22ª RAU

REUNIÃO ANUAL DE USUÁRIOS DO LNLS/CNPEM

28 E 29 FEVEREIRO 2012

RESUMOS

DE TRABALHOS CIENTÍFICOS

Apoio

FAPESP CNPq CAPES CLAF

Realização

LNLS

ABTLuS CNPEM

Ministério da
Ciência, Tecnologia
e Inovação

GOVERNO FEDERAL
BRASIL
PAÍS RICO É PAÍS SEM POBREZA

Coordenação: Comitê dos Usuários do LNLS

LNLS Users Committee

Celso Valentim Santilli (UNESP)
Álvaro Saavedra (Petrobrás – Cenpes)
Humberto D´Muniz Pereira (USP)
Maria Luiza Rocco Pereira Duarte (UFRJ)
Rosangela Itri (USP)
Reinaldo Cavasso Filho (UFABC)
Valmor Roberto Mastelaro (USP)

Comitê Científico

Scientific Committee

Celso V. Santilli (UNESP)
Carlos de la Védova Omar (UNLP)
Edson Ticianelli (USP)
Fabio Furlan (UFABC)
Guinther Kellermann (UFPR)
Maria Cristina Nonato (USP)
Mateus Cardoso (LNLS)
Reinado Cavasso (UFABC)
Richard Landers (Unicamp)
Rogerio Paniago (UFMG)

Comitê Local

Local Organizing Committee

Camila de Gusmões S. Körber
Dora Marques
Gustavo Martins Moreno
Marjorie Cavalheiro
Meire de Carvalho Migotto
Sérgio A. Carrare Junior
Vilmara Helena T. Congílio
William Barbosa

22ª RAU

REUNIÃO ANUAL DE USUÁRIOS DO LNLS/CNPEM

28 E 29 FEVEREIRO 2012

22ª Reunião Anual de Usuários do LNLS/CNPEM

Laboratório Nacional de Luz Síncrotron

Campinas, 28 e 29 Fevereiro de 2012

Realização

LNLS

ABTLuS CNPEM

Ministério da Ciência, Tecnologia e Inovação

GOVERNO FEDERAL BRASIL PAÍS RICO É PAÍS SEM POBREZA

Apoio

FAPESP

CNPq

CAPES

CLAF

Prefácio

Às 22:10 horas do dia 28 de outubro de 1996, uma segunda-feira, a luz síncrotron chegou pela primeira vez a uma estação experimental acoplada ao anel de armazenamento do LNLS. Assim anunciou o histórico boletim interno do LNLS, o LUX N^0 14 de 30/10/96, marcando o final da etapa de projeto e construção do primeiro laboratório nacional de luz síncrotron do hemisfério sul. A fonte de luz de segunda geração de 1,37 GeV, com as primeiras sete linhas de luz, foi inaugurada em 1997. A partir desse ano, a produção científica baseada em experiências realizadas pelos usuários do LNLS teve um contínuo crescimento, contribuindo para formar uma nova geração de pesquisadores das mais variadas áreas do conhecimento. Atualmente, as 16 linhas de luz em operação no LNLS atendem anualmente aproximadamente 2300 usuários que executam mais de 450 projetos de pesquisa.

O número de equipamentos de grande porte que começou a se multiplicar no entorno do LNLS serviu para a nucleação do Laboratório Nacional de Biociências (LNBio), inaugurado em 2001, do Laboratório Nacional de Ciência e Tecnologia do Bioetanol (CTBE) aberto em 2010, e do recém inaugurado Laboratório Nacional de Nanotecnologia (LNNano). Em de 2010 esse complexo de Laboratórios Nacionais ganhou o nome de Centro Nacional de Pesquisa em Energia e Materiais (CNPEM). Para os próximos anos, o CNPEM tem pela frente o desafio de projetar e construir uma nova fonte de luz síncrotron de 3^a geração, batizada com o nome de Sirius. Essa nova instalação deve contar com um anel de armazenamento de elétrons de 3 GeV, podendo comportar mais de 40 linhas de luz.

Com o objetivo de criar um canal direto de comunicação entre os usuários, os cientistas das linhas de luz e a direção do Laboratório, instituiram, em 2010, um Comitê de Usuários do LNLS. Eleitos por seus pares e empossados em agosto de 2010 por mandato de dois anos, o comitê é constituído por sete membros titulares representantes das áreas de Biologia, Ciência Atômica e Molecular e Ciências dos Materiais, e um representante da indústria. Uma das atribuições do Comitê de Usuários é a organização da RAU.

A partir desta edição, a RAU passa a ser organizada pelo Comitê de Usuários e a focar prioritariamente as pesquisas realizadas por usuários e pesquisadores do LNLS. Buscando aumentar a troca de informações e melhorar as condições de apresentação dos trabalhos, o número de sessões orais e de pôsteres foi duplicado e, com isto, a duração da 22ª RAU passou de 1½ para 2 dias. Entre os 233 trabalhos inscritos, o comitê científico selecionou 50 para apresentação no formato oral. Para as quatro Palestras Plenárias foram convidados especialistas renomados de diferentes áreas, que abordarão aspectos relacionados à espectro microscopia com luz síncrotron, a novos algoritmos para determinação de estrutura de proteínas e aos progressos recentes na análise estrutural de sistemas nanoscópicos e no estudo espectroscópico de catalisadores.

Nas Sessões Temáticas, os usuários terão a oportunidade de interagir com os cientistas das linhas de luz, conhecer as mais recentes atualizações da instrumentação, além de obter informações quantitativas relevantes sobre o funcionamento dessas linhas e sobre as características dos acessórios (antigos e novos) disponíveis para os usuários. Além disso, os coordenadores dessas sessões convidaram alguns usuários para abordar aspectos técnicos relevantes para o contínuo aperfeiçoamento das linhas de luz.

Esperamos que as mudanças no formato da RAU criem um ambiente propício à participação de todos nos debates científicos, bem como nas discussões relacionadas aos projetos de melhoria e ampliação da instrumentação disponível para pesquisa científica e tecnológica no LNLS.

Agradecemos aos membros do Comitê Científico pelo empenho na análise dos resumos submetidos, participação na elaboração da programação final e indicação dos palestrantes convidados. Agradecemos também aos organizadores dos dois eventos satélites: First School of SAXS Data Analysis & Workshop on Advanced X-ray Spectroscopy Methods. Agradecemos ainda aos funcionários da Central de Apoio e Eventos, às áreas de Comunicação, Convênios, Projeto e Tecnologia da Informação da ABTLuS que, com afinco e competência, trabalharam durante meses para o bom andamento da 22ª RAU. Finalmente, agradecemos ao LNLS, CNPq, Capes, FAPESP, CLAF e à PETROBRAS pelo apoio financeiro.

Comitê de Usuários

Orientações aos Participantes

Guidelines to Participants

Prezado Participante / Dear Participant
Seja bem-vindo à 22ª Reunião Annual de Usuários. O Comitê Organizador pede sua atenção para as informações abaixo.
Welcome to 22nd LNLS Users Annual Meeting. Please, read carefully the following instructions.

1. Credenciamento / *Registration*

O credenciamento no evento (retirada de material, crachás de identificação e assinaturas dos recibos para agências de fomento - FAPESP/Capes/CNPq) será no seguinte horário:
Registration at the event (identification badge, personal kit and signature on the receipt for the ones who have financial support) will be done following the schedule bellow:
28/02, Terça-feira, das 8h às 18h / *Thursday, 8AM to 6PM*

2. Crachá de identificação/ *Identification Badge*

O crachá de identificação deve ser usado durante toda a reunião.
The identification badge must be used at all time during the meeting.

3. Sessões / *Sessions*

As Comunicações Orais e Sessões Temáticas ocorrerão em diferentes salas do hotel Premium Norte: Amadeus, 02, 05, 08 e 09 do Centro de Convenções, conforme Programação.
The Oral Communications and Thematic Session will be held in rooms: Amadeus, 02, 05, 08 e 09 at the Convention Centre, Premium Norte Hotel.

4. Sessão de Pôsteres / *Posters Session*

A sessão de pôsteres ocorrerá nos dias 28 e 29 de fevereiro. Seguem os horários para fixação e retirada dos mesmos. *The poster session will be on February 28th and 29th, following the schedules for fixing and dismantle:*

Data *Date*	**Coordenação** *Coordination*	**Horário montagem** *Mounting*	**Horário de retirada** *Dismantle*
28/fev – 18h as 19:30 *Feb 28th – 6PM to 7h30PM*	Karim Dahmouche	Das 8h às 12h *8AM to 12PM*	19:40 *7:40PM*
29/fev – 10:10 as 11:40 *Feb 29th – 10:10 to 11:40AM*	Luis G. Martinez	Das 8h às 9h *8AM to 9AM*	Até 13h *till 1PM*

A localização onde o pôster deverá ser fixado estará sinalizada por etiquetas com a numeração correspondente à página do resumo no Livro de Resumos.
Os organizadores da RAU não se responsabilizam por qualquer perda ou dano do pôster e também por embalar, remover ou transportar o material.
The local where the poster must be fixed will be signaled by a tag with the corresponding page number of the Abstract Book.
RAU staffs are not responsible for any loss or damage of your poster and also for packing, removing or shipping it.

5. Hotel / *Hotel*

O hotel oferece desktops no Lobby para uso de hóspedes e participantes da 22ª RAU.
O uso do estacionamento está disponível durante a reunião – vagas limitadas.
The hotel offers desktop computer at the lobby for the use of guests and participants of the event. The parking lot is available during the meeting.

6. Almoço / *Lunch*

Os almoços dos dias 28/02 e 29/02 serão servidos no restaurante do hotel, a partir do horário indicado na programação.
Lunch will be served at the hotel restaurant, following the schedule in the program.

7. Coquetel / *Cocktail*

Dia 28/02, terça-feira / Thursday 28th
Será oferecido um coquetel de confraternização durante a sessão de pôster.
On February 28th, a cocktail will be served with the poster session.

8. Segurança / *Security*

Pedimos a todos que fiquem atentos à segurança de seus objetos pessoais de valor. O CNPEM e o Hotel Premium Norte não poderão se responsabilizar pela segurança de tais objetos.
Please, pay attention at your personal belongings. CNPEM and Premium Norte Hotel cannot be responsible for the safety of such objects.

O Comitê de Organização deseja a todos os participantes uma agradável e produtiva reunião.
The Organization wishes all participants a pleasant and productive meeting.

Agenda, 28 de Fevereiro

08:00 - 09:00	**Recepção / Inscrições**
09:00 - 09:15 Sala Amadeus	**Abertura** Antônio José Roque da Silva Diretor LNLS
09:15 - 09:45 Sala Amadeus	**Status e Perspectivas do LNLS** Yves Petroff Diretor Científico LNLS
09:45 - 10:15 Sala Amadeus	**Projeto Sirius** Antônio Ricardo Droher Rodrigues Coordenador Projeto Sirius
10:15 - 10:20	**Foto Oficial**
10:20 - 10:40	**Café**
10:40 - 11:40 Sala Amadeus	**Plenária I** **Maria C. Asensio (Synchrotron SOLEIL, France)** Nano-ARPES at Synchrotron SOLEIL: A new concept in scanning photoelectron microscopy.
11:40 - 12:40 Sala Amadeus	**Plenária II** **Yang Zhang (Univ. of Michigan, USA)** Genome-wide protein structure prediction and structure-based function annotations.
12:40 - 14:00	**Almoço**
14:00 - 15:00	**Sessões Temáticas I**
15:00 - 16:40	**Comunicações Orais I**
16:40 - 17:00	**Café**
17:00 - 18:00	**Sessões Temáticas II**
18:00 - 19:30	**Sessão Pôster I e Coquetel**

Agenda, 29 de Fevereiro

08:30 - 10:10	**Comunicações Orais II**
10:10 - 11:40	**Sessão Pôster II e Café**
11:40 - 12:40 Sala Amadeus	**Plenária III** **Andrea E. Russel (Univ. of Southampton, UK)** In situ characterisation of Pd@Pt core-shell ORR catalysts: the effects of shell structure on stability.
12:40 - 14:00	**Almoço**
14:00 - 15:00 Sala Amadeus	**Plenária IV** **Greg Beaucage (Univ. of Cincinnati, USA)** Quantification of branched structures using small-angle x-ray and nêutron scattering.
15:00 - 15:30 Sala Amadeus	**Parcerias LNNano / LNLS** Fernando Galembeck Diretor LNNano
15:30 - 16:00 Sala Amadeus	**Articulação entre os Laboratórios do CNPEM** Carlos Alberto Aragão de Carvalho Filho Diretor Geral ABTLuS
16:00 - 16h30 Sala Amadeus	**Mesa Redonda** Avaliações e Discussões com o Comitê de Usuários do LNLS

Comunicações Orais, 28 de Fevereiro

Biologia Estrutural

Sessão 1	**Sala Amadeus**
Chairperson:	**Rodrigo Villares Portugal**
15:00-15:20	Assessment of *Escherichia coli* Selenophosphate Synthetase oligomeric states by analytical ultracentrifugation and small angle X-ray scattering **Ivan Rosa Silva (pág. 13)**
15:20-15:40	Crystal structure of importin-α complexed with a classic nuclear localization sequence obtained by oriented peptide library screening **Agnes Alessandra Sekijima Takeda (pág. 4)**
15:40-16:00	Structure of *Dioclea virgata* lectin: relations between carbohydrate binding site and nitric oxide production **Plinio Delatorre (pág. 6)**
16:00-16:20	Influence of membrane compositon on its flexibility **Barbara Bianca Gerbelli (pág. 10)**
16:20-16:40	Cloning, expression, purification and initial crystallographic studies of UbiG: a methyltransferase involved in Ubiquinone biosynthesis in *Escherichia coli* **Mariana Amalia Figueiredo Costa (pág. 21)**

Propriedades Estruturais, Eletrônicas e Magnéticas de Sólidos

Sessão 2	**Sala 2**
Chairperson:	**Valmor Roberto Mastelaro**
15:00-15:20	Speciation of metals in a nanostructured iron-cobaltite mixed conductor used for SOFC design **Analía Leticia Soldati (pág. 165)**
15:20-15:40	Study of the influence of reduction agents in the Eu reduction in the $BaAl_2O_4$ host **Marcos Vinícius dos Santos Rezende (pág. 177)**
15:40-16:00	Effects of temperature and chemical environment in the electronic properties of Pt/C and PtRu/C electrocatalysts **Edson Antonio Ticianelli (pág. 187)**
16:00-16:20	Local structure of $Pb(Fe_{1/2}Nb_{1/2})O_3$ and $Pb(Fe_{2/3}W_{1/3})_{1-X}Ti_xO_3$ multiferroic materials probed by X-ray absorption spectroscopy **Alexandre Mesquita (pág. 159)**
16:20-16:40	Structural characterization of ternary compounds based in rare earth oxides using x-ray spectroscopy, Rutherford backscattering and scanning electron microscopy **Danilo Roque Huanca (pág 244)**

Superfícies, Interfaces e Nanossistemas

Sessão 3	**Sala 5**
Chairperson:	**Maria Luiza Miranda Rocco**
15:00-15:20	A dispersive XANES and XRD investigation of the reducibility and crystallization processes of iron oxides promoted by gold **Juan Carlos Fierro-Gonzalez (pág. 210)**
15:20-15:40	Epitaxial graphene on SiC(0001): a photoelectron diffraction (XPD) study **Luis Henrique de Lima (pág. 241)**
15:40-16:00	Reciprocal space maps of thin layers of CdTe / Si - The effect of growth temperature and thickness **Joelma Oliveira Mello (pág. 229)**
16:00-16:20	Understanding the stability of cobalt supported catalysts during ethanol reforming as addressed by *in situ* XAFS analysis **Cícero Naves de Ávila Neto (pág. 228)**
16:20-16:40	Room temperature observation of orbital momentum enhancement of Co/Au(110) by XMCD **Rogerio Magalhaes Paniago (pág. 227)**

Ciência Atômica

Sessão 4	**Sala 8**
Chairperson:	**Danilo de Paiva Almeida**
15:00-15:20	Photoexcitation, photoionization and photofragmentation studies on pyrosulfuryl chloride, $(ClSO_2)_2O$, between 12 and 300 eV **Rosana Mariel Romano (pág. 67)**
15:20-15:40	Photoabsorption and time-of-flight mass spectroscopy for gas-phase trimethyl phosphate following valence shell excitation **Manoel Gustavo Petrucelli Homem (pág. 62)**
15:40-16:00	Fragmentation and desorption from condensed alcohols due to soft X-rays: Relevance to solid state astrochemistry **Guilherme Camelier Almeida (pág. 50)**
16:00-16:20	Interação da radiação estelar com moléculas congeladas na superfície de grãos de poeira **Thiago Monfredini (pág. 66)**
16:20-16:40	Photostability of Glycine to Lyman α radiation **Ana Mónica Ferreira da Silva Napole Rodrigues (pág. 52)**

Materiais Estruturais e Aplicações na Indústria	
Sessão 5	**Sala 9**
Chairperson:	**Álvaro Saavedra**
15:00-15:20	Luminescência excitada por raios X do $SrAl_2O_4$ dopado com Eu e Dy **Claudiane dos Santos (pág. 107)**
15:20-15:40	Theoretical and experimental investigation of the disordered quaternary oxide $CoMo_{0.5}W_{0.5}O_4$ **Yordy Enrique Licea Fonseca (pág. 105)**
15:40-16:00	Phase characterization of recycled Zircaloy **Luis Gallego Martinez (pág. 100)**
16:00-16:20	Local structure of $SrTi_{1-X}Fe_XO_3$ nanocubes analyzed by XAS technique **Luís Fernando da Silva (pág. 99)**
16:20-16:40	Investigação da ativação de catalisadores de Ni ou Ni-Co suportados em alumina modificados com Zn por XANES *in situ*. **Daniela Coelho Oliveira (pág. 117)**

Comunicações Orais, 29 de Fevereiro

Geociência, Meio-ambiente e Aplicações em Materiais Biológicos	
Sessão 1	**Sala Amadeus**
Chairperson:	**Simone Coutinho Cardoso**
08:30-08:50	Functional and Biophysical studies on four Ceratoplatanins from the fungus *Moniliophthora perniciosa*, causal agent of the Witche's Broom Disease **Mario Ramos de Oliveira Barsottini (pág 43)**
08:50-09:10	Bioacumulacion de As en larvas de sapo comun argentino (Rhinella arenarum) expuestos cronicamente durante su desarrollo **Guillermina Azucena Bongiovanni (pág. 77)**
09:10-09:30	Arsenic speciation by X-ray spectroscopy using resonant Raman scattering **Héctor Jorge Sánchez (pág. 76)**
09:30-09:50	Determination and correlation of spatial distribution of trace elements in normal and neoplastic breast tissues evaluated by μ-XRF. **Marina Piacenti Silva (pág. 82)**
09:50-10:10	Elemental content changes in Hemolymph of *Rhodnius prolixus* due to mercury contamination: A study using SR-TXRF **Regina Cély Rodrigues Barroso (pág. 81)**

Matéria Mole e Fluídos Complexos

Sessão 2	**Sala 2**
Chairperson:	**Márcia C. A. Fantini**
08:30-08:50	Estudo da ordem de longo alcance e propriedades termodinâmicas de multicamadas de ácidos fosfônicos pela técnica de difração de raios-x dispersiva em energia **Muriel de Pauli (pág. 91)**
08:50-09:10	Unimolecular micelles and electrostatic nanoassemblies stemming from hyperbranched polyethyleneimin **Agustin Silvio Picco (pág. 89)**
09:10-09:30	Thermoplastic starch and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) bionanocomposites before and after prolonged storage **Karim Dahmouche (pág. 88)**
09:30-09:50	SAXS as a tool to understand the phase behavior of ethoxylated complex salts **Ana Maria Percebom (pág. 93)**
09:50-10:10	Structural investigations of sodium caseinate micelles in complex environments **Cristian Huck Iriart (pág. 92)**

Superfícies, Interfaces e Nanossistemas

Sessão 3	**Sala 5**
Chairperson:	**Richard Landers**
08:30-08:50	Surface functionalisation of polypropylene by inner-shell monochromatic irradiation with mild oxygen flux **Rajajeyaganthan Ramanathan (pág. 213)**
08:50-09:10	Formation of an extended $CoSi_2$ thin nanohexagons array coherently buried in silicon single crystal **Félix Gregorio Requejo (pág. 247)**
09:10-09:30	Evolução estrutural de nanopartículas $Pt_{0.3}Pd_{0.7}$ sob condições reacionais **Jocenir Boita (pág. 207)**
09:30-09:50	Transição sol-gel termorreversível em sistemas a base de titania **Renata Ferreira Lins (pág. 242)**
09:50-10:10	Study of depth-dependent local structures in thin films by grazing-incidence X-ray absorption spectroscopy **Claudia Elena Rodríguez Torres (pág. 209)**

Biologia Estrutural

Sessão 4	**Sala 8**
Chairperson:	**Ricardo Aparicio**
08:30-08:50	Structural Studies of Schistosoma mansoni Adenylate Kinases **Ivo de Almeida Marques (pág. 14)**
08:50-09:10	Self-Assembling of Amyloid-like Proteins **Elisa Morandé Sales (pág. 17)**
09:10-09:30	The crystal structure of the hexameric purine nucleoside phosphorylase from *Bacillus subtilis* in complex with adenosine **Priscila Oliveira Giuseppe (pág. 24)**
09:30-09:50	Mitochondrial localization and structure-based phosphate activation mechanism of Glutaminase C with implications for cancer metabolism **Amanda Petrina Scotá Ferreira (pág. 18)**
09:50-10:10	Microscopia eletrônica de transmissão aplicada à biologia molecular estrutural **Rodrigo Villares Portugal (pág. 26)**

Propriedades Estruturais, Eletrônicas e Magnéticas de Sólidos

Sessão 5	**Sala 9**
Chairperson:	**Fábio Furlan Ferreira**
08:30-08:50	In situ XRD studies of the carburization process of tungsten carbides catalysts **Cristiane Barbieri Rodella (pág. 186)**
08:50-09:10	X-ray multiple diffraction phenomenon in the evaluation of small structural changes in a new single crystal used as optical bandpass filters **Claudio Marcio Rocha Remédios (pág. 170)**
09:10-09:30	Phase stability and structural distortions of nanostructured iron-cobaltite mixed conductor **Laura Cecilia Baqué (pág. 164)**
09:30-09:50	Avaliação das transformações térmicas na estrutura porosa de espumas de alumina a partir do monitoramento in situ por SAXS **Aline Ribeiro Passos (pág. 190)**
09:50-10:10	Characterization of pharmaceutical polymorphs by means of X-ray powder diffraction **Fabio Furlan Ferreira (pág. 192)**

Sessões Temáticas, 28 de Fevereiro

Sessão Temática I:	**Linhas de Luz XRD / XPD**
Sessão 1A	**Sala 02**
Chairperson:	**Guinther Kellermann**
14:00 - 14:15	Status e perspectivas das linhas de difração de raios X XRD1 e XRD2 do LNLS **Beatriz Leonila Diaz Moreno**
14:15 - 14:25	Status e perspectivas da linha de Difração de Pó XPD do LNLS **Fabiano Yokaichiya**
14:25 - 14:35	Linha de difração e espectroscopia (XDS) **Eduardo Granado Monteiro da Silva**
14:35 - 14:40	Otimização das condições de medidas de difração de raios X em policristais em modo de transmissão **Fábio Furlan Ferreira**
14:40 - 14:45	High resolution X-ray Spectrometer **Germán Tirao**
14:45 - 14:50	Time resolved experiments: choosing your bunch **Carlos Sato Baraldi Dias**
14:50 - 14:55	Novas possibilidades da difração múltipla de raios X com radiação síncrotron no LNLS **Lisandro Pavie Cardoso**

Sessão Temática I:	**Linhas de Luz TGM / SGM / PGM**
Sessão 1B	**Sala 05**
Chairperson:	**Maria Luiza Rocco Duarte Pereira**
14:00-14:15	Status e perspectivas da linha TGM **Paulo de Tarso Fonseca**
14:15- 14:30	Status e perspectivas da linha SGM **Flávio Garcia**
14:-14-45	Status e perspectivas da linha PGM **Julio Criginski Cezar**
14:45-15:00	Comentários e discussões

Sessão Temática I:	**Linhas de Luz MX1 / MX2**
Sessão 1C	**Sala 08**
Chairperson:	**Humberto D'Muniz Pereira**
14:00 - 14:15	Biologia estrutural no Brasil: Quo Vadis? **Humberto D'Muniz Pereira**
14:15 - 14:30	Linha de luz MX2: Automação, características e perspectivas **Mario Murtakami**
14:30 - 14:45	D03B-MX1: Presente e futuro **André Ambrosio**
14:45 - 15:00	Comentários e discussões

Sessão Temática II:	**Linhas de Luz XAFS / DXAS**
Sessão 2A	**Sala 02**
Chairperson:	**Félix G. Requejo**
17:00 - 17:10	Grupo de linhas XAFS: status e perspectivas **Narcizo Marques de Souza Neto**
17:10 - 17:20	XAFS1: status e perspectivas **Daniela Coelho**
17h20 – 17h30	XAFS2: status e perspectivas **Santiago Figueroa**
17h30 – 17h35	XAFS2: status e perspectivas **Narcizo Marques de Souza Neto**
17h35 – 17h50	Descrição e perspectivas das linhas XAFS no SIRIUS **Narcizo Marques de Souza Neto**
17h50 – 18h00	Discussões Gerais

Sessão Temática II:	**Linhas de Luz XRF**
Sessão 2B	**Sala 05**
Chairperson:	**Guillermina Bongiovanni**
17:00 - 17:30	Status, upgrading e apresentação de últimos desenvolvimentos e setups **Carlos A. Pérez**
17:30 - 17:50	Inovações: obtenção de imagens em 3D no LNLS **Ricardo T. Lopes**
17h50 – 18h00	Discussões sobre as perspectivas da linha XRF

Sessão Temática II:	**Linhas de Luz SAXS1 / SAXS2**
Sessão 2C	**Sala 08**
Chairperson:	**Aldo Craievich**
17:00 - 17:15	Status, use and perspectives of SAXS beam lines **Harry Westfhal**
17:15 - 17:30	Quantitative evaluation of relevant characteristics of SAXS1 and SAXS2 beam lines **Mateus Cardoso e Leide Cavalcanti**
17:30 - 18:00	Short communications submitted by users: 1. Design of a sample holder for SAXS measurements under static magnetic field: **Marcela B. Fernández van Raap e P. Mendoza Zélis** 2. Instrumentation for SAXS studies of surfaces: **Rafael G. Oliveira** 3. A program for pre-analysis of data output from the Mar-CCD165 SAXS detector: **Guinther Kellermann** 4. SAXSTER: A Web Server for protein template recognition aided by threading and small-angle X-ray scattering data: **Marcelo Augusto dos Reis, Ricardo Aparicio e Yang Zhang** 5. Other communications and/or comments

Sessão Temática II:	**Linhas de Luz SXS**
Sessão 2D	**Sala 09**
Chairperson:	**Jonder Morais**
17:00 - 17:20	Status e perspectivas da linha SXS **Flávio Vicentin**
17:30 as 18:00	Mesa redonda com usuários presentes I) Discussão sobre eventuais necessidades de novas instrumentações II) Apreciação crítica sobre aspectos técnicos do funcionamento atual das linhas III) Comentários sobre o atendimento técnico e administrativo recebido pelos usuários durante a realização de suas experiências no LNLS IV) Sugestões referentes à formação e treinamento dos usuários

Sumário

Parte I Biologia Estrutural

Parte II Biologia Molecular e Química de Proteínas

Parte III Ciência Atômica e Molecular

Parte IV Geociência, Meio-ambiente e Aplicações em Materiais Biológicos

---

Parte V Matéria Mole e Fluídos Complexos

Parte VI Materiais Estruturais e Aplicações na Indústria

Parte VII Métodos e Instrumentação

Parte VIII Propriedades Estruturais, Eletrônicas e Magnéticas de Sólidos

---

Parte IX Superfícies, Interfaces e Nanossistemas

Parte X Projetos dos Bolsistas de Verão

Parte I

Biologia Estrutural

Structural determination of Selenocysteine Synthase Complex (SelA) of Escherichia coli.

Serrão, V.H.B[1], Manzine, LR[1], Thiemann, O. H.[1], Portugal, R. V.[2], Bettini J.[2], and van Heel, M.[3]

[1] Universidade de São Paulo - São Carlos - São Carlos SP Brazil
[2] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[3] Imperial College of Science, Technology and Medicine - South Kensington, London United Kingdom

The biosynthesis of the 21th amino acid, Selenocysteine (Sec U), requires complex enzymatic machinery composed in eubacteria of: Selenocysteine Synthase (SELA), Selenocysteine Specific Elongation Factor (SELB), Selenophosphate Synthetase (SELD) and a specific Selenocysteine Inserting tRNA (tRNAsec). The Selenocysteine residue is incorporated into a nascent protein at a UGA like stop codon signaling as a Sec incorporation site by the presence of a Selenocysteine Insertion Sequence (SECIS), embedding the UGA codon in the coding region in bacteria and in a 3 UTR in archaea and eukarya. SELA plays a central role in this pathway by modifying the Serine residue charged into the tRNAsec by Seryl-tRNA Synthetase (SerRS) and converting it into Selenocysteine. This enzyme forms a homodecameric complex that specifically recognizes and binds to Seryl-tRNAsec. The specific interaction of SELA and its tRNA remains unclear. Our aim is the structural investigation by Atomic Force Microscopy, Negative Staning and Cryo-Eletronic Microscpy of Escherichia coli SELA and SELA-tRNAsec. Microscopy datas determined dimensional parameters as maximum dimension, molecular mass and radius of gyration. Recently study saw prospects of assuming one tRNA for monomeric protein of SELA, the models of AFM and Cryo-Microscopy may help to decide the number of tRNA interections of SELA.

Acknowledgements: Acknowledgements to Dr. Alexandre Cassago and Marcos Michel Souza because resolve the problem about cloning and purification; Professor Luís Maurício T. R. Lima for the fluorescenses help and Dr. Humberto Pereira D'Muniz for the interpretation of the structural and help of others works. This work was supported by CAPES and FAPESP.

Crystal structure of importin-α complexed with a classic nuclear localization sequence obtained by oriented peptide library screening

Takeda, A. A. S.[1], Yang, S. N. Y.[2], Harris, J. M.[3], Jans, D. A.[4], Kobe, B.[5], and Fontes, M. R. M.[1]

[1] Universidade Estadual Paulista - Botucatu - Botucatu SP Brazil
[2] University of Melbourne - Melbourne AU Australia
[3] Queensland University of Technology - Brisbane Australia
[4] Monash University - Clayton Australia
[5] University of Queensland - Brisbane QU Australia

Importin-α (Impα) plays a role in the classical nuclear import pathway, binding to cargo proteins with activities in the nucleus. Different Impα paralogs responsible for specific cargos can be found in a single organism. The cargos contain nuclear localization sequences (NLSs), which are characterized by one or two clusters of basic amino acids (monopartite and bipartite NLSs, respectively). In this work we present the crystal structure of Impα from *M. musculus* (residues 70-529, lacking the autoinhibitory domain) bound to a NLS peptide (pepTM). The peptide corresponds to the optimal sequence obtained by an oriented peptide library experiment designed to probe the specificity of the major NLS binding site. The peptide library used five degenerate positions and identified the sequence KKKRR as the optimal sequence for binding to this site for mouse Impα (70-529). The protein was obtained using an *E. coli* expression system and purified by affinity chromatography followed by an ion exchange chromatography. A single crystal of Impα -pepTM complex was grown by the hanging drop method. The data were collected using the Synchrotron Radiation Source LNLS, Brazil and processed to 2.3. Molecular replacement techniques were used to determine the crystal structure. Electron density corresponding to the peptide was present in both major and minor binding sites The peptide is bound to Impα similar as the simian virus 40 (SV40) large tumour (T)-antigen NLS. Binding assays confirmed that the peptide bound to Impα with low nM affinities. This is the first time that structural information has been linked to an oriented peptide library screening approach for importin-α; the results will contribute to understanding of the sequence determinants of classical NLSs, and may help identify as yet unidentified classical NLSs in novel proteins.

Acknowledgements: Supported by: FAPESP, CNPq .

Three-dimensional structure of lectin from *Dioclea violacea* and comparative vasorelaxant effects with *Dioclea rostrata*

Rocha, B.A.M.[1], Delatorre, P.[2], Bezerra,M. J. B.[1], Rodrigues, N.V.[3], Pires, A.F.[3], Bezerra, G.A.[1], Alencar, K. L. L.[1], Nascimento, K. S.[1], Naganao, C.S.[1], Marins, J.L.[4], Sampaio, A.H.[1], Assreuy, A.M.S.[3], and Cavada, B.S.[1]

[1] Universidade Federal do Ceará - Fortaleza CE Brazil
[2] Universidade Federal da Paraíba - João Pessoa PB Brazil
[3] Universidade Estadual do Ceará - Fortaleza CE Brazil
[4] Universidade Federal de Pelotas - Pelotas RS Brazil

Lectins are a structural heterogeneous group of proteins possessing at least one non-catalytic domain that binds reversibly to a specific mono or oligosaccharide. Diocleinae lectins exhibit glucose/mannose monosaccharide binding specificity and studies of their chemical and physicochemical properties revealed a high degree of identity in their amino acid sequences and three dimensional structures. This study investigated structural/functional relationships between lectins obtained from *Dioclea violacea* (DVL) and *Dioclea rostrata* (DRL). The purified lectin (DVL) was solubilized in 20 mM Tris-HCl pH 7.6 with 5 mM $CaCl_2$ and $MnCl_2$ buffer and incubated during one hour before the crystallization experiments with the ligand X-Man (5-bromo-4-chloro-3-indolyl-α-D-mannose) at 3 mM. Crystals of DVL grew in condition 33 of Crystal Screen I (4M Sodium formate) and belong to the orthorhombic space group I222. The structure of DVL at 2.6 resolution was obtained by molecular replacement using the coordinates of DRL (PDB code 2ZBJ), after the last refinement the structure presented R factor of 0.23 and R free of 0.27. The crystal structures reveal differences between them and could be related to relaxant activity. The conformation of residues HIS51, HIS131 and GLU205 and others positioned at CRD lead to different lectin binding activities. In fact, the pocket in DVL is small and deep and promotes weak interaction with carbohydrates, while DRL pocket is large and shallow, allowing strong interaction between CRD and sugars. This can explain why DVL and DRL elicited different degrees of aorta relaxation showing maximal effects of 43 % and 96 %, respectively.

Acknowledgements: This work was supported by CNPq and CAPES. We would like to ackowledge Dr. Karl Gruber for you contributions to this work.

Structure of *Dioclea virgata* lectin: relations between carbohydrate binding site and nitric oxide production

Delatorre, P.[1], Nóbrega,R.B.[2], Rocha, B.A.M.[2], Gadelha, C. A. A.[1], Santi-Gadelha, T.[1], Pires, A.F.[3], Assreuy, A.M.S.[3], Nascimento, K. S.[2], Naganao, C.S.[2], Sampaio, A.H.[2], and Cavada, B.S.[2]

[1] Universidade Federal da Paraíba - João Pessoa PB Brazil
[2] Universidade Federal do Ceará - Fortaleza CE Brazil
[3] Universidade Estadual do Ceará - Fortaleza CE Brazil

Lectins are proteins/glycoproteins with at least one noncatalytic domain binding reversibly to specific monosaccharides or oligosaccharides. By binding to carbohydrate moieties on the cell surface, lectins participate in a range of cellular processes without changing the properties of the carbohydrates involved. The lectin of *Dioclea virgata* (DvirL), both native and complexed with X-man, was submitted to X-ray diffraction analysis and the crystal structure was compared to that of other Diocleinae lectins in order to better understand differences in biological properties, especially with regard to the ability of lectins to induce nitric oxide (NO) production. The DvirL diffraction analysis revealed that both the native crystal and the X-Man-complexed form are orthorhombic and belong to space group I222. The cell parameters were: a=65.4 , b=86.6 and c=90.2 (native structure), and a=61.89 , b=87.67 and c=88.78 (X-Man-complexed structure). An association was observed between the volume of the carbohydrate recognition domain (CRD), the ability to induce NO production and the relative positions of Tyr12, Arg228 and Leu99. Thus, differences in biological activity induced by Diocleinae lectins are related to the configuration of amino acid residues in the carbohydrate binding site and to the structural conformation of subsequent regions capable of influencing site-ligand interactions. In conclusion, the ability of Diocleinae lectins to induce NO production depends on CRD configuration.

Acknowledgements: This work was supported by CNPq and CAPES.

Interaction Indole-3-Acetic Acid IAA with lectin *Canavalia maritima* seeds reveal new function of lectins in plant physiology

SILVA FILHO, J. C.[1], TEIXEIRA, C. S.[2], Santi-Gadelha, T.[1], Rocha, B.A.M.[2], Nóbrega,R.B.[2], Gadelha, C. A. A.[1], Alencar, K. L. L.[2], Cavada, B.S.[2], and Delatorre, P.[1]

[1] Universidade Federal da Paraíba - João Pessoa PB Brazil
[2] Universidade Federal do Ceará - Fortaleza CE Brazil

Lectins are a class of proteins of non-immune origin characterized by its capability in interacts specifically and reversibly to mono and oligosaccharides. In plant several possible roles have been suggested including their function in seed maturation, cell wall assembly, defense mechanisms, or rhizobial nodulation of legume roots. Nearly all application and proposed of the plant lectins are based on their specific carbohydrate binding. However, it has been reported that lectins from legumes, might interact with other molecules, such as non proteic amino acids and hydrophobic compounds. This study show the first the crystal structure based on molecular replacement of the *Canavalia maritima* (CML) complexed with IAA correlated with possible role in plant development. Purified CML was dissolved in 20 mMTrisHCl pH 7.6 containing 5 mM IAA, the suitable co-crystals from CML-IAA complex grew in condition 4 of screen I (0.1 M TrisHCl pH 8.5 and 2.0 M ammonium sulfate). This crystal belong to the orthorhombic space group I222 with unit-cell parameters a = 67.1 ; b = 70.7 , c = 97.7 , The structure was refined at 2.1 of resolution to a final R factor of 20.63 % and an R free of 22.54 %. To check the relative position of the IAA molecule in relation to the biological assemble of the CML, the tetrameric structure was generate by crystallographic symmetry. IAA molecules are positioned in the central cavity. The IAA is stabilized by interacting through hydrogen bounds and Van der Waals forces with the amino acids residues Ser 108 and Asn131, and two water molecules. The hydrophilic interactions occur between IAA and side chains of Ser 108, Asn131 and water molecules 26 and 31 by H-bonds. The OG oxygen from Ser108 display H-bonds with O2 and O3 oxygen atoms from IAA, 3.1 and 2.8 respectively. The tetrameric structure of CML complexed with IAA revels which this protein can act during the seedling in plant development.

Acknowledgements: This work was supported by CNPq and CAPES.

Structural and Biophysical Studies with the MjTX-I, a Lys49-Phospholipase A_2 Homologue From *Bothrops moojeni* Venom

Salvador, G. H. M.[1], Fernandes, C.A.H.[1], Marchi-Salvador, D. P.[2], Fernandez, R.M.[1], Soares, A. M.[3], Oliveira, C. L. P[4], and Fontes, M. R. M.[1]

[1] Universidade Estadual Paulista - Botucatu - Botucatu SP Brazil
[2] Universidade Federal da Paraíba - João Pessoa PB Brazil
[3] Universidade de São Paulo - Ribeirão Preto - Ribeirão Preto SP Brazil
[4] Universidade de São Paulo - São Paulo - São Paulo SP Brazil

Phospholipases A_2 (PLA_2) are small proteins found in a great diversity of organisms and belong to a superfamily of proteins involved in many important pharmacological processes, such as neurotoxicity, myotoxicity, platelet aggregation, and anticoagulant activity. Ophidic accidents caused by snakes from *Bothrops* genus are not efficiently neutralized by conventional serum therapy, and then detailed studies with this class of proteins may be very important to supplement this conventional therapy. Miotoxin-I (MjTX-I) is a basic Lys49-PLA_2, isolated from *Bothrops moojeni* snake venom, which induces a drastic local myonecrosis. Crystal structure of MjTX-I shows four molecules in the asymmetric unit, an unusually oligomeric conformation for snake venom Lys49-PLA_2s. However, bioinformatic techniques indicate a dimer as the biological oligomeric conformation. To get additional information of its biological conformation, we also performed Dynamic Light Scattering, Size Exclusion Chromatography and Small Angle X-ray Scattering experiments. These techniques showed a monomer as the most probable biological conformation in water; however small changes in pH and ionic strength result in different oligomeric assemblies. These novel informations for Lys49-PLA_2s may result in important conclusions for this intriguing class of toxins.

Acknowledgements: This work was supported by FAPESP, CNPq and LNLS.

BASES ESTRUTURAIS DO TRANSPORTE NUCLEAR DAS PROTEÍNAS KU70 E KU80 MEDIADAS PELA IMPORTINA-α

Takeda, A. A. S.[1], Barros, A.C.[1], Chiung-Wen Chang[2], Kobe, B.[2], and Fontes, M. R. M.[1]

[1] Universidade Estadual Paulista - Botucatu - Botucatu SP Brazil
[2] University of Queensland - Brisbane QU Australia

O heterodímero Ku é um importante componente do sistema de reparo de DNA em eucariotos, especificamente do mecanismo de reparo de DNA por junção de terminais não homólogos (NHEJ). As proteínas Ku70 e Ku80 compõem esse heterodímero e são responsáveis por manter a dupla fita de DNA unida, permitindo a atuação de outras proteínas no processo de reparo. A estrutura do heterodímero Ku foi elucidada por cristalografia, porém pouco se sabe a respeito do processo de importação nuclear desses componentes. Ambas proteínas apresentam sequências de localização nuclear (NLS) conservadas e estudos identificaram as NLS das proteínas Ku70 e Ku80 como sequências bipartida e monopartida, respectivamente. Comparados aos outros NLS clássicos, Koike e colaboradores sugeriram o NLS da Ku70 como uma variante de NLS bipartida por apresentar menos resíduos básicos que as NLS clássicas, embora toda sua extensão seja essencial para o processo de importação nuclear pela via clássica de importação nuclear, mediada pelas importinas α (Impα) e β. Para determinar as bases estruturais do reconhecimento das proteínas Ku70 e Ku80 pela Impα, elucidamos as estrutura dos complexos Impα com peptídeos NLS correspondentes aos das proteínas Ku70 e Ku80. Nesse trabalho foi realizada a expressão e purificação da Impα (Impα) truncada (aminoácidos 70-529) de *Mus musculus* bem como a co-cristalização com os peptídeos NLS das proteínas Ku70 e Ku80, respectivamente. Dados de difração de raios X foram coletados em comprimento de onda de 1,43 no Laboratório Nacional de Luz Síncrotron (Campinas, Brasil) e processados a 2,6 e 2,3 de resolução, respectivamente. Os cristais eram isomorfos ao cristal da Impα nativa e estruturas foram resolvidas pelo método de síntese de Fourier partindo da estrutura do complexo Impα N1N2 NLS (PDB ID 1PJN) como modelo inicial. Resultados obtidos das estruturas finais dos complexos Impα-Ku70NLS e Impα-Ku80NLS demonstraram claramente que ambas as sequências NLS são monopartidas, indicando que é possível a importação nuclear, pela via clássica, das Ku70 e Ku80 de maneira independente. Foi demonstrado também que a Ku70 tem mais alta afinidade pela Impα do que a Ku80, dado este consistente pelo maior número de interações do N-terminal mais longo da Ku70 em relação a Ku80.

Acknowledgements:

Influence of membrane compositon on its flexibility

Gerbelli, B. B.[1], Teixeira da Silva, E.R.[1], Oliveira, C. L. P[1], and Oliveira, E. A.[1]

Universidade de São Paulo - São Paulo - São Paulo SP Brazil

Lamellar phases and vesicles composed of lipids have been used as model systems to investigate biological process related to cell membrane as well as promising carriers for drugs and gene therapy. The composition of the membrane determines its three dimensional shape and its properties such as rigidity and compressibility which play an important role on membrane fusion, protein adhesion, interactions between proteins, etc. We present systematic study of a lamellar system composed mainly of lecithin which is a biocompatible phospholipid and simusol, which is a mixture of fatty acids that acts as a cosurfactant introducing flexibility to the membrane. Using X ray scattering we determine the lamellar periodicity as a function of the hydration for different formulations of the membrane; ranging from 100 % to 50 % mass fraction of lecithin. The X-ray spectra are fitted using a 4 Gaussian model [1]that allows us to determine the lamellar periodicity and the Caillé parameter [2]. The ideal swelling law relating the membrane volume fraction (ϕ_m) to the lamellar periodicity (D) is given by $\phi_m=\delta_m/D$, where δ_m is the thickness membrane, however, when steric interactions are dominant with respect to electrostatic and van der Waals interactions, deviations from this behavior are expected [3]. We present experimental data illustrating the swelling behavior for the membrane compositions and the respective behavior of the hydration limit, membrane Luzzati [4], of the Caillé parameter and qualitative interpretation of the interaction forces the systems studying the parameter membrane square amplitude fluctuation[5].

[1] Private communication with Prof. Dr. Cristiano Luis Pinto de Oliveira.
[2] Caille A. et all, Acad. Sci. Paris B274 (1972) 891.
[3] E. Kurtisovski et all, PRL 98, 258103 (2007).
[4] Nagle et all, Curr Opin Struct Biol. 2000 Aug;10(4):474-80.
[5] H. I. Petrache. Structure and interactions of fluid phospholipids bilayers measured by high resolution X-ray scattering. PhD thesis, Carnegie Mellon University, 1998.

Acknowledgements: This work was supported by Capes and INCTFCx

Avaliação das Modificações Estruturais em PLA2s Induzidas por Cimentos Dentários Através do Espalhamento de Raios X à Baixos Ângulos

santos, D. A.[1], Lopes, M. B.[2], Soares, V.C.G.[3], Toyama MH[3], and Santos, M.L.[1]

[1] Universidade Federal de Sergipe - Itabaiana SE Brazil
[2] Universidade Norte do Paraná - Londrina PR Brazil
[3] Universidade Estadual de Campinas - Campinas SP Brazil

Fosfolipases A2 (PLA2s) são importantes enzimas que desempenham papel-chave em diversos processos celulares. PLA2s secretórias, obtidas de venenos de serpentes, tem sido utilizadas como proteínas modelo no estudo de processos inflamatórios in vitro, inclusive pela possibilidade de provocar necrose pulpar induzida por cimentos dentários (Lopes M.B., et al. Braz Oral Res 2011;25:210). Neste sentido, procuramos avaliar o efeito das modificações estruturais induzidas pelo mineral trióxido agregado (MTA), componente majoritário de cimentos dentários, sobre a estrutura de uma fosfolipase A2 de *Bothrops pirajai* (proteína modelo). Para isso, dados de Espalhamento de Raios X à Baixos Ângulos (SAXS) foram coletados na linha D11A-SAXS1 para a proteína modelo nativa e após o tratamento com o MTA e hidróxido de cálcio (usado como controle). Os dados foram processados com o programa Fit2D e outros softwares do pacote ATSAS. As análises preliminares dos dados não demonstraram grandes modificações nos valores de Rg, porém nítidas modificações em distâncias em torno de 5 foram observadas nas funções pR após o tratamento da PLA2 com Ca^{2+} e MTA. Os formatos das funções de distribuição de distância indicam uma configuração alongada para o provável dímero sugerido pelas análises com o programa SAXS MoW, assim como já foi observado em trabalhos anteriores (Santos M.L., et al. Molecules 2011;16:738). Os modelos de baixa resolução estão atualmente em construção e serão importantes para a identificação das prováveis modificações estruturais induzidas pelo MTA.

Acknowledgements: Pelo apoio técnico e financeiro do LNLS para a realização das medidas.

PREPARAÇÃO E CARACTERIZAÇÃO ESTRUTURAL DE SISTEMAS DE VESÍCULAS CONSTITUÍDOS POR LIPÍDIOS NEUTROS

Oseliero, P. L.[1], Gerbelli, B. B.[1], and Oliveira, C. L. P[1]

Universidade de São Paulo - São Paulo - São Paulo SP Brazil

Membranas lipídicas são um dos principais constituintes de sistemas biológicos. São responsáveis, por exemplo, pela interface e compartimentação das células sendo também encontradas em dispositivos celulares importantes como o Complexo de Golgi e mitocôndrias. Neste sentido, o estudo das propriedades físicas de membranas pode permitir a compreensão tanto de sua funcionalidade quanto o entendimento de diversos processos biológicos. Devido ao fato de membranas reais serem extremamente complexas, faz-se necessário realizar os estudos nas chamadas "membranas modelo", que nada mais são que membranas mais simples e cuja preparação pode ser controlada. Um dos lipídios mais utilizados para este tipo de aplicacão é a *fosfatidil colina* (PC) que em certas condições pode formar vesículas unilamelares, similares as membranas citoplasmáticas. Em experimentos recentes obtivemos a indicação de que em regime diluído (~0.5 a 2.5%, concentração em massa), sistemas constituídos por lipídio (PC) e *Simulsol* ® (na proporção 70/30, respectivamente) e água apresentam formação de vesículas unilamelares [1]. Realizando experimentos de espalhamento dinâmico de luz (DLS) constatamos que as amostras apresentaram alta polidispersidade de tamanho, variando de ~50 nm até ~2000 nm. Neste trabalho objetivamos a obtenção de protocolos de preparação de vesículas com baixa polidispersidade, o controle do seu diâmetro e também o desenvolvimento de ferramentas para análise dos dados obtidos. Para a preparação das amostras foi usada a técnica de filme fino seguida da técnica de extrusão [2] . Para a caracterização do sistema extrusado usamos as técnicas de DLS e espalhamento de raios X a baixo ângulo (SAXS). A partir da análise dos dados experimentais foi possível encontrar os parâmetros estruturais das vesículas obtidas como, por exemplo, dimensões, polidispersidade e perfil de densidade eletrônica. Estes estudos iniciais servem de base para uma caracterização sistemática deste sistema de membranas modelo, variando, por exemplo, a temperatura, força iônica, entre outros parâmetros, permitindo sua correlação com outras técnicas experimentais.

1- Oliveira CLP et al, submetido para o *Activity Report* do LNLS 2011.
2- Ting F. Zhu et al, *Preparation of Large Monodisperse Vesicles*, PlosOne, vol 4, issue 4, 2004.

Acknowledgements: Agradecemos as agências CNPq, FAPESP e INCTFCx.

Assessment of *Escherichia coli* Selenophosphate Synthetase oligomeric states by analytical ultracentrifugation and small angle X-ray scattering

Silva, I. R.[1], Faim, F. M.[1], Oliveira Neto M.[1], Borges, J.C.[2], and Thiemann, O. H.[1]

[1] Universidade de São Paulo - São Carlos - São Carlos SP Brazil
[2] Instituto de Quimica de Sao Carlos - São Carlos SP Brazil

Selenium is an essential micronutrient for many organisms and is present in selenium-containing proteins as selenocysteine (Sec) and RNAs as selenouridine. Specific selenium incorporation into selenoproteins and RNAs requires the generation of a biologically active selenium donor compound, selenophosphate, which is produced from the activation of selenide with adenosine 5-triphosphate (ATP) in a reaction catalyzed by Selenophosphate Synthetase (SELD). Therefore, SELD is a key enzyme of the selenium pathway in the cell. The *Escherichia coli* SELD open reading frame was cloned into pET28a (Novagen) expression vector and the recombinant protein was over expressed in *Escherichia coli* BL21(DE3) strain. In order to purify the protein, we used metal-chelate affinity chromatography followed by a gel filtration step. Analytical Ultracentrifugation (AUC) and Small Angle X-ray Scattering (SAXS) were employed to study the oligomeric states of the soluble protein. The results of AUC revealed dimer-tetramer and tetramer-octamer equilibrium at low concentrations of protein, with dissociation constants of 70 2 and 560 40 M, respectively. Moreover, the SAXS results pointed the oligomeric state of the protein at higher concentrations as predominantly dimeric and the p(r) and the SAXS envelope revealed the SELD as elongated. We also performed initial crystallization trials with protein samples at 7 mg/ml in 96-well sitting-drop crystallization plates at room temperature using a crystallization robot. Needle crystals appeared after some days. X-ray diffraction for these crystals were tested in the MX2 beamline at the Brazilian Synchrotron Laboratory (LNLS Campinas). We are now working to improve these crystals in order to obtain suitable crystals for structure determination.

Acknowledgements: We wish to thank LNLS and LNBio for technical support. This work has been supported by FAPESP, CNPq and CAPES.

Structural Studies of Schistosoma mansoni Adenylate Kinases

Marques, I. A.[1], Pereira, H.M[2], and Garrat, R. C.[2]

[1] Universidade Federal de Goiás - Goiânia GO Brazil
[2] Universidade de São Paulo - São Carlos - São Carlos SP Brazil

Parasitic diseases are a major cause of death in developing countries, however receive little or no attention from pharmaceutical companies for the development of novel therapies. In this respect, the Center for Structural Molecular Biology (CBME) of the Institute of Physics of São Carlos (IFSC / USP) has developed expertise in all stages of the development of active compounds against target enzymes from parasitic diseases. The present work focuses on the adenylate kinase enzymes (ADK's) from Schistosoma mansoni. These enzymes are widely distributed and catalyze the reaction of phosphoryl exchange between nucleotides in the reaction 2ADP to ATP + AMP, which is critical for the cells life cycle. Due to the particular property of the reaction catalyzed, the ADK's are recognized as reporters of the cells energetic state, translating small changes in the balance between ATP and ADP into a large change in concentration of AMP. The genome of S. mansoni was recently sequenced by the Sanger Center in England. On performing searches for genes encoding adenylate kinases we found two such genes. The corresponding gene products were named ADK1 (197 residues) and ADK2 (239 residues), and the two sequences share only 28 percent identity. Both have been cloned into the pET-28a(+)vector, expressed in E. coli and purified. Preliminary tests of activity have been performed only for ADK1 showing it to be catalytically active. Crystallization trials were performed for both proteins and thus far, crystals of ADK1 have been obtained which diffract to 2.05 at the LNLS beamline MX2 and the structure solved by molecular replacement. Understanding, at the atomic level, the function of these enzymes may help in the development of specific inhibitors and may provide tools for developing diagnostic tests for schistosomiasis.

Acknowledgements: CAPES, CNPq and FAPESP

The *cys* regulon of *Xanthomonas citri*

Moutran, A.[1] and Balan, A.[1]

Laboratório Nacional de Biociências - Brazil

In *Escherichia coli*, genes involved in metabolic pathway of sulfate and sulfonate compounds are clustered in a *cys* regulon, which includes three ABC transport system (operons: *sbpcysWUA*; *ssuABC* and *tauABC*), thirteen genes involved in the sulfur reduction (*ssuDE*; *tauD* and *cysDNCHIJGK*) and two regulatory proteins that belong to LysR transcription family: CysB and Cbl. Notably, a search and comparative analysis of these genes in the genomes of the citrus pathogen *Xanthomonas citri* and other phylogenetically related Xanthomonas species revealed the presence of genes involved with alkanesulfonate, sulfate ester and taurine, only in *X. citri*, suggesting that proteins from this regulon might be associated with pathogenicity in citrus. Using the molecular modeling associated with a system biology view, we modeled all the protein structures of the *X. citri cys* regulon as well as characterized the important residues forming the putative active sites. Comparison with orthologs from different microorganisms was made in order to get a phylogenetic relationships. We showed that proteins that are responsible for the affinity and specificity of the alkanesulfonate, sulfate and taurine transport systems conserved the residues involved in the sulfate coordination but are organized in different branches in evolution. Inside these phylogenetic branches, proteins involved in the sulfate transporter are highly conserved when compared to the others. Moreover, we identified that the taurine-binding protein (TauA) of the *X. citri* belongs to a different evolutionary branch from that one that described for *E. coli*. These differences were also noticed for components of the tau operon, including a putative new regulator. The function and mechanism of action of each protein is discussed in order to bring light for the sulfur assimilation processes and their importance for *X. citri* physiology.

key words: *cys* regulon, *Xanthomonas citri*, molecular modeling, phylogeny

Acknowledgements: FAPESP, CNPq and ABTLuS.

The weathervane model, a functional and structural organization of the two-component alkanesulfonate oxidoreductase SsuD from *Xanthomonas citri*

Pegos, V.R.[1], Oliveira,P.S.L.[2], and Balan, A.[3]

[1] Universidade Estadual de Campinas - Campinas SP Brazil
[2] Laboratório Nacional de Biociências -
[3] Laboratório Nacional de Biociências - Brazil

In *Xanthomonas citri*, the phytopathogen responsible for the canker citrus disease, we identified in the *ssuABCDE* operon, genes encoding the alkanesulfonate ABC transporter as well as the two enzymes responsible for oxidoreduction of the respective substrates. SsuD and SsuE proteins represent a two-component system that can be assigned to the group of $FMNH_2$ -dependent monooxygenases. However, despite of the biochemical information about SsuD and SsuE orthologs from Escherichia coli, there is no structural information of how the two proteins work together. In this work, we used ultracentrifugation, SAXS data and molecular modeling to construct a structural/functional model, which consists of eight molecules organized in a weathervane shape. Through this model, SsuD ligand-binding site for $NADPH_2$ and FMN substrates is clearly exposed, in a way that might allow the protein-protein interactions with SsuE. Moreover, based on molecular dynamics simulations of SsuD in apo state, docked with $NADPH_2$, FMN or both substrates, we characterized the residues of the pocket, the mechanism of substrate interaction and transfer of electrons from $NADPH_2$ to FMN. This is the first report that links functional and biochemical data with structural analyses.

Acknowledgements: FAPESP, LNBio and LNLS

Self-Assembling of Amyloid-like Proteins

Sales, E.M.[1], Damalio, J.C.P.[2], Barbosa, L.R.S.[1], Spinozzi, F.[3], Mariani, P.[3], Araújo, A.P.U.[2], and Itri, R.[1]

[1] Universidade de São Paulo - São Paulo - São Paulo SP Brazil
[2] Universidade de São Paulo - São Carlos - São Carlos SP Brazil
[3] Università Politecnica delle Marche - Ancona Italy

Septins are proteins from the GTP-binding family and participate in cell division cycle performing functions such as secretion and cytoskeletal division. They can also be found in neurodegenerative conditions as Alzheimers and Parkinsons diseases, forming highly organized fiber-like aggregates known as amyloids. In this work, we used small angle x-ray scattering (SAXS) to investigate the formation and time evolution of septins aggregates under the influence of temperature and concentration.

The SAXS measurements were performed with the GTPase domain of human Septin 2 (SEPT2G) at 0.5 and 1 mg/mL and temperatures between 4 and 45° C. At 0.5 mg/mL and 4°C, the protein self-aggregates as a dimer, being stable over one hour of observation. When the temperature was increased to 15° C, the results demonstrate that cylinder-like aggregates are formed and coexist with some dimer population and a small amount of larger aggregates. However, the number of very large aggregates increases with time concomitantly with the decrease of cylinder amount in the solution. At 37°C cylinder-like aggregates are not longer present in solution, whereas a significant amount of dimers decreases from 50% to 20% in less than 1 hour. At 45°C such an effect is even more accentuated: the percentage of dimers is only 6% in solution into a favor of 94% of very larger aggregates.

When we analyze the protein at 1 mg/mL, at 4°C cylinder-like aggregates (36 nm-long and 12 nm-cross section) are already formed, coexisting with dimers and, as occurred for lower concentration, the two populations remained unchanged over one hour of observation. Out results also indicate that the dimensions of these cylinders increase with the concentration and the percentage of cylinders and larger aggregates are higher than those found for 0.5 mg/mL. In conclusion, our results showed the coexistence of dimers of SEPT2G with small fibers and larger aggregates in solution that evolve not only with concentration and temperature but also with time.

Acknowledgements: This work is supported by FAPESP and CNPq.

Mitochondrial localization and structure-based phosphate activation mechanism of Glutaminase C with implications for cancer metabolism

CASSAGO, A[1], Ferreira, A. P. S.[2], Ferreira, I. M.[3], Fornezari, C.[4], Gomes, E.R.M.[2], Greene, K. S.[5], Pereira, H.M[6], Garratt, R. C.[6], Dias, SMG[2], and Ambrosio, A.L.B.[2]

[1] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[2] Laboratório Nacional de Biociências - Brazil
[3] Laboratório Nacional de Biociências - Campinas SP Brazil
[4] Universidade Estadual de Campinas - Campinas SP Brazil
[5] Cornell University - Ithaca NY United States of America
[6] Universidade de São Paulo - São Carlos - São Carlos SP Brazil

Glutamine is an essential nutrient for cancer cell proliferation, especially in the context of citric acid cycle anaplerosis. In this manuscript we present results that collectively demonstrate that, of the three major mammalian glutaminases identified to date, the lesser studied splice variant of the gene gls, known as Glutaminase C (GAC), is important for tumor metabolism. We show that, although levels of both the kidney-type isoforms are elevated in tumor versus normal tissues, GAC is distinctly mitochondrial. GAC is also most responsive to the activator inorganic phosphate, the content of which is supposedly higher in mitochondria subject to hypoxia. Analysis of X-ray crystal structures of GAC in different bound states suggests a mechanism that introduces the tetramerization-induced lifting of a gating loop as essential for the phosphate-dependent activation process. Surprisingly, phosphate binds inside the catalytic pocket rather than at the oligomerization interface. It also mediates substrate entry by competing with glutamate. A greater tendency to oligomerize differentiates GAC from its alternatively spliced isoform and the cycling of phosphate in and out of the active site distinguishes it from the liver-type isozyme, which is known to be less dependent on this ion.

Acknowledgements: Aknowledgements: LNBio (LPP, LEC and Robolab), LNLS (beamlines W02B-MX2 and D01A-SAXS1) and FAPESP (for financial support).

Structural and functional analyses of the putrescine binding protein PotF from *Xanthomonas citri*

Santana, L.D.F.[1] and Balan, A.[1]

Laboratório Nacional de Biociências - Brazil

The focus of our group is to determinate the role of ABC transporters in the physiology and growth of *Xanthomonas citri*, a phytopathogenic bacteria that infects citrus plants causing significant losses for the economy. One of the ABC transporters identified in the *X. citri* genome and that was showed to be active during the infection in Citrus sinensis plants was the putrescine transporter. This transporter consists of two internal membrane proteins PotG and PotH that form a pore, a cytoplasmic protein that gives energy for the transport and the periplasmic-binding protein PotF, which is responsible for the affinity and specificity of the system. Its function is associated to the microbial carcinogenesis, biofilm formation, escape from phagolysosomes, bacteriocin production, toxin activity and protection from oxidative and acid stress. In this work, we show for the first time, the expression, purification, functional and structural analyses of the *X. citri* PotF protein. The PotF was expressed from *Escherichia coli* cells strain Arctic, as a 40 kDa soluble protein, after induction of IPTG for twenty four hours at thirteen °C. Using immobilized metal affinity chromatography for purification, the protein was eluted in the fractions with 10-500 mM of imidazole. To test the folding and cability to bind putrescine, spectroscopic analyses were performed using circular dichroism and intrinsic fluorescence. The data showed that PotF suffers conformational changes in presence of ligands and in different pH, suggesting a possible interaction with the tested ligand. Moreover, based on bioinformatics studies and molecular modeling analyses, we showed that *X. citri* PotF is highly conserved when compared to orthologs present in other bacteria, including the residues that form the ligand-binding site. The production of PotF in a soluble and stable form will allow us to start the crystallization trials in attempt to solve its structure.

Acknowledgements: This work was supported by PIBIC and CNPq

Structural analysis of recombinant human protein QM

Gualberto, D. C. H.[1], Pereira, L.M.[2], Fernandes, J. L.[1], Silva, F. S.[1], Saraiva, K. W.[1], Silva, I. D. C. G.[3], and Affonso, R.[1]

[1] Instituto de Pesquisas Energéticas e Nucleares - São Paulo SP Brazil
[2] Universidade Federal de São Paulo - Diadema SP Brazil
[3] Universidade Federal de São Paulo - Sao Paulo SP Brazil

The ribosomal protein QM belongs to a family of ribosomal proteins, which is highly conserved from yeast to humans. The presence of the QM protein is necessary for joining the 60S and 40S subunits in a late step of the initiation of mRNA translation. Although the exact extra-ribosomal functions of QM are not yet fully understood, it has been identified as a putative tumor suppressor. This protein was reported to interact with the transcription factor c-Jun and thereby prevent c-Jun actives genes of the cellular growth. In this study, the human QM protein was expressed in bacterial system, in the soluble form and this structure was analyzed by Circular Dichroism and Fluorescence. The results of Circular Dichroism showed that this protein has less alpha helix than beta sheet, as described in the literature. QM protein does not contain a leucine zipper region; however the ion zinc is necessary for binding of QM to c-Jun. Then we analyzed the relationship between the removal of zinc ions and folding of protein. Preliminary results obtained by the technique Fluorescence showed a gradual increase in fluorescence with the addition of increasing concentration of EDTA. This suggests that the zinc is important in the tertiary structure of the protein. More studies are being made for better understand these results.

Acknowledgements: This work was supported by FAPESP (project 2010/52666-4) and CQMA- IPEN

Cloning, Expression, Purification and Initial Crystallographic Studies of UbiG: a Methyltransferase Involved in Ubiquinone Biosynthesis in *Escherichia coli*

Costa, M. A. F.[1], Magalhães, R. D.[1], Ferreira-Júnior, J.R.[2], Barros, M.H.[3], and Nagem, R. A. P.[1]

[1] Universidade Federal de Minas Gerais - Belo Horizonte MG Brazil
[2] Universidade de São Paulo - São Paulo - São Paulo SP Brazil
[3] Universidade de São Paulo - São Paulo - Sao Paulo SP Brazil

Ubiquinone is a molecule that functions as an electron carrier in the respiratory chain in living organisms. Some clinical phenotypes, including, encephalomyopathy, has been associated with ubiquinone deficiency, raising the interest in the biosynthetic pathway of this molecule. This pathway was proposed mainly from the results of the genetic analysis of mutants of *E. coli.* UbiG is a methyltransferase involved in ubiquinone biosynthesis in *E. coli.* In this work we have cloned, expressed, purified and made initial crystallographic assessments of UbiG for later determination of its three-dimensional structure. The gene encoding UbiG was amplified from *E. coli* genomic DNA by polymerase chain reaction. The 753 bases pairs amplicon was inserted into the expression plasmid pMCSG7 by ligation independent cloning system and transformed into BL21(DE3) *E. coli* strain. The expression of UbiG, verified by SDS polyacrylamide gel, showed a protein of approximately 29kDa after IPTG induction. The recombinant UbiG, in the soluble fraction of the cellular lysate, was purified by affinity chromatography and the molecular weight of recombinant UbiG of approximately 29 kDa was confirmed by mass spectrometry. After removal of His-tag by TEV protease, another affinity chromatography was performed and UbiG, without His-tag, was observed in flow-through fraction. In Size-Exclusion Chromatography (SEC), the recombinant UbiG showed a unique peak with correct molecular weight of a monomer. Analysis of CD indicated that recombinant UbiG has 31,80% of alpha helix at 20^{O}C and DLS showed that 70.9% of the sample is still monomeric in solution even five days after purification. Initial crystallization studies were performed with Crystal Screen 1 and Crystal Screen 2 from Hampton Research. Needle-shaped microcrystals of UbiG were obtained using a precipitant solution consisting of 0,1M lithium sulfate, 0,1M Tris pH 7,5 and 30% w/v polyethylene glycol 4,000.

Acknowledgements: This work was supported by FAPESP and CNPq

Estudos estruturais das Glutaminases por Microscopia Eletrônica

CASSAGO, A[1], Ferreira, I. M.[2], Ferreira, A. P. S.[3], Bettini J.[1], Portugal, R. V.[1], Dias, SMG[3], and Ambrosio, A.L.B.[3]

[1] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[2] Laboratório Nacional de Biociências - Campinas SP Brazil
[3] Laboratório Nacional de Biociências - Brazil

A proliferação celular em mamíferos é controlada por fatores de crescimento através de vias de sinalização específicas para os diferentes tipos celulares. Entretanto, em células tumorais, essas mesmas vias tornam-se constitutivamente acionadas direcionando, entre outros, a biossíntese de lipídeos, proteínas e ácidos nucléicos, indispensáveis para a proliferação celular. A multiplicação celular acelerada é associada à glicólise aeróbica, também conhecida como Efeito Warburg em que a maioria do carbono derivado do consumo de açúcar é secretado na forma de lactato. Somado ao Efeito Warburg, a glutaminólise auxilia as células tumorais a suprirem tanto a demanda por metabólitos do ciclo do ácido tricarboxílico, como por NADH e glutationa. Dessa maneira, tanto a glicólise aeróbica como a glutaminólise são mecanismos rápidos e eficientes na incorporação de biomassa em neoplasmas. Nosso estudo foca nas enzimas glutaminases, componente do primeiro passo da glutaminólise. Duas isoenzimas são expressas, a GLS1 e GLS2, sendo que a GLS1 formada por duas isoformas produtos de splicing alternativo, KGA Kidney type Glutaminase e GAC Glutaminase C, enquanto a GLS2 pela isoforma LGA Liver type Glutaminase. Dados do nosso laboratório tem mostrado que a isoforma GAC apresenta maior eficiência catalítica em relação ao substrato glutamina e em resposta ao ativador fosfato (o qual, entre outros, leva a tetramerização da enzima) quando comparada a KGA, enquanto a LGA é aparentemente insensível a este ativador. Mais, temos verificado que, na presenca de fosfato, tanto KGA quanto GAC formam oligômeros maiores que tetrâmeros. Estes super-oligômeros são aparentemente importantes para a atividade, dado que mutações que levam à um aumento na atividade de glutaminase da GAC também facilitam a formação dos mesmos. Visando um melhor entendimento da organização quaternária, massa molecular e estrutura destes super-oligômeros empregamos a técnica de microscopia eletrônica de transmissão aliada a análises de raio de Stokes (Rs) por Dynamic Light Scattering e cromatografia por exclusão de tamanho (Superose 6 PC 3.2/30 GE). Resultados preliminares indicaram que os super-oligômeros se associam como octâmeros pelas extremidades N- e C-terminal das proteínas.

Acknowledgements: Esse trabalho é financiado pela FAPESP (2010/059870)

Structural Studies of Alternative Oxidase (AOX) from *Moniliophthora perniciosa*, the Causal Agent of Witches' Broom Disease in Cacao: a Membrane-Associated Protein

Oliveira, J. F.[1], Prado, P. F. V.[1], Tiezzi, H.O.[1], Thomazella, D. P. T.[2], Teixeira,P.J.P.L[2], Dias, SMG[1], Pereira, G. A. G.[2], and Ambrosio, A.L.B.[1]

[1] Laboratório Nacional de Biociências - Campinas SP Brazil
[2] Universidade Estadual de Campinas - Campinas SP Brazil

Alternative oxidase (AOX) is a protein attached to the inner mitochondrial membrane that receives electrons directly from reduced ubiquinone and catalyzes the reduction of oxygen to water. AOX is a non-proton motive terminal quinol oxidase that enables cell respiration to continue even in the presence of inhibitors targeting the complexes of the respiratory chain. This protein is present in higher plants, pathogenic fungi and some parasites. The structural characterization of AOX becomes interesting due to its potential as a fungicide target. AOX is predicted to be a monotopic interfacial membrane protein interacting with a single leaflet of the lipid bilayer, rather than transmembrane. Amino acid sequence analysis reveals the presence of two conserved glutamate-histidine motifs, identifying it as a member of the diiron carboxylate protein family. The AOX model is defined by two pairs of helices forming a four helix bundle and an additional hydrophobic connecting sequence between the two helical pairs is proposed to act as the membrane anchoring region. In this work we aim at production, purification and crystallization of the AOX protein from *M. perniciosa* for further structural studies of this membrane-associated protein, by X-ray protein crystallography.

Juliana F. Oliveira and Paula F. V. Prado contributed equally to this work.

Acknowledgements: LNBio and FAPESP

The crystal structure of the hexameric purine nucleoside phosphorylase from *Bacillus subtilis* in complex with adenosine

Giuseppe, P. O.[1], Meza, A. N.[1], Martins, N. H.[1], Santos, C. R.[1], and Murakami, M. T.[1]

Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

Purine nucleoside phosphorylases (PNPs) play a key role in the purine-salvage pathway in both prokaryotes and eukaryotes. Its ribosyltransferase activity is of great biotechnological interest due to potential application in the synthesis of nucleoside analogues used in the treatment of antiviral infections and in anticancer chemotherapy. Trimeric PNPs are found mainly in vertebrates and are specific for 6-oxo-purines whereas hexameric PNPs are prevalent in prokaryotes and exhibit a broad range of substrates including 6-oxo and 6-amino purines. BsPNP233, the hexameric PNP from *B. subtilis*, is able to catalyze the bioconversion of ribavirin, an anti-viral drug, and is relatively thermostable, being a good target for industrial use. Here we report the crystal structures of BsPNP233 in the apo form and in complex with adenosine solved at 2.65 and 1.91 resolution, respectively. The apo and ligand-bound BsPNP233 subunits superposed with an overall r.m.s. deviation of 0.31 for all $C\alpha$ atoms, which suggests that no major conformational changes occur upon substrate binding. Based on the crystal structure of BsPNP233 in complex with adenosine we have defined the active site residues implicated in binding the ribose (H4*, R43*, M64, R87, E178, M179, E180) and the nitrogenous base (S90, C91, G92, S202, V177, F159). These residues are highly conserved among the bacterial hexameric PNPs, suggesting they share the same mode of interaction with the substrates. This work will probably contribute to a better understanding of the molecular basis for the broad substrate specificity of hexameric PNPs and to projects aiming the rational design of PNPs for industrial purposes.

Acknowledgements: This work was supported by CNPEM/ABTLuS. We gratefully acknowledge Dr. Humberto M. Pereira for kindly provide the adenosine used in this work.

Determination of the structure of Thiol-Specific Antioxidant (Tsa 2) of *Saccharomyces cerevisiae*.

Breyer, C.A.[1] and Oliveira, M.A.[2]

[1] Universidade Federal de São Carlos - São Carlos SP Brazil
[2] Universidade Estadual Paulista Julio de Mesquita Fillho - Assis SP Brazil

The Peroxiredoxin (Prx), is a group of antioxidant proteins that have been widely studied for its role in the decomposition of several species of peroxides such as hydrogen peroxide, peroxynitrite and organic hydroperoxides using two highly reactive cysteines, named cysteine peroxidatic (Cys_P) and resolve cysteine ($Cys\ _R$), present in the active site. In *Saccharomyces cerevisiae* were identified five Prx isoforms, three cytosolic (Tsa1, Tsa2 and Ahp1), a mitochondrial (mTPx) and a nuclear one (nTPx). Tsa1 and Tsa2 are homodimers that in heat shock or oxidative stress form complex structures of high molecular-weight with chaperone function. These proteins are very similar (86% identity and 96% similarity) but despite this structural similarity it has been shown that they present different functions: Tsa1 is mainly involved in the response to oxidative stress while Tsa2 is involved in signal transduction. Tsa1 was already crystallized and a structural model was generated, but Tsa2 structural studies were not performed. The research goal is the determination of the structure of Tsa2. The initial screening experiments of crystallization using the kits CS1 and CS2 (Hampton Research) showed favorable results when the conditions were 0,1M sodium acetate trihydrate pH 4.6 and 8% polyethylene glycol 4000. To improve our results the crystallization condition is been refined using variations of pH and concentration of polyethylene glycol 4000. We believe that the results of this study may contribute significantly to the understanding of the formation of overoxidized forms and cellular functions of Tsa2.

Acknowledgements: This work was supported by FAPESP

Microscopia Eletrônica de Transmissão Aplicada à Biologia Molecular Estrutural

Bettini J.[1] and Portugal, R. V.[1]

Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

O estudo de complexos biológicos macromoleculares por técnicas de microscopia eletrônica de transmissão vem sendo feito ao longo das últimas décadas. A utilização de sais de metal pesado para o preparo de amostras biológicas é uma técnica efetiva para melhoria do contraste apresentado por imagens de macromoléculas biológicas. Embora a técnica de coloração negativa permita um significativo avanço na visualização das imagens, ainda apresenta sérias limitações, entre elas a possibilidade de deformação estrutural da molécula. Com o desenvolvimento da técnica de preparação de amostras em gelo amorfo, o uso da microscopia eletrônica de transmissão, como ferramenta de biologia molecular estrutural, atingiu um novo patamar. O congelamento rápido da amostra evita a formação de cristais de gelo, preservando a integridade estrutural da molécula. O preparo de amostras em gelo amorfo, aliado aos métodos de análise de partícula única e o recente aumento de poder computacional disponível em computadores e clusters, fez com que a crio-microscopia eletrônica (crio-ME) de partícula única se firmasse como uma importante técnica de biologia molecular estrutural. Esta técnica possibilita a resolução de estruturas de complexos macromoleculares com massa de centenas de kDa a vários MDa, permitindo ainda a análise de diferentes conformações estruturais encontradas em solução. O Centro Nacional de Pesquisa em Energia e Materiais (CNPEM) está implantando no Laboratório Nacional de Nanotecnologia (LNNano) a infraestrutura necessária para a análise de complexos macromoleculares por microscopia eletrônica de transmissão.

Acknowledgements: Centro Nacional de Pesquisa em Energia e Materiais (CNPEM)

Redox dependent changes in the Structure of the Yeast Tsa1p peroxidase

Tairum Jr, C.A.[1], Bagini, R.H.[2], Netto, L.E.S.[3], and Oliveira, M.A.[2]

[1] Universidade de São Paulo - São Paulo - São Paulo Brazil
[2] Universidade Estadual Paulista Julio de Mesquita Fillho - Assis SP Brazil
[3] Universidade de São Paulo - São Paulo - São Paolo SP Brazil

Peroxiredoxins (Prx) comprises a group of peroxidases ubiquitously distributed among the organisms. These proteins make use of a reactive cysteine residue to efficient reduce hydroperoxides. Some Prx possesses a second cysteine residue (resolving cysteine) which can make a disulfide bond during the catalytic cycle. Since the two cysteines residues are far apart in the reduced state (10), it is necessary the partial unfolding of α-helix containing peroxidatic cysteine. Therefore, 2-Cys Prx alternate between two states:locally unfolded (LU), when the cysteines are oxidized to disulfide, and fully folded (FF), when the cysteines residues are reduced. However, forces that drive structural transitions are still poorly understood. Recently, we have shown that to the peroxiredoxin Tsa1 from *Saccharomyces cerevisiae*, the substitution of an arginine residue (146) by a glutamine, resulted in a decay of Tsa1 reactivity and alterations of it quaternary structure, as asserted by biochemical assays and size exclusion chromatography. Aiming to investigate in detail the molecular effects of the R146Q substitution, we have screened several crystallization conditions. The refinement of an initial hit (100mM Tris-HCl pH 7.0/10

Acknowledgements: This work was supported by FAPESP and CNPq.

Parte II

Biologia Molecular e Química de Proteínas

Scattering Studies on cryoglobulins stability and aggregation properties

Bicev, R. N.[1], BRANDÃO, H.[2], ANDRADE, L. E. C.[3], Oliveira, E. A.[1], and Oliveira, C. L. P[1]

[1] Universidade de São Paulo - São Paulo - São Paulo SP Brazil
[2] Universidade de São Paulo - São Paulo - Sao Paulo SP Brazil
[3] Universidade Federal de São Paulo - Sao Paulo SP Brazil

Cryoglobulins are proteins of the immunoglobulin(Ig) type, which play an important role in infections, autoimmune diseases and neoplastic disorders[1]. When in abnormal concentrations in the blood, cryoglobulins can aggregate and precipitate at temperatures below $37°C$, forming large complexes with dimensions in the range of 40 nm up to 1 μm depending on the temperature, leading to damage of arteries and veins of small caliber. The objective of this study is to investigate the aggregation dynamics of crygoblulin solutions through scattering techniques as SAXS (small angle X-Ray scattering). For the SAXS measures it was used the protein in aqueous and the system temperature was varied between $38.5°C$ and $4°C$. The protein concentration was 10mg/mL.The GNOM [2] program was used for the first data analysis. This program performs the Fourier transform (IFT) of the scattering data, which provides the overall particle size, radius of gyration and some indications of the particle shape. The IFT analysis can be used to the so called ab initio modeling which provides a three-dimensional model for particle shape. This model was an attempt to obtain a real space representation for the particle system. Although it was possible to verify difference in the particle diameter for the different temperatures, the models provide a branched structure which can indicate polydispersity of shapes/sizes and also flexible structures. Interestingly, the construction of Kratky Plots, $(I \cdot q^2 \ vs \ q)$, wich provide the compactness degree of a structure, indicated that the particles were highly flexible. Therefore another model procedure, which models the protein as polymer-like structure[3], have to be used. Using the recently developed Ensemble Optimization Method (EOM) [4] it was possible to obtain a very good fit for the experimental dataset, the distributions of radius of gyration and also three-dimensional representations of the possible configurations for the protein in solution in each temperature.

[1]Dammacco F. et al. Eur J Clin Invest 2001; 31:628-38.
[2]Semenyuk V and Svergun DI. J. Appl. Cryst., 1991, 24, 537-540;
[3]SCHMIDT, Manfred; BURCHARD, Walter. Macromolecules, 1981, 14, 210-211
[4]BERNADÓ, Pau et al. JACS, 2007, 129, 17, 5656-5664.

Acknowledgements: This work was supported by CAPES, Cnpq, FAPESP, INCT-GFCx.

Study of protein and metabolic profile of sugarcane workers

Polachini, G. M.[1], Santos, U. P.[2], Zeri, A. C. M.[3], Paes Leme, A.F.[3], and Tajara, E.H.[1]

[1] Faculdade de Medicina de São José do Rio Preto - São José do Rio Preto SP Brazil
[2] Universidade de São Paulo - São Paulo - Sao Paulo SP Brazil
[3] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

The National Alcohol Program (Proálcool) is a successful Brazilian renewable fuel innitiative aiming to reduce the countrys oil dependence. Producing ethanol from sugar cane, the program has shown positive results although accompanied by potential damage. The environmental impact mainly derives from the particulate matter emissions due to sugarcane burning, which is potentially harmful to human health. The physical activity of sugarcane workers is repetitive and exhaustive and is carried out in presence of dust, smoke and soot. The efforts by the sugarcane workers during the labor process result in increased risks of nervous, respiratory and cardiovascular system diseases and also in premature death. The aim of the present study was to investigate the effect of occupational stress on protein and metabolic profile of sugarcane workers. Forty serum samples were analyzed by 1-DE and LC MS/MS proteomic shotgun strategy and nuclear magnetic resonance (NMR). A set of proteins was found to be altered in workers after crops when compared with controls. The analysis of NMR spectra by Chenomx also showed differences in the expression of metabolites. For example, lactate displayed higher levels in control subjects than in sugarcane workers, and vice versa for the acetate. The concentrations of the two metabolites were lower after the crop, except in the case of acetate, which remained uniform in the control subjects before and after the crop. The present findings can have important application for rational designs of preventive measures and early disease detection in sugarcane workers.

Acknowledgements: This work was supported by CNPq and FAPESP.

Characterization of the Sulfate Uptake and Assimilation Pathway from *Xanthomonas citri* - targets for bacterial growth inhibitors

TAMBASCIA, C.[1] and Balan, A.[1]

Laboratório Nacional de Biociências - Brazil

Microorganisms require sulfur for growth and obtain it either for inorganic sulfate or organosulfur compounds. ATP-Binding Cassete (SulT family) or major facilitator superfamily-type (SulP) transporters are responsible for the sulfate transport into the cell. In *Xanthomonas citri*, the phytopathogenic bacterium that causes the canker citrus disease, there are no reports related to the importance of these transporters during in vitro or in vivo infection. We identified in *X. citri* genome all the genes that belong to the well-characterized *cys* regulon from *Escherichia coli* and *Salmonella typhimurium*, which includes three ABC transporters and all the enzymes necessary for sulfate oxidereduction to sulfide and cysteine. Once these genes have been shown to be extremely important for bacteria growth and development in different environments, we chose the *sbpcysWUA* and *cysDNCHIJG* operons, which encodes the ABC inorganic sulfate ABC transporter and all the enzymes necessary for conversion of sulfate in cysteine, respectively. As a step for crystallization trials and resolution of their tridimensional structures, the referred genes were amplified and cloned into the cloning vector pGEM T-easy. In addition, using bioinformatics tools and molecular modeling we characterized all the protein functions as well as built tridimensional models of their structure for determination of the active sites. The importance of each protein is discussed aiming the discovery of a good target for development of inhibitors that could block the bacterium growth.

Acknowledgements: This work has been supported by FAPESP.

Caracterização estrutural e funcional da enzima Liver-Type Glutaminase

Ferreira, I. M.[1], Dias, SMG[1], and Ambrosio, A.L.B.[1]

Laboratório Nacional de Biociências - Brazil

Descobertas por Hans Krebs há quase cem anos, as glutaminases mitocondriais de mamíferos se mostraram enzimas altamente complexas em termos de sequência primária, levando à especulação sobre possíveis funções adicionais dentro das células além da atividade catalítica sobre o aminoácido glutamina. Mamíferos contêm dois genes distintos, mas estruturalmente relacionados, que codificam para pelo menos três diferentes isoenzimas conhecidas como Kidney-type Glutaminase (ou KGA), Glutaminase C (ou GAC) e Liver-type Glutaminase (também conhecida como LGA). Uma das características mais importantes dessas proteínas é o padrão de expressão alterado em tecidos tumorais. Resultados recentes obtidos em nosso laboratório, que já estuda de maneira aprofundada as isoformas KGA e GAC, demonstram que LGA possui propriedades catalíticas distintas quando comparadas com demais, inclusive na resposta ao ativador fosfato inorgânico. Sua seqüência primária sugere ainda a possibilidade de que LGA possa interagir com outras proteínas em diferentes organelas além da mitocôndria, participando inclusive de maneira direta na regulação de expressão gênica. Dentro desse contexto, e de acordo com a linha de pesquisa corrente, o projeto proposto visa estudos estruturais, funcionais e mutacionais da glutaminase LGA, de maneira a descrever e entender os detalhes que a diferencia das outras duas enzimas, e que, em conjunto com o conhecimento acumulado na literatura, possam vir auxiliar no entendimento do fenômeno da expressão seletiva em diferentes tecidos e múltipla localização intracelular.

Acknowledgements: Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP)

ANALYSIS OF MEMBRANE PROTEOME AND SECRETOME IN CELLS OVER-EXPRESSING ADAM17 USING QUANTITATIVE PROTEOMICS

Kawahara, R.[1], Yokoo, S[2], Simabuco, F. M.[3], Sherman, N[4], and Paes Leme, A.F.[2]

[1] Laboratório Nacional de Biociências - Brazil
[2] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[3] Laboratório Nacional de Biociências - Campinas SP Brazil
[4] University of Virginia - Charlottesville VA United States of America

A disintegrin and metalloproteinase (ADAM) protease is involved in proteolytic ectodomain shedding of several membrane-associated proteins and modulation of key cell signaling pathways in the tumor microenvironment. In this study, we examined the effect of over-expressing the full length human ADAM17 in membrane and secreted proteins. To this end, we constructed a stable Flp-In T-RExHEK293 cells expressing ADAM17 by tetracycline induction. These cells were grown in Dulbeccos modified Eagles medium containing light lysine, arginine or heavy, L-Arg -13C615N4 and L-Lys -13C615N2 (SILAC: stable istope labeling with amino acid in cell culture) media and they were treated with an ADAM17 activator, phorbolester (PMA). Controls such as Flp-In T-RExHEK293 cell without PMA treatment and without ADAM17 cloned were cultivated in light medium. The ADAM17 over-expression was induced with tetracycline 500 ng/ml for 24 hours. Cells in a heavy condition were treated with PMA 50 ng/ml for 1 hour and vehicle DMSO was used as control in a light cell condition. The extracellular media were collected, concentrated and used to evaluate the secretome and a cell surface biotinylation-based approach was used to capture cell surface-associated proteins. The biotinylated proteins were eluted with dithiothreitol, alkylated with iodoacetamide and then digested with trypsin. The resulting peptides were subjected to LC-MS/MS analysis on an ETD enabled Orbitrap Velos instrument. The results showed different proteins up or down regulated in membrane and secretome analysis which might represent potential molecules involved in signaling or ADAM17 regulation events.

Acknowledgements: Mass Spectrometry Laboratory, LNBio

Preliminary identification of secreted proteins by Leptospira interrogans serovar Kennewicki strain Pomona Fromm

Ricardi, L.M.P.[1], Portaro FC[2], Morais, Z.M.[3], Vasconcellos, S.A.[3],
Barbosa,A.S.[4], and Abreu, P. A. E.[1]

[1] Instituto Butantan - São Paulo sp Brazil
[2] Instituto Butantan - São Paulo SP Brazil
[3] Universidade de São Paulo - São Paulo - Sao Paulo SP Brazil
[4] Instituto Butantan - São Paulo SP Brazil

This project aimed to identify secreted proteins by pathogenic Leptospira interrogans serovar Kennewicki strain Pomona Fromm (LPF) by proteomic analyses. The strain LPF, whose virulence was maintained by passages in hamsters, were cultured in EMJH medium. The supernatants were centrifuged, dialyzed and subjected to lyophilization. Protein samples were resolved first by IEF at pH 3 to 10, immobilized pH gradient 13-cm strips. Strips were then processed for the second-dimension separation on SDS-polyacrylamide gels. Proteins from gel spots were subjected to reduction, cysteine-alkylation, and in-gel tryptic digestion, and analyzed by LC/MS/MS spectrometry. Liquid chromatography-based separation followed by automated tandem mass spectrometry was also used to identify secreted proteins. In silico analyses were performed using the PSORTbV.3.0 program and SignalP server. One major obstacle to secretome studies is the difficulty to obtain extracts of secreted proteins without citoplasmatic contamination. In addition, the extraction of low concentration proteins from large volumes of culture media, which are rich in salts, BSA and other compounds, frequently interfere with most proteomics techniques. For these reasons, several experimental approaches were used to optimize the protocol applied. In spite of this fact, our analysis resulted in the identification of 200 proteins with high confidence. Only 5 of 63 secreted proteins predicted by in silico analysis were found. Other classes identified included proteins that possess signal peptide but whose cellular localization prediction is unknown or may have multiple localization sites, and proteins that lack signal peptide and are thus thought to be secreted via nonconventional mechanisms or resulting from cytoplasmic contamination by cell lysis. Many of these are hypothetical proteins with no putative conserved domains detected. To our knowledge, this is the first study to identify secreted proteins by leptospires using a proteomic approach. The identification of these proteins will contribute to the elucidation of the pathogenic mechanisms and development of novel strategies for the treatment and prevention of leptospirosis.

Acknowledgements: LNBio/LNLS, CNPq, CAPES and FAPESP (2010/51215-9)

Exploration of soil metagenome diversity for prospection of enzymes involved in lignocellulosic biomass conversion

Alvarez, T.M.[1], Paixão, D. A. A.[2], Franco Cairo, J.P.L[2], Buchli, F.[2], Ruller,R.[3], Prade, R.[4], and Squina, F. M.[1]

[1] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[2] Laboratório Nacional de Ciência e Tecnologia do Bioetanol - Campinas SP Brazil
[3] Laboratório Nacional de Ciência e Tecnologia do Bioetanol - CAMPINAS SP Brazil
[4] Oklahoma State University - Sillwater OK United States of America

Metagenomics allows access to genetic information encoded in DNA of microorganisms recalcitrant to cultivation. They represent a reservoir of novel biocatalyst with potential application in environmental friendly techniques aiming to overcome the dependence on fossil fuels and also to diminish air and water pollution. The focus of our work is the generation of a toolkit of lignocellulolytic enzymes from soil metagenome, which could be used for second generation ethanol production. Environmental samples were collected at a sugarcane field after harvesting, where it is expected that the microbial population involved on lignocellulose degradation was enriched due to the presence of straws covering the soil. Sugarcane Bagasse-Degrading-Soil (SBDS) metagenome was massively-parallel-454-Roche-sequenced. We identified a full repertoire of genes with significant match to glycosil hydrolases catalytic domain and carbohydrate-binding modules. Soil metagenomics libraries cloned into pUC19 were screened through functional assays. CMC-agar screening resulted in positive clones, revealing new cellulases coding genes. Through a CMC-zymogram it was possible to observe that one of these genes, nominated as E-1, corresponds to an enzyme that is secreted to the extracellular medium, suggesting that the cloned gene carried the original signal peptide. Enzymatic assays and analysis through capillary electrophoresis showed that E-1 was able to cleave internal glycosidic bonds of cellulose. New rounds of functional screenings through chromogenic substrates are being conducted aiming the generation of a library of lignocellulolytic enzymes derived from soil metagenome, which may become key component for development of second generation biofuels.

Acknowledgements: This work is funded by FAPESP

Mass Spectrometry reveals Thioredoxin-1 as a new partner of ADAM17 that can modulate its sheddase activity

Aragão, A. Z. B.[1], Simabuco, F. M.[2], Yokoo, S[3], Smetana, J. H. C.[1], Rodrigues, E.[4], Mercadante, A. Z.[4], and Paes Leme, A.F.[3]

[1] Laboratório Nacional de Biociências - Brazil
[2] Laboratório Nacional de Biociências - Campinas SP Brazil
[3] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[4] Universidade Estadual de Campinas - Campinas SP Brazil

ADAMs are a family of membrane-associated metalloproteinases with a complex multi-domain structure: a metalloproteinase domain, a disintegrin domain, a cysteine-rich region, an epidermal growth factor-like repeat, a transmembrane domain and a cytoplasmic tail. These proteases are responsible for shedding the ectodomains of cell surface proteins, modulating regulatory mechanisms. Many ADAMs are highly associated with tumorigenesis and tumor progression. The aim of this study is identify novel binding partners that can modulate ADAM17 activation via cytoplasmatic domain. We performed the cloning and overexpression of the ADAM17 cytoplasmic tail in HEK-293 cell line and the ligands were determined by LC-MS/MS after proteins immunoprecipitation (IP) with anti-FLAG M2 Affinity Gel (Sigma). Thioredoxin-1 (Trx-1) and others ligands were identified at least in two independent experiments, and this binding is independent of phosphorylation. The IP of Trx-1 was confirmed by Western blot, furthermore Trx-1 immunolocalized with full length ADAM17-HA and cytoplasmic tail-FLAG recombinant proteins in HEK293 and HeLa cells. Trx-1 is part of the system peroxiredoxin/thioredoxin/thioredoxin reductase, one of the mechanisms by which cells maintain the reduced cellular environment, inactivating the reactive oxygen species (ROS). We investigate whether ADAM17 activity is modulate by Trx-1 on AP reporter assay that was performed using HEK293 and SCC-9 cells transfected stably with HB-EGF-AP in co-transfection with transient recombinant Trx-1-HA. The results indicate that Trx-1 can modulate negatively the activity or maturation of ADAM17 in presence of PMA, which is known to increase ROS. In summary, this study identifies Trx-1 and suggest that this protein can modulate ADAM17 activity in normal and tumorigenic cells lines.

Acknowledgements: This study was supported by Fapesp

Expression, purification and spectroscopic characterization of the Ragulator Complex

Nogueira, M. L. C.[1], Ospina-Bedoya M.[2], Silva, A. L. S.[1], Camilotti, D.[1], SILVA, C. A.[1], Sforça, ML[1], Smetana, J. H. C.[3], and Zeri, A.C. ; Zeri, A.C.M, de Mattos Zeri, A.C.[1]

[1] Laboratório Nacional de Biociências - Campinas SP Brazil
[2] Universidad de Antioquia - Medellín Colombia
[3] Laboratório Nacional de Biociências - Brazil

The mammalian target of rapamycin (mTOR) signaling pathway integrates both intracellular and extracellular signals, serves as a central regulator of cell metabolism in humans and its deregulation is linked to diseases like cancer and diabetes. The small GTPases Rag are mediators of signaling by amino acid (leucine). These GTPases are anchored on the surface of the lysosome through an interaction with a complex of three proteins, p18, MP1 and p14, called Ragulator. The p18 protein is responsible for interaction with the lysosomal membrane through its N terminal post translational modification. The objective of this project is to study the interaction of p18 and other components of the Ragulator complex. The p18 protein was expressed in inclusion bodies, which were isolated and solubilized in urea. p18 was renatured with its partners MP1/p14 and this complex, the Ragulator, was subjected to spectroscopic characterization using circular dichroism and dynamic light scattering.

Acknowledgements: This work was supported by CAPES and FAPESP

Estudo da importância da interação da Liver-type Glutaminase com a Glutaminase Interacting Protein-1 para o metabolismo celular

Saez, R. C.[1], Gonçalves, K. A.[1], and Dias, SMG[1]

Laboratório Nacional de Biociências - Brazil

Células tumorais apresentam um metabolismo energético e biossintético diferenciado quando comparado ao das células não transformadas, sendo caracterizado pela intensa glicólise mesmo na presença de oxigênio (Efeito Warburg). Uma das consequências do aumento da glicólise é a diminuição no aporte de piruvato para a mitocôndria, o que contribue para o truncamento do ciclo do ácido tricarboxílico (TCA). Para a manutenção da alta taxa mitótica, as células neoplásicas utilizam a via da glutaminólise para manter o ciclo do TCA, uma importante fonte de metabólitos precursores de macromoléculas, em funcionamento. Já foram identificadas três isoformas das glutaminases em mamíferos: a Kidney-type glutaminase (KGA), Glutaminase C (GAC), e a Liver-type glutaminase (LGA). A LGA foi recentemente caracterizada como um alvo do regulador transcricional p53, um conhecido supressor de tumor, tendo sido proposto como o intermediador das funções de regulador do metabolismo energético e de defesa antioxiante do p53. Estes achados indicam que a supressão de sua expressão pode ser um dos fatores dirigentes ou de suporte ao crescimento tumoral. Além disso, esta isoenzima apresenta outros domínios além do catalítico, como repetições de contatos proteína-proteína do tipo ankirin, e domínios de interação com regiões PDZ. Estudos revelaram que a proteína GIP-1 (Glutaminase Interacting Protein)/TIP-1 (Tax interacting protein 1) é um parceiro de interação da enzima LGA, cuja interação foi confirmada em células nervosas. O entendimento das funções extra-enzimáticas da LGA ajudará a compreender a importância desta enzima para o processo de crescimento celular assim como processos celulares ainda desconhecidos. Este trabalho envolve a caracterização da interação da LGA com a GIP-1 em células epiteliais mamárias não-transformadas (HMEC) e transformadas (SKBR3) através das técnicas de co-imunoprecipitação e co-localização. Para tanto, as proteínas LGA e GIP foram clonadas em pCDNA 3.1 V-5/His TOPO (LGA), pEGFP (LGA), pCDNA 6 Flag (GIP-1) e pDsRe-Monomer (GIP-1). O objetivo a longo prazo é determinar a importância desta interação para a localização celular da LGA assim como de sua função no balanço redox da célula.

Acknowledgements: À FAPESP pelo apoio financeiro.

MOLECULAR MASS DISTRIBUTION AND EPITOPES OF THE BETA LACTOGLOBULIN SUBMITTED TO HYDROLYSIS PRE-TRANSGLUTAMINASE TREATMENT

Villas-Boas, M.B[1], Paes Leme, A.F.[2], Benede, S.[3], Molina, E.[3], Zollner, R.L[1], and Netto, F.M.[1]

[1] Universidade Estadual de Campinas - Campinas SP Brazil
[2] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[3] Universidad Autónoma de Madrid - Spain

The β-Lactoglobulin (β-Lg) is a whey protein with important nutritional properties but very resistant to pepsin digestion and consequently highly antigenic. This protein can be modified by transglutaminase (TG) although it is required a pre-treatment to increase their susceptibility to the TG action. In the present study the hydrolysis pre-TG treatment was used to improve the TG accessibility on β-Lg and the MM distribution and antigenic fragments were evaluated. For pre-TG treatment, the β-Lg (Davisco Inc.) was hydrolyzed with bromelain (3% of β-Lg w/w in distilled water; 25 U enzyme g $^{-1}$ of substrate, pH 7.5, 240 min) and then polymerized by TG (7% hydrolysate, 10U TG g^{-1} protein, 50 C/180 min). The samples were evaluated by SDS-PAGE/tricine and by RP-nanoUPLC (nanoAcquity UPLC, Waters) coupled with nano-electrospray tandem mass spectrometry on a Q-Tof Ultima API mass spectrometer (MicroMass/Waters) at LNBio. The products were also submitted to pepsin digestion and the peptide identification was performed by RP-HPLC-tandem mass spectrometry (RP-HPLC-MS/MS, Brucker) with support from CIAL. The β-Lg hydrolysed by bromelain and polymerized by TG had a broad MM distribution. The intact mass analysis indicated that the nonmodified βLg -A showed 18.362 Da and the nonmodified βLg -B 18.274 Da, which is in agreement with the theoretical corresponding masses. The use of bromelain pre-TG treatmen resulted in polymers with MM from 61.052 to 67.654 Da, although some nonmodified protein was still present. In addition, the nonmodified β-Lg showed fragments that present high antigenicity (such as Leu$_{95}$ - Leu$_{104}$, Asp$_{95}$ - Phe$_{105}$, Tyr$_{42}$ - Leu$_{54}$, lle$_{29}$ - Val$_{41}$), previously identified as IgE-binding epitopes. After hydrolysis following by TG treatment the fragment Tyr$_{42}$ - Leu$_{54}$ was still present, however the other fragments that were observed in the nonmodified β-Lg were not detected by LC-MS/MS, suggesting that structural change occurred in the protein after hydrolysis and polymerization and also resulted in low amount of fragments that could promote antigenic response.

Acknowledgements: FAPESP, CNPq and LNBio, CNPEM/ABTLus (Brazil), CIAL (Spain)

Investigation of biological partners by ESI Q-TOF Mass Spectrometry of *Saccharomyces cerevisiae* Cytosolic Thioredoxin Peroxidase I (cTpxI) and III (cTpxIII) by oxidative stress

Andrade,L.M.[1], Ishikawa, AK[2], and Oliveira, M.A.[1]

[1] Universidade Estadual Paulista Julio de Mesquita Fillho - Assis SP Brazil
[2] Universidade Estadual Paulista Julio de Mesquita Fillho - - São Vicente SP Brazil

One of the oxidative protective mechanisms present in the cell is the peroxiredoxin family. This class of enzymes, present in prokaryotes and eukaryotes, promotes the elimination of H_2O_2 and alkyl hydrogen peroxides using reactive cysteines named peroxidatic cysteine (Cys_p) and resolving cysteine (Cys_r). Five peroxiredoxins have been discovered in *Saccharomyces cerevisiae*, three are cytosolic, one is mitochondrial, and another is nuclear. The present work aims the identification of $cTPxI^{c170S}$ and $cTPxIII^{c120S}$ biological partners linked by mixed disulfide bonds in response to H_2O_2 and t-BOOH oxidative stress. We generated mutant $cTPxI^{c170S}$ and $cTPxIII^{c120S}$, purified by IMAC, treated with DTT, incubated with crude protein extracts of yeast ΔcTPxI/ΔcTPxII or ΔAHPI and challenge to H_2O_2 or t-BOOH to promote complexes formation. After the complexes were submitted to analysis by ESI Q-TOF mass spectrometry and processed using MASCOT MS/MS Ion Search. At present our results indicate interactions between $cTPxI^{c170S}$ and GSF2, a membrane protein that provides the secretion of hexose transporters; OMS1, a mitochondrial protein with a conserved methyltransferase motif; the hypothetical protein YGR031WP; TDH3p, a triose-phosphate dehydrogenase protein and RPS18ap, protein component of the small (40S) ribosomal subunit. Attached to $cTPxIII^{c120S}$ it was identified Crn1p an protein that binds actin filaments (F-actin) and cross-links F-actin to form long actin filament bundles and identified its own isoform cTPxI.

Acknowledgements: FAPESP

Functional and Biophysical studies on four Ceratoplatanins from the fungus *Moniliophthora perniciosa*, causal agent of the Witche's Broom Disease

Barsottini, M[1], Oliveira, J. F.[2], Tiezzi, H.O.[2], Zaparoli, G.[1], García, O[1], Ambrosio, A.L.B.[2], Pereira, G. A. G.[1], and Dias, SMG[2]

[1] Universidade Estadual de Campinas - Campinas SP Brazil
[2] Laboratório Nacional de Biociências - Campinas SP Brazil

Ceratoplatanin (CP) is a secreted protein of 12.4 kDa initially identified in culture filtrates of the ascomycete *Ceratocystis fimbriata f. sp. platani*, etiological agent of the canker stain disease. CP is also the founding member of the namesake protein family, which contains fungal-secreted proteins involved in various stages of the host-fungus interaction and may act as phytotoxins or elicitors of defense response. Besides the low molecular weight, CPs have a high percentage of hydrophobic residues and share two conserved intramolecular disulfide bonds. It has been suggested that CPs have important physiological functions, including interaction with cell wall or cell membrane and manipulation of the host's defense system. Furthermore, a recent work showed that the ceratoplatanin from *C. fimbriata* has some degree of affinity for the saccharide 4-N-acetylglucosamine. However, its precise molecular function remains elusive. Five putative CPs have been identified in *Moniliophthora perniciosa* a basidiomycete fungus responsible for great economic losses in cocoa industry in the form of Witches' Broom Disease (WBD) , four of which had their crystal structures resolved by our group. In this work we report biophysical and functional studies on these MpCPs aiming at understanding their role and importance during the WBD progression.

Acknowledgements: LNBio and FAPESP

Using Mass spectrometry for Identification of ABC transporters from *Xanthomonas citri* and mutants expressed in different growth conditions

Faria, J. N.[1], Paes Leme, A.F.[2], and Balan, A.[1]

[1] Laboratório Nacional de Biociências - Campinas SP Brazil
[2] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

Xanthomonas citri is a phytopathogenic bacterium that infects citrus plants causing significant losses for the economy. In our group, we have focused on the identification and characterization of ABC transport proteins of this bacterium, in order to determinate their function for growth *in vitro* and *in vivo*, during infection. ABC transporters represent one of the largest families of proteins, which transport since small molecules as ions up to oligopeptides and sugars. In prokariotic cells many works have reported the ABC transport function in pathogenesis, resistance, biofilm formation, infectivity and DNA repair, but until our knowledge, there is no data related to these transporters and *X. citri*. So, In order to determinate which transporters are expressed in *X. citri*, we started a proteomic analysis based on mono and bi-dimensional gels associated to mass spectrometry analyses. After growing *X. citri* and two different mutants deleted for *ssuA* and *nitA* genes in LB and minimum media, cellular extracts were obtained and used for preparation of mono and bi-dimensional gels. Seven bands covering the expected mass of ABC transporter components (20 kDa to 50 kDa) in SDS-PAGE were cut off the gel, treated with trypsin and submitted to the MS for protein identification. The results of 2D gels were good enough and will serve as a standard for development of similar experiments in large scale.

Acknowledgements: Associação Brasileira de Luz Sincrotron ABTLuS, Laboratório Nacional de Biociências

---

Inibição da Glutaminase C por BPTES

Fornezari, C.[1], Dias, SMG[2], Ferreira, A. P. S.[2], Ambrosio, A.L.B.[2], Oliveira,P.S.L.[2], and Honorato, R.V.[2]

[1] Universidade Estadual de Campinas - Campinas SP Brazil
[2] Laboratório Nacional de Biociências - Campinas SP Brazil

Glutaminase C (GAC), uma das três isoenzimas das glutaminases até então descritas em mamíferos, é chave no metabolismo de tumores devido a sua alta eficiência na conversão de glutamina na presença de fosfato inorgânico. Esse processo é fundamental especialmente para suprir a alta demanda biossintética das células cancerosas, representando, assim, um alvo em potencial para o desenvolvimento de novas terapias para o câncer. O BPTES é um composto orgânico que atua como inibidor não-competitivo sobre a atividade enzimática da GAC de sua isoforma por splicing alternativo, a enzima KGA (Kidney-type glutaminase). No presente trabalho apresentamos a estrutura cristalográfica da GAC ligada ao BPTES, resolvida por substituição molecular e refinada à resolução máxima de 2.85 , com dados coletados na linha D03B-MX1. Combinando a estrutura cristalográfica com estudos de dinâmica molecular, identificamos novos resíduos de aminoácidos que podem influenciar na atividade catalítica da enzima. Diante disso, foram realizadas mutações sítio-dirigidas nestes resíduos e as glutaminases mutantes foram submetidas à ensaios de atividade. Ainda, analisando a flexibilidade de um importante loop adjacente ao sítio catalítico da enzima em combinação com os dados cinéticos dos mutantes, apresentamos um mecanismo mais completo de ação para essa enzima.

Acknowledgements: Ao apoio do CNPEM

Estudo da importância da interação da Liver-type Glutaminase com a Glutaminase Interacting Protein-1 para o metabolismo celular

Saez, R. C.[1], Gonçalves, K. A.[1], and Dias, SMG[1]

Laboratório Nacional de Biociências - Campinas SP Brazil

Células tumorais apresentam um metabolismo energético e biossintético diferenciado quando comparado ao das células não transformadas, sendo caracterizado pela intensa glicólise mesmo na presença de oxigênio (Efeito Warburg). Uma das consequências do aumento da glicólise é a diminuição no aporte de piruvato para a mitocôndria, o que contribue para o truncamento do ciclo do ácido tricarboxílico (TCA). Para a manutenção da alta taxa mitótica, as células neoplásicas utilizam a via da glutaminólise para manter em funcionamento o ciclo do TCA, uma importante fonte de metabólitos precursores de macromoléculas. Já foram identificadas três isoformas das glutaminases em mamíferos: a Kidney-type glutaminase (KGA), Glutaminase C (GAC), e a Liver-type glutaminase (LGA). A LGA foi recentemente caracterizada como um alvo do regulador transcricional p53, um conhecido supressor de tumor, tendo sido proposto como o intermediador das funções de regulador do metabolismo energético e de defesa antioxiante do p53. Estes achados indicam que a supressão de sua expressão pode ser um dos fatores dirigentes ou de suporte ao crescimento tumoral. Além disso, esta isoenzima apresenta outros domínios além do catalítico, como repetições de contatos proteína-proteína do tipo ankirin, e domínios de interação com regiões PDZ. Estudos revelaram que a proteína GIP-1 (Glutaminase Interacting Protein)/TIP-1 (Tax interacting protein 1) é um parceiro de interação da enzima LGA, cuja interação foi confirmada em células nervosas. O entendimento das funções extra-enzimáticas da LGA ajudará a compreender a importância desta enzima para o processo de crescimento celular assim como processos celulares ainda desconhecidos. Este trabalho envolve a caracterização da interação da LGA com a GIP-1 em células epiteliais mamárias não-transformadas (HMEC) e transformadas (SKBR3) através das técnicas de co-imunoprecipitação e co-localização. Para tanto, as proteínas LGA e GIP foram clonadas em pCDNA 3.1 V-5/His TOPO (LGA), pEGFP (LGA), pCDNA 6 Flag (GIP-1) e pDsRe-Monomer (GIP-1). O objetivo a longo prazo é determinar a importância desta interação para a localização celular da LGA assim como de sua função no balanço redox da célula.

Acknowledgements: À FAPESP pelo apoio financeiro.

Parte III

Ciência Atômica e Molecular

Fragmentation of the CH_2Cl_2 molecule by proton impact and VUV photons

Alcantara, K.F de[1], Sigaud, L.[1], A.B. Rocha[1], ACF Santos[1], W. Wolff[1], and Gomes, A. H. A.[1]

Universidade Federal do Rio de Janeiro - Rio de Janeiro RJ Brazil

A absorção de um fóton VUV por uma molécula ou sua interação com uma partícula carregada, dá origem a uma fragmentação molecular eficiente que apresenta muitas questões teóricas abertas. Medidas do rendimento iônico e distribuições de energia dos produtos da fragmentação em uma colisão íon-molécula forneceram informações úteis sobre os estados final e inicial da molécula, a quantidade de energia transferida pela partícula incidente para a mesma, e como essa energia está distribuída entre os estados moleculares. Um estudo comparativo para a fragmentação da molécula CH_2Cl_2 foi realizado para colisões com feixe de H^+ de 0,2-2,0 MeV e fótons de 12-90 eV. Foram determinados os rendimentos parciais dos produtos da fragmentação em função da energia dos projéteis. Os resultados demonstram que quanto maior a energia dos prótons, mais o padrão de fragmentação se assemelha ao espectro correspondente por impacto de fótons com energias mais baixas. Por exemplo, no impacto de prótons de 2,0 MeV, o padrão de fragmentação se assemelha ao padrão correspondente por impacto de fótons de $h\nu = 60$ eV . A partir da análise da forma dos picos, conclui-se que os produtos de fragmentação encontrados, foram obtidos com baixa energia cinética (< 1 eV). Os principais fragmentos observados, no caso do impacto de prótons e fótons acima de 30 eV, foram associados à liberação de um átomo de cloro. Combinando a informação das energias moleculares orbitais, estima-se a contribuição relativa dos orbitais moleculares na ionização por impacto de prótons do CH_2Cl_2. É demonstrado pela primeira vez, que o padrão de fragmentação para os produtos carregados nos espectros por impacto de prótons, podem ser diretamente comparados com o padrão de fragmentação correspondente para o impacto de fótons, através do momento transferido, que depende da velocidade do projétil com v^{-1}. Esta é uma clara indicação de que a principal variável dinâmica por trás do rendimento parcial é o momento transferido em altas velocidades.

Referências

Alcantara, K F ; Wolff, W ; Gomes, A H A ; Sigaud, L ; Soriano, S ; Oliveira, V ; Rocha, A B ; Santos, A C F . Fragmentation of the CH Cl molecule by proton impact and VUV photons. Journal of Physics. B, Atomic Molecular and Optical Physics (Print), v. 44, p. 165205, 2011.

Acknowledgements: CNPq, CAPES, FAPERJ e LNLS

Fragmentation and desorption from condensed alcohols due to soft X-rays: Relevance to solid state astrochemistry

Almeida,G.C.[1], Rocco, M.L.M.[1], Andrade, D. P. P.[2], Boechat-Roberty , H.M.[1], Nazareth A.M.[1], Amaral, L.[1], and Bergantini, A.[2]

[1] Universidade Federal do Rio de Janeiro - Rio de Janeiro RJ Brazil
[2] Universidade do Vale do Paraíba - São José dos Campos SP Brazil

Methanol and ethanol, the simplest organic alcohols, are important precursors of more complex prebiotic species and are found abundantly in icy mantles on interstellar and protostellar dust. These molecules have been detected through infrared spectroscopy in some low- and high-mass protostars, such as W33A and RAFGL 7009, and also in comets, as Hale-Bopp and other Solar system bodies, such as the Centaur 5145 Pholus grains. All of these astronomical environments are subjected to some kind of ionizing agents, such as cosmic rays, electrons and photons (e.g. stellar radiation field). The aim of this work is to experimentally study the ionization, dissociation and ion desorption processes induced by photons and electrons on alcohols, CH_3OH and CH_3CH_2OH, as part of a systematic experimental study of condensed (ice phase) prebiotic molecules. We have employed soft X-ray photons at the oxygen K edge and variable electron energies to simulate the effects of stellar radiation field on the astrophysics ices. These results were also compared with effects produced by charged particles from cosmic rays. Ion photodesorption experiments on the icy surface were carried out at the Brazilian Synchrotron Light Source (LNLS), using the Spherical Grating Monochromator (SGM) beam line, operated in the single-bunch mode of the storage ring, with a period of 311 ns and bunch width of 60ps. Several fragments such as CH_2^+, O^+, H^+ and H_3^+ have been identified and their desorption rates per impact were determined and compared with previous results obtained using different ionization agents, such as electrons, heavy ions and photons at different energies in order to provide data to astrochemical models.

Acknowledgements: This work was supported by D08A-SGM-9918, CNPQ, CAPES and FAPERJ

Photofragmentation dynamics of gaseous dimethyl sulfoxide at 15 eV Induced by Synchrotron Radiation

Guerra, A. C. O.[1], Leite, T.C.M.[1], A.L.F. de Barros[2], Ferreira, G. B.[3], and Turci, C. C.[1]

[1] Universidade Federal do Rio de Janeiro - Rio de Janeiro RJ Brazil
[2] Centro Federal de Educação Tecnológica - Rio de Janeiro RJ Brazil
[3] Universidade Federal Fluminense - Niterói RJ Brazil

Dimethyl sulfoxide (DMSO) is a solvent widely used in chemical and biological laboratories and in industrial processes, as well. DMSO $[(H_3C)_2 - SO]$ is a sulfur analog of acetone $[(H_3C)_2 - CO]$. Being the simplest alkylsulfoxide, the DMSO is a model system for the understanding of more complex sulfoxide molecules. In this work the DMSO was excited with synchrotron light and the photoelectron-photoion coincidence spectrum was acquired at 15 eV. Our goal is to study the S–C bonding breaking process, especially in the H_3CSO^+ and CH_3^+ channels. The main question is how the 10a → ∞ transition affects the cleavage of S–C bond and consequently the production of those fragments. The experiments have been performed using the Toroidal Grating Monochromator (TGM) beamline at the Brazilian Synchrotron Light Laboratory (LNLS) in Campinas-SP (research proposal D05A-TGM-11047). High purity samples were obtained commercially and used without any further purification. They were introduced into the Wiley-McLaren time-of-flight mass spectrometer (TOF-MS) from the vapours of the room temperature liquids after removing air and volatile impurities by a series of freeze-pump-thaw cycles. The work pressure was maintained at 1.0×10^{-6} mbar during data acquisition. The basis pressure was 1.0×10^{-8} mbar. The results confirm that at 10a → ∞ transition the main produced fragment is the H_3CSO^+. It means that at 15 eV the S-C bonding breaking is the principal photofragmentation process.

Acknowledgements: LNLS (D05A-TGM-11047), FAPERJ, CNPq

Photostability of Glycine to Lyman α radiation

Ferreira-Rodrigues, A. M.[1], M.G.P. Homem[2], Naves de Brito, A.[3], C.R. Ponciano[4], and E. F. da Silveira[4]

[1] Universidade Federal do Estado do Rio de Janeiro - Rio de Janeiro RJ Brazil
[2] Universidade Federal de Santa Catarina - Florianópolis SC Brazil
[3] Universidade de Brasília - Brasília DF Brazil
[4] PUC - Rio de Janeiro - Rio de Janeiro RJ Brazil

The amino acids already detected in Solar System bodies and researched in Interstellar Medium are of particular importance for the chemistry related to the origin of life since they are constituents of all living organisms. To interpret the viability of amino acids in pre-biotic astrochemistry is important to investigate the stability of these compounds in extraterrestrial surroundings. This study investigates, in the laboratory, the stability of glycine to the action of ultraviolet radiation, in spectral region around the wavelength of the Lyman α line (1216) produced by a hydrogen lamp. ^{252}Cf-PDMS of positive and negative desorbed ions was performed for glycine, before and during the irradiation, and the dependence of the ion desorption yields on the irradiation time is determined. As a result, the relative photostability curves of the molecular and dimer ions are observed to be a single exponential decay with a time constant 376 min for positive desorbed ions and 675 min for negative ones. The photodissociation cross section found for glycine molecule at room temperature, when positive secondary ions are considered, is 17 Mb; this value drops to 9 Mb when negative secondary ions are analyzed. This new methodology offers a complementary way of understanding the photonic interaction in amino acids, allowing discussion on polymerization and/or radiation induced phase transition effects.

Reference: A.M. Ferreira-Rodrigues, M.G.P. Homem, A. Naves de Brito, C.R. Ponciano and E.F. da Silveira, Int. J. of Mass Spectrom. (2011) 306(1), 77-81. DOI:10.1016/j.ijms.2011.06.022

Acknowledgements: This work was partially supported by Brazilian agencies CNPq and FAPERJ and to LNLS by lend the hydrogen lamp.

Fotoionização múltipla da molécula CF_2Cl_2 na proximidade da borda $Cl1s$

Gomes, A. H. A.[1], Alcantara, K.F de[1], ACF Santos[1], W. Wolff[1], Luna, H[1], and Natalia Ferreira[1]

Universidade Federal do Rio de Janeiro - Rio de Janeiro RJ Brazil

As moléculas de Freon tem atraído muita atenção para estudos devido ao seu efeito de degradação da camada de ozônio quando esta é quebrada na atmosfera através de fenômenos fotoquímicos. O CF_2Cl_2 (Freon-12) é uma molécula de bastante interesse no estudo desses fenômenos pois tem vasta utilização como propelente em aerossóis e como gás refrigerante. Excitação e ionização de moléculas em camada interna geralmente resultam na criação de íons moleculares simples ou multiplamente carregados muito instáveis que se fragmentam em espécies mais leves com ou sem separação de carga [1]. Com o intuito de estudar o papel da correlação eletrônica na fragmentação molecular após a criação de uma vacância em camada interna profunda, neste trabalho apresentamos medidas para a fotoionização da molécula CF_2Cl_2 em torno da borda 1s do cloro. Foram utilizadas técnicas de coincidência múltipla (PEPICO e PEPIPICO) e as medidas foram realizadas na linha SXS do Laboratório Nacional de Luz Síncrotron (LNLS). Foram medidos os rendimentos iônicos parciais em função da energia do fóton. Um alto grau de fragmentação, levando à quase total atomização da molécula, foi observado. Também foram determinadas as energias cinéticas dos fragmentos produzidos.

Referências: [1] K.F. Alcantara, W. Wolff, A. H. A. Gomes. L. Sigaud, S. Soriano, V. Oliveira. A. B. Rocha e A.C. F. Santos, J. Phys. B (2001).

Acknowledgements: Trabalho com apoio parcial do CNPq, CAPES e LNLS (proposta SXS-9288).

Depth Analysis of Chemical Environments using Resonant Raman Spectroscopy in Total Reflection Geometry

Leani, J.J.[1], H. J. Sánchez[1], R.D. Pérez[1], and Pérez, C. A.[2]

[1] Universidad Nacional de Cordoba - Córdoba Cba Argentina
[2] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

Total Reflection of X-rays is a largely proved spectroscopic technique that allows the study of material surfaces. Making use of this phenomenon, different depths of a sample surface could be studied by means of the correct election of the incident radiation angle. In this way, analysis of the reflected intensity could provide a method for studying surface properties, as variations of electron density with depth (e.g., corrosion, porosity, aging, etc.) with a resolution from Amstrongs to hundred nanometers deep. X-ray resonant Raman scattering (RRS) is an inelastic scattering process which presents fundamental differences compared to other scattering interactions between X-rays and atoms. Both total reflection and resonant Raman scattering techniques are used combined with the aim of discriminate oxidation states in nano-layers of materials.

Samples of pure Cu and Fe oxidized in water and salty water, respectively, were studied in the Brazilian synchrotron using monochromatic radiation and an energy dispersive setup. The measurement were carried out in total reflection geometry scanning the incident radiation angle around the critical angle with incident energy lower and close to the K absorption edge of both elements in order to study the RRS emissions.

For the first time, both resonant Raman scattering and total reflection techniques are used combined as a hybrid tool allowing discrimination of oxidation states in nano-layers of materials using a low resolution spectrometer. The main contribution of this article relies on the possibility of obtaining structural information with nanometric resolution, or even mstrongs, by using a typical energy dispersive setup. In this way, a lot of possibilities appear from the combination of RRS spectroscopy with other X-ray techniques, even threedimensional analysis by RRS combined with confocal setups. Currently, further investigations are carried out in order to reach a complete understanding of the processes involved with the aim of turn this practical method into a true and complete analytical tool.

Acknowledgements: This work has been partially supported by the Brazilian Synchrotron Light Laboratory (LNLS).

Study of the Ionic Fragmentation of Dimethyl Diselenide, $CH_3SeSeCH_3$, with Synchrotron Radiation around the Se 3p Region.

Geronés, Mariana[1], Rodriguez Pirani, Lucas[1], Erben, Mauricio F.[1], Angelica Moreno Betancourt[1], Romano, Rosana M.[1], Cavasso Filho, R. L.[2], and Della Védova, Carlos O.[1]

[1] Universidad Nacional de La Plata - La PLata B.A. Argentina
[2] Universidade Federal do ABC - Santo André SP Brazil

In this work we present a study of the dissociative photoionization of the volatile selenium compound $CH_3SeSeCH_3$ by using multicoincidence time-of-flight mass spectrometry and synchrotron radiation in the Se 3p edge. Gaseous selenium species detected in the atmosphere include dimethyl selenide, dimethyl selenone, methaneselenol and the title compound, dimethyl diselenide [1,2]. Various plants can accumulate Se up to the thousands of ppm. These are called accumulators and they have potential to remediate areas contaminated with this metalloid (phytoremediating) [3] being an attractive solution for cleaning such sites. Certain plants can also convert the Se into volatile species, such as dimethyl selenide or dimethyl diselenide, mainly harmless to the environment, by a process called phytovolatilization.[4,5] Below the Se 3p threshold, located at approximately 179.0 eV, the TIY spectrum exhibits two signals at 164.3 eV and 170.2 eV which should correspond to transitions involving the spin-orbit splitting of the 3p term of selenium into $3p_{1/2}$ and $3p_{3/2}$ levels. The analysis of the PEPICO spectra of $CH_3SeSeCH_3$ over the whole range of photon energies analyzed here reveals a preferential production of H^+ ions, while signals corresponding to ionic fragments $H_2{}^+$, $CH_x{}^+$ (x= 2, 1 and 0) , Se^+ and $HCSe^+$ appear as less intense bands. In addition, peaks corresponding to the $H_3{}^+$ and $Se_2{}^+$ ions have been observed having very weak relative intensity. It should be noted that only a singly charged molecular ion can produce $Se_2{}^+$ from ionized $CH_3SeSeCH_3$ by the loss of two CH_3 groups. The molecular ion, $CH_3SeSeCH_3{}^+$, can not be observed in any PEPICO spectra measured in these photon energies. Naturally occurring isotopomer fragments, due to the presence of Se isotopes, have been observed due to the suitable mass resolution attained in the experiments. (1) Zieve, R et al J. Sci. Total Enuiron. 1981, 19,277-284(2) Zieve, R et al J. Trace Subst. Enuiron. Health 1984, 18, 262-267.(3) G. S. Bañuelos et al Plant Soil, 1996, 183, 49.(4) K.M. Carvalho et al J. Environ. Sci. Health, 2001, 36, 1403.(5) M. P. De Souza et alPlant Physiol., 2000, 122, 1281.

Acknowledgements: This work was supported by LNLS, CONICET, CIC, ANPCyT, UNLP.

3D Spatially-Resolved Characterization of Chemical Environment distributions by Inelastic X-Ray Scattering in Confocal Setup

Leani, J.J.[1], H. J. Sánchez[1], R.D. Pérez[1], and Pérez, C. A.[2]

[1] Universidad Nacional de Cordoba - Córdoba Cba Argentina
[2] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

3D-micro X-ray fluorescence spectroscopy enables non-destructive three-dimensional investigation of elemental distribution in samples in the micrometer regime. In the last few years, accurate quantification procedures have been developed [1,2]. The most important problem in these quantification procedures is the existence of light elements in the sample from which no fluorescence is detected. This dark matrix problem is not yet solved and is now the most serious limitation of this technique [2]. Resonant Raman scattering is an inelastic scattering process that becomes dominant when atoms are irradiated with incident energy lower and close to an absorption edge. Recently, a spectroscopic technique in formation based in this process showed to be useful to distinguish surrounded chemical environments [3,4]. We present first results regarding the possibility of determining the oxidation state of an element, in a three-dimensional regime, by resonant Raman scattering using an energy dispersive system combined with a confocal setup. A depth scanning of a multilayer sample in confocal setup was carried out in the XRF Beamline of the LNLS (Campinas, Brazil) [5]. The sample consisted of different layers of Cu oxides over a Cu substrate. The sample was irradiated with monochromatic photons having energy close but lower than the K absorption edge of Cu. The Raman peaks were analyzed, residuals were determined and a FFT smoothing procedure, taking into account the instrument functions of the detecting system, was applied. The results show an oscillation pattern that depends on the oxidation state of cooper. The result is relevant since allows the discrimination of the oxidation state of the elements present in a sample in a 3D-micrometer regime by means of resonant Raman scattering combined with a confocal setup. This result could be used as a tool to determine the dark matrix present in the sample with the aim of establishing a reliable quantification procedure.

1. W. Malzer and B. Kanngieher, Spectrochimica Acta Part B 60, 1334 (2005). 2. I. Mantouvalou et al., Anal. Chem. 80, 819 (2008). 3. Leani J.J. et al., J. Anal. At. Spectrom., 26, 378 (2011). 4. Leani J.J. et al., X-Ray Spectrom. 40, 254 (2011). 5. C.A. Pérez et al., X Ray Spectrom; 28 320 (1999).

Acknowledgements: This work was partially supported by the LNLS (Campinas. Brazil).

MEDIDAS ABSOLUTAS DE SEÇÃO DE CHOQUE DE FOTOABSORÇÃO DE MOLÉCULAS POLIATÔMICAS: ISOPRENO, ACETONITRILA E HALOTANO

Rodrigues, F. N.[1], Rodrigues, A.M. S.[2], Lucas, C.A.[3], Pontes, F.C.[4], and de Souza, G.G.B.[2]

[1] Instituto Federal de Educação, Ciencia e Tecnologia do Rio d - Rio de Janeiro RJ Brazil
[2] Universidade Federal do Rio de Janeiro - Rio de Janeiro RJ Brazil
[3] Universidade Federal Fluminense - Niterói RJ Brazil
[4] Universidade do Estado do Rio de Janeiro - Rio de Janeiro RJ Brazil

Nas últimas décadas as técnicas de espalhamento de elétrons de alta energia e de fotoabsorção por radiação têm sido usadas extensivamentes, sendo indispensáveis (e complementares) para entender diferentes aspectos de ciências como a astronomia, a biologia, a química e a física. Alguns estados eletrônicos que não são acessíveis por técnicas ópticas podem ser estudados por espectroscopia de perda de energia de elétrons (EPEE), ferramenta refinada para o estudo de excitações eletrônicas em átomos e moléculas. Neste trabalho EPEE, com alta energia de impacto (1 keV), foi usada na determinação de espectros da molécula de Isopreno (C_5H_8) abrangendo até 100 eV de perda de energia, num ângulo de espalhamento igual a 1,5^o. Utilizando luz síncrotron, obtivemos espectros de fotoabsorção na região da valência. Utilizando a regra da soma S(-2) colocamos o espectro numa escala absoluta de força do oscilador óptica (seção de choque)[1]. O mesmo método experimental foi adotado para a obtenção, em escala absoluta, da Superfície de Bethe para as moléculas de Acetonitrila (CH_3CN)[2] e Halotano ($CF_3CHClBr$). A superfície de Bethe é uma representação tridimensional envolvendo as forças do oscilador, a energia e os ângulos de espalhamento. Estas superfícies permitem ainda a determinação de propriedades físicas como o índice de refração e a constante de Verdet. No caso da molécula acetonitrila, observou-se pela primeira vez uma transição não-dipolar em 10,8 eV. Os resultados da FOG para a molécula Halotano apresentados também são originais. Em todos os casos foram obtidos as seções de choque de fotoabsorção absolutas.

[1] - MARTINS, G. ; Ferreira-Rodrigues, A. M. ; Rodrigues, F. N. ; de Souza, G. G. B. ; et al., Physical Chemistry Chemical Physics, v. 11, p. 11219-11231, 2009.

[2] - Rodrigues, F. N., Ferreira-Rodrigues, A. M., Lucas, C. A., Beochat-Roberty, H. M.,Pontes, F. C., de Souza, G. G. B., UV Excitation and Fragmentation of Acetonitrile Molecule, 2011 in preparation

Acknowledgements: Faperj, CNPq.

Fotoestabilidade de compostos naturais fotoativos: cumarinas e corantes

Moraes, M. O. S.[1], Ferreira-Rodrigues, A. M.[2], Ricardo, W.[3], de Souza, G.G.B.[4], and de Castilho, R.B.[1]

[1] Universidade Federal do Amazonas - Manaus AM Brazil
[2] Universidade Federal do Estado do Rio de Janeiro - Rio de Janeiro RJ Brazil
[3] Universidade do Estado do Amazonas - Manaus AM Brazil
[4] Universidade Federal do Rio de Janeiro - Rio de Janeiro RJ Brazil

No presente trabalho, iniciou-se uma pesquisa precursora que irá contribuir para o entendimento da dinâmica de interação da luz com os psoralenos, assunto de grande relevância na área da saúde e afins devida a suas propriedades fotossensibilizantes. Os psoralenos são compostos furocumarínicos presentes em várias frutas e, particularmente, no óleo de bergamota, possuem atividade fotobiológica e fototerapêutica, sendo utilizados no tratamento PUVA (psoraleno + UV-A), técnica que atualmente fornece bons resultados contra doenças de pele, como psoríase, vitiligo e em alguns tipos de câncer. O 8-metoxi-psoraleno é comumente usado em medicamentos. Com o objetivo de investigar a fotoestabilidade dos psoralenos em alta e baixa energia, foi feito a fragmentação iônica do 8-metoxi-psoraleno (8-MOP) empregando um espectrômetro de massa por tempo de voo. O experimento foi realizado nas dependências do Laboratório Nacional de Luz Síncrotron - LNLS, na linha de luz TGM (Toroidal Grating Monochromator) que opera na faixa de energia do ultravioleta (12 - 310 eV) e foi ajustada na primeira grade que corresponde ao comprimento de onda de 100 a 35 nm (12 - 35 eV). A técnica de coincidência fotoelétron-fotoíon (PEPICO) foi utilizada para a observação da fragmentação iônica do 8-MOP em energia de 12, 14, 16, 18 e 21 eV, obtendo espectros de massa por tempo de voo. Os espectros apresentaram vários fragmentos $m/z = 216.2$, 201, 188, 173 e 145, e foram surgindo, nesta ordem, à medida que aumentava a energia do feixe ionizante. Estes fragmentos são formados a partir da fragmentação do íon molecular 8-MOP (216.2) por uma cadeia de reações que envolvem a eliminação de grupos neutros e rearranjos moleculares. Entretanto, observou-se que o pico base era o próprio íon molecular (216.2), em todos os espectros obtidos, esta observação nos leva a considerar sobre a estabilidade eletrônica da estrutura molecular do 8-MOP, que por efeito de ressonância das ligações pi alternadas impedem a abertura dos anéis, mantendo sua alta estabilidade.

Acknowledgements: LNLS/CNPq

Mecanismo de Emissão do Cintilador BaY_2F_8:2%Pr^{3+} via Espectroscopia de Absorção de Raios X

Andrade, AB[1], de Mello, A.C.S.[1], Baldochi, S. L.[2], Valerio, M.E.G.[1], and Rezende, M. V. dos S.[1]

[1] Universidade Federal de Sergipe - São Cristóvão SE Brazil
[2] Instituto de Pesquisas Energéticas e Nucleares - São Paulo SP Brazil

Neste trabalho foram usadas as técnicas XAFS (X-Ray Absorption Fine Struture) e XEOL (X-Ray Excited Optical Luminescence), realizadas na linha XAFS2 do LNLS (Laboratório Nacional de Luz Síncrotron), para o estudo dos processos que originam a luminescência do cintilador BaY_2F_8:2%Pr^{3+}. Novas e importantes propriedades a respeito do mecanismo luminescente do material foram observadas. O espectro XEOL do BaY_2F_8:2%Pr^{3+} apresenta as emissões típicas do íon Pr^{3+}, com emissões em 482, 525, 555, 607, 642 e 722 nm correspondentes as transições $^3P_2$ - $^3H_5$, $^3P_1$ + $^1I_6$ - $^3H_5$, $^3P_2$ - $^3F_4$, $^1D_2$ - $^3H_5$, $^3P_2$ - $^3F_4$ e $^1D_2$ - $^3H_5$, respectivamente. A intensidade de emissão XEOL medida em função da energia dos fótons de raios X apresentou as bordas de absorção L1, L2 e L3 do Ba^{2+} e, com menor intensidade, a borda L3 do Pr^{3+}. A explicação para este comportamento está relacionada com a baixa concentração de Pr^{3+}, já que se trata de um dopante. A XEOL apresenta, no entanto uma característica muito diferente da curva de absorção de Raios X medida no modo de transmissão após as bordas de absorção, a intensidade XEOL (já normalizada pela intensidade do feixe de raios X incidente) cresce monotonicamente com a energia de excitação, revelando que a eficiência de cintilação é tanto maior quanto maior for a energia dos fótons. Estes resultados permitem propor um modelo para o mecanismo de cintilação do BaY_2F_8:2%Pr^{3+} quando excitado por raios X baseado no processo de geração de cargas devido a absorção dos fótons de raios X, no tráfego de portadores entre as bandas de condução/valência e armadilhas e no processo de recombinação radiativa dos portadores leves que transferem a energia para o Pr^{3+}. Este por sua vez absorve a energia e vai para o estado excitado, decaindo para o estado fundamental através das suas emissões características.

Acknowledgements: Trabalho parcialmente financiado pelo CNPq, CAPES, FAPITEC/SE e LNLS

Mn coordination and oxidation state determination in spinel $Mn_{2-x}V_{1+x}O_4$ series by XANES. Comparison with high-resolution Kβ Emission Spectroscopy.

Tirao G.[1], Ceppi, S.[1], Mesquita, A.[2], Pomiro, F.[3], and Pannunzio Miner, E. V.[1]

[1] Universidad Nacional de Cordoba - Cordoba Argentina
[2] Universidade Federal de São Carlos - São Carlos SP Brazil
[3] Universidad Nacional de Cordoba - Córdoba CO Argentina

The spinel $Mn_{2-x}V_{1+x}O_4$ series with $x = 0, 1/3$, and 1, prepared by solid state reaction, were studied by Pannunzio-Miner et al. [1] using several techniques in order to explain their magnetic susceptibility and electrical properties behaviors. All the samples presented positive magnetoresistance (MR) at room temperature, in particular, the highest value (around 1 %) was observed in the MnV_2O_4 sample. This feature could be justify by the distribution of Mn/V cations in the tetrahedral and octahedral sites, assuming that the Mn and V cations were in the 2+ and 3+ oxidation states, respectively.

In order to study the Mn chemical environment, Mn-K XANES spectra were measurement at the D04B-XASF1 beamline. The Mn oxidation state and coordination were determined using the edge energy half way up the normalized-edge step in the usual way (i.e. where the absorption is equal to 0.5) and the area of the extracted pre-edge structure, respectively, comparing with reference spinels. In addition, these results were used to compare this conventional technique with the high-resolution Kβ Emission Spectroscopy applied in previous works [2,3].

Acknowledgements: This work was partially supported by the Brazilian Synchrotron Light Source (LNLS) (project D04B - XAFS1-10693) and by the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET).

---

[1] E. V Pannunzio-Miner, J. M. De Paoli, R. E. Carbonio, R. D. Sánchez, J. Applied Physics. 105, (2009) 113906.

[2] S. Limandri, S. Ceppi, G. Tirao, G. Stutz, C.G. Sánchez, J.A. Riveros. Chem. Phys. 367, 93 (2010).

[3] G. Tirao, S. Ceppi, A.L. Cappelletti, E.V. Pannunzio Miner. J. Phys. Chem. Solids 71, 199205 (2010).

Propriedades fotoinduzidas por VUV na liga SbTe

Almeida, D. P.[1] and Moura, P. R.[1]

Universidade Federal de Santa Catarina - Florianópolis SC Brazil

Inicialmente, a liga amorfa de SbTe foi preparada por moagem MECânica e usada para produzir filmes finos amorfos de mesma composição por evaporação resistiva. Em seguida, investigamos os efeitos fotoinduzidos em filmes finos calcogênicos amorfos excitados com radiação VUV na linha de luz TGM, para promover os efeitos de fotobranqueamento ou de fotoescurecimento. As propriedades estruturais da liga na forma de po foram analisadas usando DRX. As propriedades estruturais e da liga, na forma de filmes finos, foram analisadas por EDS. Visando comparar as mudanças causadas pela irradiação nos filmes. Suas propriedades estruturais e opticas foram novamente investigadas pelos mesmos procedimentos. Compreender esses mecanismos tem fundamental importância para o desenvolvimento de novos dispositivos.

Acknowledgements: This work was supported by LNLS

Photoabsorption and time-of-flight mass spectroscopy for gas-phase trimethyl phosphate following valence shell excitation

Homem, M. G. P.[1], Iza, P.[2], Rosa, L. F. S.[1], Farenzena, L. S.[1], Cavasso Filho, R. L.[3], Hasse, A.[1], Lee, M. T.[4], and Iga, I.[4]

[1] Universidade Federal de Santa Catarina - Florianópolis SC Brazil
[2] ESCUELA SUPERIOR POLITECNICA DEL LITORAL - Guayaquil Guaya Ecuador
[3] Universidade Federal do ABC - Santo André SP Brazil
[4] Universidade Federal de São Carlos - São Carlos SP Brazil

In this work we report an experimental study on photoabsorption of trimethyl phosphate (TMP) molecules in the vacuum-ultraviolet energy range. More specifically, absolute photoabsorption cross sections and photoionization yields are measured and reported in the (11.11-21.45) eV energy range. The photoionization and neutral-decay cross sections in absolute scale are also derived and reported. Details of our experimental setup and procedure for cross-section determination can be found in our previous work [1]. Essentially, the measurements were performed using a double-ion-chamber technique [2]. The experimental cross-section results are analyzed in comparison with PES measurements. Oscillator strengths sum rules over the extrapolated experimental data gives a value of 71.6 au for the static dipole polarizability of TMP, which is in excellent agreement with the value of 72.3 au reported in literature. In addition, the ionic dissociation in the same energy range has been studied by time-of-flight mass spectrometry [3]. The detected product cations are $C_3H_9O_4P^+$, $C_3H_8O_4P^+$, $CH_3O_4P^+$, $C_2H_6O_3P^+$, PO_4^+, $CH_5O_2P^+$, PO_3^+ and CH_3^+. The observed ionic branching ratios are converted in absolute scale by using the measured photoionization cross sections. The presence of two ionic metastable states corresponding to the $C_3H_9O_4P^+$ and $CH_3O_4P^+$ fragments are reported and their metastable ion mean lives are estimated in (152±5) ns and (248±30) ns. The results and discussion will be presented during the workshop.

[1] M. G. P. Homem, P. Iza, L. S. Farenzena, R. L. Cavasso-Filho, M. T. Lee and I. Iga, J. Phys. B: At. Mol. Opt. Phys. **42**, 235204 (2009). [2] J. A. R. Samson and Lifeng Yin, J. Opt. Soc. Am B **6**, 2326 (1989). [3] F. Burmeister, L. H. Coutinho, R. R. T. Marinho, M. G. P. Homem, M. A. A. Morais, A. Mocellin, O. Bjorneholm, S. L. Sorensen, P. T. Fonseca, A. Lindgren and A. Naves de Brito, J. Electron Spectrosc. Relat. Phenom. **180**, 6 (2010).

Acknowledgements: This work was supported by the LNLS under proposal D05A-TGM 10071. The authors acknowledge the help from staff of the LNLS and the financial supports from the Brazilian agencies CNPq and FAPESP.

Interação da Molécula DL-prolina em Fase Condensada com Fótons na Região do Ultravioleta de Vácuo

Silveira,T.R.[1], Marinho, R. R. T.[1], E. M. Nascimento[1], and Prudente, F. V.[1]

Universidade Federal da Bahia - Salvador BA Brazil

Existem modelos que tentam explicar como biomoléculas mais simples teriam sido formadas. Uma das possíveis conseqências dos modelos de evolução química no espaço seria que a vida na Terra tenha sua origem no espaço, isto é, as biomoléculas precursoras da vida teriam sido formadas no espaço e trazidas para a Terra pelos impactos de cometas e meteoritos. Já foram encontrados desde elementos leves como C, H, O e N até moléculas como cianeto de hidrogênio (HCN), formaldeído, pirimidinas, polímeros, entre outros. Como os cometas perdem grãos ao entrar em contato com a atmosfera terrestre eles podem ter desempenhado um importante papel de fontes de moléculas orgânicas para desenvolvimento da vida na era primitiva. A astronomia observacional apresentou nos últimos anos resultados em relacção à descoberta de moléculas complexas. Existe uma diferença considerável no número de observações diretas de moléculas orgânicas em fase condensada e em fase gasosa no espaço, sendo a primeira muito mais abundante. Este fato está intimamente ligado a fotoestabilidade destas moléculas quando expostas ao campo de radiação no espaço de radiação que compreende comprimento de ondas desde o infravermelho a raios cósmicos. Produzindo filmes de amino ácidos podemos estudar como moléculas em fase condensada se comportam quando expostas a radiação ultravioleta de vácuo (VUV). Nesse trabalho, apresentaremos um estudo da fotoestabilidade do composto orgânico DL-prolina em função de sua interação com a radiação VUV. Os filmes foram produzidos pela técnica drop-casting, os experimentos foram realizados na linha de luz TGM do LNLS, onde selecionamos fótons com energia de 150 eV, e para analisar os efeitos da degradação dos filmes utilizamos um espectrômetro infravermelho com transformada fourier (FT-IR).

Acknowledgements: LNLS, CNPq, FAPESB e CAPES

Sistema para as Medidas de Fotoionização e Produção do Formaldeído

Tanaka, H. J.[1], Prudente, F. V.[1], Marinho, R. R. T.[1], and E. M. Nascimento[1]

Universidade Federal da Bahia - Salvador BA Brazil

O estudo da fotoionização de moléculas de interesse biológico tem aumentado muito nos últimos anos, devido ao interesse básico na natureza fundamental de estruturas eletrônicas e de processos moleculares de espalhamento. Consideramos a hipótese de que moléculas simples dariam origem a moléculas mais complexas por meio de reações fotoquímicas induzidas por radiação interestelar. Apresentaremos neste trabalho as medidas da fotoionização do argônio (Ar), do xenonio (Xe) e do formaldeído (CH_2O); e a produção do formaldeído a partir de paraformaldeído em pó. Os dados foram coletados no Laboratório Nacional de Luz Sincrotron (LNLS), utilizando a linha D0-5A TGM (Toroidal Grating Monochromator). As seções de choque de fotoionização foram medidas utilizando uma câmara de dupla ionização (double-ion chamber). Este trabalho faz parte de um projeto mais amplo de estudos de moléculas de interesse biológico, motivado pela hipótese de que partindo de moléculas simples, processos físico-químicos podem ter dado origem a moléculas mais complexas responsáveis pela geração da vida terrestre.

Acknowledgements: LNLS, CAPES

A study about dimers formation of formic acid in gas phase and in the valence region

Arruda, M. S.[1], Prudente, F. V.[2], Marinho, R. R. T.[2], and E. M. Nascimento[2]

[1] Universidade Federal do Recôncavo da Bahia - Amargosa/ BA Brazil
[2] Universidade Federal da Bahia - Salvador BA Brazil

Study of simple pre-biotic molecules takes great importance for understanding about complex organic molecules formation like amino acids, proteins and nucleobases within the DNA and RNA. A hypothesis for the appearance of nucleobases is that they could have been synthesized from simpler organic composites contained in interstellar medium (ISM), meteorites and asteroids. Lots of experiments have demonstrated that it is possible to produce complex pre-biotic molecules from simpler molecules under environments that simulate the ISM. Thus, we have performed a theoretical and experimental study about photoionization and photofragmentation processes of simple pre-biotic molecules that are important in the synthesis of complex biomolecules. In this work particularly, we performed photoionization and photofragmentation process of formic acid-D2 (CDOOD) in order to verify if some molecular fragmentations coming from dimers that could be formed before ionization region at TOF mass spectrometer. Experimentally, we measured these molecules mass spectra in gaseous phase. These spectra were got as function of pressures in experimental chamber, temperature samples and photon energy, in the vacuum ultraviolet region, between 11 and 20 eV. These data had been obtained in the Brazilian Laboratory of Syncrotron Light, by using mass spectrometer of flight time. The mass spectra had been obtained by using the photonelectron photonion coincidence technique, PEPICO. For a better understanding of experimental results, we have made a theoretical analysis of the photofragmentation by using Density Functional Theory.

Acknowledgements: LNLS

Interação da radiação estelar com moléculas congeladas na superfície de grãos de poeira

Monfredini, T.[1], Mendoza, E. F.[1], Almeida,G.C.[1], Andrade, D. P. P.[2], W. Wolff[1], Rocco, M.L.M.[1], and Boechat-Roberty , H.M.[1]

[1] Universidade Federal do Rio de Janeiro - Rio de Janeiro RJ Brazil
[2] Universidade do Vale do Paraíba - São José dos Campos SP Brazil

O envoltório de estrelas evoluídas, como as nebulosas planetárias, é composto por várias espécies moleculares, resultado de reações químicas tanto na fase gasosa quanto na superfície de grãos de poeira. A abundância de uma dada molécula nesses ambientes depende das taxas de formação, destruição e fotodessorção do manto de gelo sobre a superfície dos grãos de poeira.

Sabe-se que os hidrocarbonetos policíclicos aromáticos (PAHs), compostos contendo dois ou mais anéis benzênicos, são formados principalmente nas camadas de gás e poeira que circundam as estrelas evoluídas ricas em carbono. Moléculas precursoras dos PAHs e PAHs metilados, como benzeno (C_6H_6), diacetileno (C_4H_2), triacetileno (C_6H_2), metil-acetileno (C_3C_2H) e metil-diacetileno (CH_3C_4H) foram detectadas na nebulosa protoplanetária CRL 618. Neste trabalho estudamos a dessorção de íons devido à interação de raios X com o metil-benzeno, ou tolueno ($C_6H_5CH_3$), congelado à temperatura de 27 K. Empregamos a espectrometria de massas por tempo de voo (MS-TOF), utilizando fótons com energias de 275 a 320 eV provenientes da linha SGM, no modo single bunch. Nossos resultados mostram que as moléculas metil-diacetileno e metil-acetileno observadas na CRL618 podem ser fragmentos do tolueno. Estudamos a variação do rendimento iônico em função da energia dos fótons e determinamos as taxas de produção de íons em função do fluxo de fótons na nebulosa planetária CRL618.

Acknowledgements: Agradecemos ao LNLS, pelo suporte técnico, e à CAPES, pelo suporte financeiro.

Photoexcitation, photoionization and photofragmentation studies on Pyrosulfuryl chloride, $(ClSO_2)_2O$, between 12 and 300 eV

Angelica Moreno Betancourt[1], Romano, Rosana M.[1], Erben, Mauricio F.[1], Cavasso Filho, R. L.[2], Geronés, Mariana[1], Berrueta Martinez, Y.[1], Rodriguez Pirani, Lucas[1], and Della Védova, Carlos O.[1]

[1] Universidad Nacional de La Plata - La PLata B.A. Argentina
[2] Universidade Federal do ABC - Santo André SP Brazil

Recent investigations in our research group have been dedicated to the elucidation of photochemical reaction mechanisms between small molecules, relevant as atmospheric contaminants or components. For example the photochemical gas-phase reaction between SO_2, O_2 and Cl_2 was studied and the reaction mechanisms were proposed on the basis of the isolation and identification of the products.1 Molecules of the type $ClSO_2$ $(OSO_2)_nCl$, with n=1,2 and the novel peroxide $ClSO_2OOSO_2Cl$ were determined, among others, as the main photoproducts. It was proposed that this reaction could play an important role in atmospheric chemistry, particularly in regions of high Cl_2 and SO_2 abundances. It was also suggested that it could account for chemical processes to explain the unexpectedly low oxygen content of the Venus stratosphere.2 Pyrosulfuryl chloride, was prepared by the reaction of SO_3 and CCl_4,1 and subsequently purified by fractional distillation first, and then by trap-to-trap distillations in vacuum conditions. The identity and purity of the sample were checked by IR and Raman spectroscopy. The photoexcitation and photofragmentation in the energy region between 12 and 300 eV was studied. The Total Ion Yield (TIY) spectra show the S 2p, Cl 2p and S 2s edges, at 182.4, 212.4 and 236.6 eV, respectively. The most abundant ion detected in the PEPICO spectra, after the photoexcitation of the sample in the 12-21 eV energy region, was the $ClSO_2^+$ fragment (43.4% at 13 eV and 44.0% at 21 eV). At higher ionization energies, the atomization processes dominate the PEPICO spectra, being the abundances of O^+, S^+ and Cl^+ 46.5, 15.9 and 22.2

1. R. M. Romano, C.O. Della Védova, H. Beckers, H. Willner. Inorganic Chemistry. 2009. 48 (5), 1906.
2. W. B. Demore, M.-T. Leu, R. H. Smith, Y. L. Yung., 1985, 63, 347-353.

Acknowledgements: This work has been largely supported by LNLS under Proposal TGM-10702. We thank Arnaldo Naves de Brito and TGM beamline staff for their assistance throughout the experiments, and Facultad de Ciencias Exactas, Universidad Nacional de La Plata, CONICET and ANPCyT for financial support.

Dissociative photoionization of FSO_2NCO following sulfur 2p and 2s edges

Angelica Moreno Betancourt[1], Romano, Rosana M.[1], Cavasso Filho, R. L.[2], Erben, Mauricio F.[1], Berrueta Martinez, Y.[1], Gerонés, Mariana[1], Rodriguez Pirani, Lucas[1], and Della Védova, Carlos O.[1]

[1] Universidad Nacional de La Plata - La PLata B.A. Argentina
[2] Universidade Federal do ABC - Santo André SP Brazil

As a part of project aimed to the study of the photochemical and electronic properties of molecules that possess the -XSO_2- group (X = halogen) namely Photoexcitation, photoionization and photofragmentation studies of molecules with atmospheric interest, in the present work we present a study of the fluorosulphuryl isocyanate, FSO_2NCO. Very recently, a similar experimental study was carried out at LNLS for the related molecule $ClSO_2NCO$. The sample was prepared by the fluorination of $ClSO_2NCO$ using SbF_3 and subsequent trap-to-trap distillation in a vacuum line.1 The purity of the compound was carefully checked by infrared spectroscopy. The experiments have been performed using synchrotron radiation from the TGM beam line in the range 100-300 eV. The Total Ion Yield spectrum (TIY) of FSO_2NCO is dominated by a group of bands centered at 171.0, 172.4, 173.8, 175.2, and 176.2 eV and a small shoulder at 177.2 eV. The S 2p threshold is located at approximately 183.0 eV. In addition, the S 2s threshold was also observed in the TIY spectrum at 237.2 eV. The photoelectron-photoion coincidence (PEPICO) and photoelectron-photoion-photoion coincidence (PEPIPICO) spectra were measured at the most important S 2p transitions, below and above the ionization edge. The analysis of the PEPICO spectra reveals a decrease of the intensity of the heaviest ions when the incident photon energies were increased. The most noticeable change observed by going toward higher energies is the increment of the signal corresponding to the O+ ion from 13 % at 160 eV to 41 % at 237 eV. On the other hand, several islands were observed in the PEPIPICO spectra, presenting the C^+/O^+, N^+/O^+, F^+/O^+, NC^+/O^+, CO^+/O^+, S^+/O^+, NCO^+/O^+ and SO^+/O^+ coincidence the higher intensities.

1. R. M.S. Alvarez,E.H. Cutín, H.G. Mack and C. O. Della Védova, J. Mol. Struct, 323 (1994) 29-38.

Acknowledgements: This work has been largely supported by LNLS under Proposal TGM-10702. We thank Arnaldo Naves de Brito and TGM beamline staff for their assistance throughout the experiments, and Facultad de Ciencias Exactas, Universidad Nacional de La Plata, CONICET and ANPCyT for financial support.

Laser Cooling in Unfriendly Environments - Advances in Synchrotron Spectroscopy of Laser Cooled Atoms

Cavasso Filho, R. L.[1], Naves de Brito, A.[2], Coutinho, L.H.[3], and Oliveira, E. T. M.[1]

[1] Universidade Federal do ABC - Santo André SP Brazil
[2] Universidade de Brasília - Brasília DF Brazil
[3] Universidade Federal do Rio de Janeiro - Rio de Janeiro RJ Brazil

During the last two decades, the construction of 2nd Generation Electron Storage Rings allowed several studies related to the interaction of ultraviolet photons and neutral atoms. The majority of these studies were concentrated in the photoionization total cross section, that is, the ionization probability as a function of the photon energy. The photoelectron angular distribution, the partial cross section, is very complicated to measure with electron analyzers. Although a lot of experiments have being performed concerning the total cross section we have few experimental studies of the partial cross section. On the other hand, the partial cross section is very sensitive to relativistic and many body effects in this way, much more information could be extracted in principle. In order to overcome the limitations of the electron analyzers, to get experimental information about the angular distribution of the photoelectrons we decided to measure the ion recoil instead of looking at the electron itself. Since the momentum of the system should be conserved in the events of photoionization, measuring the ions we can get indirect information about the electrons. However the ion recoil energy is much smaller than the atomic thermal energy at room temperature. With laser cooling we can achieve thermal energies 3 orders of magnitude smaller than the typical ion recoil energy. In the first part of this talk I will present the technique of ion recoil momentum spectroscopy, the first experimental results obtained in Brazil, as well as new results obtained by our group in a German 3rd generation Electron Storage Ring, BESSY II, and the future perspectives. Thanks to the high photon flux and energy resolution available in BESSY II we could observe photoionization from the hot background atoms and resolve resonances from excited state cold atoms. As compared to standard optics laboratories, the experimental hall of Synchrotron storage rings are extremely noisy environments for experiments demanding stabilized single frequency laser sources, so we will also talk about the special laser setup developed.

Acknowledgements: We would like to thank the help from LNLS and BESSY II staff during the experiments and the financial support from LNLS, BESSY II, Friends of BESSY, FAPESP and CNPq.

Parte IV

Geociência, Meio-ambiente e Aplicações em Materiais Biológicos

Chroococcidiopsis sp. strain AAB1, a new model from the Atacama Desert for the understanding of extreme UV tolerance in an Astrobiological Context

Azua-Bustos, A.[1], Arenas, C.[1], PAULINO-LIMA, I. G.[2], and Galante, D.[3]

[1] PUC - Chile - Santiago Chile
[2] Universidade Federal do Rio de Janeiro - Rio de Janeiro RJ Brazil
[3] Universidade de São Paulo - São Paulo - Sao Paulo SP Brazil

The Atacama Desert in northern Chile is the driest and oldest desert on Earth. In a recently published report [Azua-Bustos, 2011] we showed that along its Coastal Range, fog can support hypolithic colonization rates of 80From these hypolithic communities we were able to obtain a previously unknown strain of Chroococcidiopsis which we characterized by morphological and molecular means. Due to the extreme tolerance of cyanobacteria of this genus to UV, and since the Atacama Desert has constantly high UV radiation levels all year long, we propose this strain as a pertinent model for understanding the limits UV tolerance for life as we know it. We have measured the viability of the isolate by using the DEAD/LIVE BacLight kit which allows the detection of dead cells by measuring the loss of integrity of the plasma membrane, and found that it remains almost unchanged with control cultures when desiccated. In addition, desiccated samples readily start new cultures. Transmission electron microscopy (TEM) of desiccated samples show no evident changes compared with controls. Pigments extracts from desiccated samples show a decrease in photosynthetic pigments like Chlorophyll-a, measured by fluorescence spectra and by tissue layer chromatography. Desiccated samples also synthesize sucrose, an intracellular compatible solute known to play a role in desiccation tolerance. As desiccation and extreme UV tolerance are thought to share similar metabolic routes [Rebecchi, 2007], we expect that our isolate (as suggested by preliminary experiments performed with our strain at LNLS in 2010) should be extremely tolerant to UV radiation. Future work include exposition of monolayers of our strain using the VUV line, and the determination of its comparative tolerance levels with a Chroococcidiopsis strain (N76) isolated from the Mojave Desert which we also have in culture. The experiments will consist of different exposition times in order to achieve increasing UV accumulation levels and attain the highest levels in which we still see survival as measured by the methods detailed above.

Acknowledgements: This work was suported by Fondecyt Project 1110597. AAB receives a scholarship from Conicyt and additional support from MIFAB (Santiago, Chile).

Study of a new approach to diagnose breast cancer based on synchrotron radiation scattering properties

Conceição, A. L. C.[1] and Poletti, M. E.[1]

Universidade de São Paulo - Ribeirão Preto - Ribeirão Preto SP Brazil

Breast cancer is the most frequently occurring cancer in women accounting for about 20% of all cancer deaths. This scenario is, among other factors, due to inherent limitations of the current clinical methods of diagnosis based on x-ray absorption. Meanwhile, recent researches have shown that the scattered radiation can provide information about the structures that compose a biological tissue, like breast tissue. Then, the information provided by x-ray scattering techniques can be used to identify breast cancer. In this work, we developed a classification model based on discriminant analysis of scattering profiles of 106 human breast samples histopathologically classified as normal tissue, benign and malignant lesion, at wide (WAXS) and small angle x-ray scattering (SAXS) regions.

WAXS and SAXS experiments were carried out at the D12A-XRD1 and D02-SAXS2 beam lines in the National Synchrotron Light Laboratory (LNLS) in Campinas. For WAXS experiment, was used an x-ray beam energy of 11keV allowing to record the momentum transfer interval of $0.7\text{nm}^{-1} \leq (q=4\pi.\sin(\theta/2)/\lambda) \leq 70.5\text{nm}^{-1}$ on the NaI(Tl) detector. While for SAXS experiment was used an x-ray wavelength of 1.488 $\mathring{A}$, a two-dimensional detector and several sample-detector distances, allowing to get the range of $0.07\text{nm}^{-1} \leq q \leq 4.20\text{nm}^{-1}$. The scattering profiles at both regions, for each sample were used to build the diagnosis model based on discriminant analysis.

From WAXS data, differences related to position and intensity of the peaks of the molecular structures were found, when compared normal and pathological breast tissues. While for SAXS these differences were observed in supramolecular structures. The diagnostic model combining the information at WAXS and SAXS yield two linear functions which, allow to correlate changes at molecular scale with those at supramolecular level as well as, to classify correctly all samples analyzed in this study[1]. Finally, the results achieved in this study suggest the possibility of developing new radiological techniques based on x-ray scattering, which would expand the capability of breast cancer diagnosis.

Reference

[1] CONCEIÇÃO, A. L. C., *et al.* **doi:10.1016/j.nima.2010.08.060**.

Acknowledgements: The authors would like to thank LNLS and FAPESP for financial support.

Multi-elemental analyses reveal high potassium levels on induced pluripotent stem cells derived from schizophrenic patients

Cardoso, S.C.[1], Stelling, M.P.[1], B Paulsen[1], and Rehen, S[1]

Universidade Federal do Rio de Janeiro - Rio de Janeiro RJ Brazil

Schizophrenia is a neural disorder that affects approximately 1% of the world population and its causes have not been completely elucidated yet. In this work we analyzed induced pluripotent stem cells derived from schizophrenic patients in order to unveil schizophrenias impairments at the cellular and atomic level. Multi-elemental analyses were performed and results revealed high potassium levels on schizophrenia-derived cells compared to controls (healthy subjects and standard embryonic stem cell lines). Further analyses showed that schizophrenia cells express higher levels of a mutated potassium channel, KCNH2 3.1, which affects neuronal firing and may affect cortical physiology, cognition and psychosis.

Acknowledgements: We thank Carlos Perez for the technical support during the experiment. This work was supported by CNPq, FAPERJ, INCTC and LNLS.

Arsenic Speciation by X-Ray Spectroscopy using Resonant Raman Scattering

H. J. Sánchez[1], Leani, J.J.[1], and Pérez, C. A.[2]

[1] Universidad Nacional de Cordoba - Córdoba Cba Argentina
[2] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

The toxicity of arsenic species is widely known. A realistic evaluation of the risk posed by As depends on accurate determination of As speciation, because its toxicity and mobility varies with oxidation state and chemical environment. The most toxic species are inorganic As (III) and As (V) called respectively arsenite or trivalent arsenic, and arsenate or pentavalent arsenic.

Recently, x-ray Resonant Raman Scattering spectroscopy has been successfully employed to determine the oxidation state of metals. In this work we use RRS spectroscopy to perform arsenic speciation.

The measurements were carried out in XRF station of the D09B-XRF beamline at the Brazilian synchrotron facility (LNLS, Campinas). Mineral samples of As in different oxidation states (As(III) and AS(V)), and two biological forms of arsenic (monomethylarsonic acid (MMA(V) and dimethylarsinic acid DMA(V)) were analysed. The samples were diluted, deposited on silicon wafers and allowed to dry. The amount of liquid deposited on the reflector before evaporation was 20 microliters for all the specimens. These samples were irradiated with monochromatic photons of 11816 eV, i.e., below the K-edge of arsenic in order to inspect the Raman emissions. The measuring livetime was 3600 sec for each sample.

Spectra were analysed with specific programs for spectrum analysis using non-conventional functions for data fitting, i.e., modified Voight functions (for Compton peaks), Gaussian functions for fluorescent and for low intensity peaks (such as escape peaks and other contributions), and polynomial functions for the background. Raman peaks were fitted using specific functions.

In this work we have shown that resonant Raman scattering spectroscopy can be used to analyse arsenic species. The method is very simple and reliable. The most important feature of this method relies in the possibility of using the same spectrometer of XRF analysis or TXRF analysis. In this way, practically in the same experiment of quantifying the traces of arsenic in a sample the species can also be obtained. This work is pioneer in the area and an important work of interpretation is necessary in the future. Nevertheless, this behaviour in the residuals of compounds could be used to identify the oxidation state of the elements under study, offering a possibility of chemical environment determination using RRS spectroscopy.

Acknowledgements: This work was partially supported by the LNLS (Campinas. Brazil)

Bioacumulación de As en larvas de sapo común argentino (*Rhinella arenarum*) expuestos crónicamente durante su desarrollo

Mardirosian M. N.[1], Pérez, C. A.[2], Venturino,A.[1], and Bongiovanni, G.A.[3]

[1] Laboratorio de Investigaciones Bioquímicas, Químicas y de Me - Neuquén Neuqu Argentina
[2] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[3] Unidad Ejecutora Neuquén-CONICET - Neuquén Neuqu Argentina

El arsénico (As) es un contaminante ampliamente distribuido en la naturaleza, es movilizado por agua y puede bioacumularse en especies expuestas. Este elemento resulta altamente tóxico para los procesos biológicos ya que produce estrés oxidativo y lleva a muerte o transformación celular. Debido a que el desarrollo embrionario y larval de los anfibios como el sapo, ocurre en medio acuoso, estos organismos resultan muy apropiados para realizar estudios ecotoxicológicos del As. Además son una pieza clave en la cadena alimenticia en ambientes acuáticos. Recientemente se comenzaron estos estudios en la especie autóctona *Rhinella arenarum* (sapo comón argentino). La técnica SR-TXRF permitió observar que la concentración de As comienza a aumentar a los 8 días de exposición después de la fertilización de los ovocitos. Esta técnica ha sido empleada para determinar la bioacumulación de As durante el estadio larval, después de los 8 días de incubación y el efecto sobre la concentración de otros elementos. Los resultados se suman al análisis de otros biomarcadores como expresión de quinasas relacionadas a estrés oxidativo. Estos estudios permitirán determinar la relación dosis/efecto de la exposición a 0, 1 y 10 ppm de As entre 8 y 21 días

Acknowledgements: The authors would like to thank LNLS - Brazilian Synchrotron Light Source, Campinas, Brazil, under proposal D09B-XRF-11784 /2011. This work was supported by the CONICET and the PICT 214-Préstamo BID, Argentina.

Determinación de las especies químicas de As acumuladas en mitocondrias de corteza renal por SR-XRF-XANES

Pérez, C. A.[1] and Bongiovanni, G.A.[2]

[1] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[2] Unidad Ejecutora Neuquén-CONICET - Neuquén Neuqu Argentina

La contaminación del agua con arsénico (As) es un problema global que afecta la salud de millones de personas. La exposición crónica a As produce cáncer, diabetes, hipertensión, neuropatías, hepato y nefrotoxicidad. Este tóxico produce estrés oxidativo y depolarización de la membrana mitocondrial desencadenando el proceso de muerte celular por apoptosis. En el hígado y en riñón, las especies As(III) y As(V) son mono- o di-metiladas (MMA y DMA) y posteriormente eliminadas, principalmente, por orina con mayores proporciones de DMA(V). Sin embargo, una fracción de As y/o sus metabolitos es retenida y acumulada en algunos órganos. Utilizando la técnica SR-XRF (línea D09B del LNLS) y un haz colimado de 300 m se han elaborado mapas de distribución de As y otros elementos en órganos de ratas que bebieron agua con 50 ppm As(III) durante 60 días. Se observó que As no se acumula en cerebro o páncreas, pero sí en hígado y corteza renal. Debido a que algunos metabolitos de As (compuestos metilados) son canceríenos y de mayor toxicidad que el As inorgánico, se están realizando experimentos para determinar las especies acumuladas en mitocondria, principal organela afectada por As. Los resultados obtenidos en la pesquisa D09B-XRF-9068/2010 utilizando SR-TXRF-XANES, mostraron que una parte del As retenido en riñón sería As(III) (resultados presentados en RAU21). En base a estos resultados previos y teniendo en cuenta que el ácido monometilarsónico MMA(III) sería uno de los metabolitos de mayor carcinogenicidad, se ha buscado la identificación de este metabolito en mitocondrias purificadas a partir de corteza renal de ratas crónicamente expuestas a As, por SR-XRF-XANES utilizando geometría convencional (45), también implementada en el LNLS por este grupo.

Acknowledgements: The authors would like to thank LNLS - Brazilian Synchrotron Light Source, Campinas, Brazil, under proposal D09B-XRF-11903/2011. This work was supported by the CONICET and the PICT97-PRH33-Préstamo BID, Argentina.

Determinación de As en especies autóctonas del sur de Argentina

LAMELA P.A.[1], NAVONI J.A.[2], R.D. Pérez[3], and Bongiovanni, G.A.[4]

[1] Laboratorio de Investigaciones Bioquímicas, Químicas y de Me - Neuquén Neuqu Argentina
[2] Universidad de Buenos Aires - Buenos Aires DF Argentina
[3] Universidad Nacional de Cordoba - Córdoba Cba Argentina
[4] Unidad Ejecutora Neuquén-CONICET - Neuquén Neuqu Argentina

El As es un contaminante ampliamente distribuido en la naturaleza y puede bioacumularse en especies expuestas. Debido al vulcanismo reciente (en términos geológicos) de la Cordillera de los Andes, este contaminante se encuentra en altas proporciones en muchos acuíferos subterráneos y cauces fluviales exponiendo diversas especies y unas 15 millones de personas en América Latina a concentraciones tóxicas de este cancerígeno. En el arco volcánico de la Cordillera de Neuquén (Patagonia Argentina) hemos registrado concentraciones de As en agua superficial de hasta 25 veces los estándares de calidad de agua potable para humanos y 17 veces para la vida de especies acuáticas. Los Andes continúan más allá de Tierra del Fuego, por debajo del mar, reapareciendo como islas y luego emergen nuevamente en la Antártida como los Antartandes, la gran cadena montañosa de la península Antártica. En estas regiones también se ha descripto la presencia de As en sedimentos y macro-algas. Estos antecedentes indican que la técnica SR-TXRF sería muy apropiada para determinar si hay bio-acumulación de As en especies autóctonas expuestas. Principalmente porque algunas de estas especies son consumidas por humanos y para identificar plantas que acumulan As, las cuales serán posteriormente estudiadas como posibles fitorremediadoras.

Acknowledgements: The authors would like to thank LNLS - Brazilian Synchrotron Light Source, Campinas, Brazil, under proposal D09B-XRF-11784/2011. This work was supported by the CONICET and the PICT97-PRH33-Préstamo BID, Argentina.

Calcium Distribution in Ribs of Wistar rats after Photon Irradiation Treatment for Breast Cancer Using Micro-XRF

Nogueira, L.P.[1], Barroso, R.C.[2], Almeida,A.P.[1], Braz, D.[1], deAlmeida, CE.[2], Salata, C.[2], Andrade, CBV[2], and Silva, C.M.[2]

[1] Universidade Federal do Rio de Janeiro - Rio de Janeiro RJ Brazil
[2] Universidade do Estado do Rio de Janeiro - Rio de Janeiro RJ Brazil

Therapeutic doses of radiation have been shown to have deleterious consequences on bone health. Among the treatment strategies used for breast cancer treatment, the most used are radiotherapy and chemotherapy. Radiotherapy may be given to destroy the cancer cells using high-dose x-rays. Protocols vary considerably, but generally whole body irradiation totals from 10 to15 Gy, whereas local therapy totals from 40 to 70 Gy. In clinical practice, the quantitative evaluation of bone tissue relies on measurements of bone mineral density values, which are closely associated with the risk of osteoporotic fracture. Improved survivorship rates of cancer patients receiving radiotherapy increase the importance of understanding the mechanisms and long-term effects of radiation-induced bone loss. In this work, we investigated the variation on calcium distribution in ribs of female Wistar rats (*Rattus norvegicus*) submitted to photon irradiation with a single dose of 20 Gy. The determination of the calcium distribution was performed using synchrotron radiation microfluorescence (SR-μXRF) at the X-ray Fluorescence beamline at Brazilian Synchrotron Light Laboratory (LNLS). Animals were irradiated using the linear accelerator Varian (CLINAC 2100) at the University Centre for Cancer Control of the State University of Rio de Janeiro (CUCC/UERJ). The total dose delivered was 20 Gy. The animals were about three months old and weighting about 200g. They were distributed into two groups (seven per group): control (did not receive any treatment) and irradiated (submitted to irradiation procedure) groups. Results showed that calcium content decreased within the dorsal ribs of rats submitted to radiotherapy in comparison to the control group.

Acknowledgements: The authors thank the Brazilian agencies CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico) and FAPERJ (Fundação de Amparo à Pesquisa do Estado do Rio de Janeiro) for financial support. We would also like to thank Dr. Carlos Alberto Perez for help during μXRF analysis. This research was partially supported by Synchrotron Light National Laboratory (LNLS), Brazil.

Elemental Content Changes in Hemolymph of *Rhodnius prolixus* due to Mercury Contamination: A Study Using SR-TXRF

MANTUANO, A.[1], Oliveira, A. P.[1], Barroso, R.C.[1], Almeida,A.P.[2], Braz, D.[2], Cardoso, S.C.[2], Figueiredo, M.B.[3], Azambuja, P.[3], and Gonzalez, M.S.[4]

[1] Universidade do Estado do Rio de Janeiro - Rio de Janeiro RJ Brazil
[2] Universidade Federal do Rio de Janeiro - Rio de Janeiro RJ Brazil
[3] Fundação Instituto Osvaldo Cruz - Rio de Janeiro RJ Brazil
[4] Universidade Federal Fluminense - Niterói RJ Brazil

In recent years, the effects of pollution on the health of humans and other vertebrates have been extensively studied. However, the effects on some invertebrates are comparatively unknown. Research has demonstrated that toxic metals interfere with the reproduction, development and immune defenses of some terrestrial and marine invertebrates. Depending on environmental conditions, pollution produces chronic and acute effects on different systems and organs of animals. In general, some more toxic elements like arsenic, cadmium, lead, mercury and nickel in contact with organisms change cellular structures, enzyme activities, and in some cases destroy the physiological integrities of the tissues. In insects, the effects of pollutants depend upon the species studied. In this work, we investigated the changes in elemental contents in the hemolymph of *Rhodnius prolixus* on 2 and 5 days after feeding on blood containing mercury chloride. *R. Prolixus* is an obligated hematophagous Hemiptera and one of the most important insect vectors of *trypanosoma cruzi*, the causative agent of chagas disease. The SR-TXRF measurements were performed at the X-ray fluorescence (XRF) beamline facility in Brazilian Synchrotron Light Laboratory LNLS/Brazil. The major elements Cl, K, Ca, Mn, Fe, Cu, Zn, Se, Br, Rb, K were found in all hemolymph samples analysed. Insects treated with HgCl2 had reduced Cl and Ca levels, whereas the same treatment had enhanced Br levels in comparison with non- treated control insects.

Acknowledgements: This work was partially supported by the Brazilian Synchrotron Light Laboratory - LNLS (Project XRF-10959). The authors thank to the Brazilian agencies: PAPES-FIOCRUZ, IOCFIOCRUZ, PDTIS-FIOCRUZ, CNPq and FAPERJ for financial support. We are also grateful to Dr. Carlos Alberto Perez for technical support during the experiment.

Determination and correlation of spatial distribution of trace elements in normal and neoplastic breast tissues evaluated by μ-XRF.

Silva, M. P.[1], Oliveira, M.A.[1], and Poletti, M. E.[1]

Universidade de São Paulo - Ribeirão Preto - Ribeirão Preto SP Brazil

Some trace elements, naturally present in breast tissues, participate in a large number of biological processes, which include among others, activation or inhibition of enzymatic reactions and changes on cell membranes permeability, suggesting that these elements may influence carcinogenic processes. Thus, knowledge of the amounts of these elements and their spatial distribution in normal and neoplastic tissues may help in understanding the role of these elements in the carcinogenic process and tumor progression of breast cancers. Concentrations of trace elements like Ca, Fe, Cu and Zn, previously studied at LNLS using TXRF and conventional XRF, were elevated in neoplastic breast tissues compared to normal tissues. In this study we determined the spatial distribution of these elements in normal and neoplastic breast tissues using μ-XRF technique. We analyzed 22 samples of normal and neoplastic breast tissues (malignant and benign) obtained from paraffin blocks available for study at the Department of Pathology HC-FMRP/USP. From the blocks, a small fraction of material was removed and subjected to histological sections of 60 μm thick made with a microtome. The slices where placed in holder samples and covered with ultralen film. Tissue samples were irradiated with a white beam of synchrotron radiation. The samples were positioned at 45 degrees with respect to the incident beam on a table with 3 freedom degrees (x, y and z), allowing independent positioning of the sample in these directions. The white beam was collimated by a 20 μm microcapillary and samples were fully scanned. At each step, a spectrum was detected for 10 s. The fluorescence emitted by elements present in the sample was detected by a Si (Li) detector with 165 eV at 5.9 keV energy resolution, placed at 90^o with respect to the incident beam. Results reveal that trace elements Ca-Zn and Fe-Cu could to be correlated in malignant breast tissues. Quantitative results, achieved by Spearman correlation tests, indicate a spatial correlation between these pairs of elements ($p = 0.001$) suggesting the importance of these in metabolic processes associated with the development of the tumor.

Acknowledgements: We would to acknowledge the support given by Brazilian agencies CAPES, CNPq, Fapesp and the Brazilian Synchrotron Light Laboratory (LNLS).

Loading of praziquantel in the crystal lattice of solid lipid nanoparticles - Studies by DSC and SAXS

Souza, A. L. R.[1], Sarmento, V.H.V[2], Andreani, T.[3], Cassimiro, D. L.[1], Almeida, A. E.[1], Ribeiro, C. A.[1], Gremião, M. P. D.[1], Silva, A. M.[3], and Souto, E. B.[3]

[1] Universidade Estadual Paulista - Araraquara - Araraquara SP Brazil
[2] Universidade Federal de Sergipe - Itabaiana SE Brazil
[3] Universidade de Trás-os-Montes e Alto Douro - Vila Real Portugal

Praziquantel (PZQ) is the drug of choice for oral treatment of schistosomiasis and other fluke infections that affect humans. Its low oral bioavailability demands the development of innovative strategies to overcome the first pass metabolism. In this work, solid lipid nanoparticles loaded with PZQ (PZQ-SLN) were prepared by a modified oil-in-water microemulsion method selecting stearic acid as lipid phase after solubility screening studies. The mean particle size (Z-Ave) and zeta potential (ZP) were 500 nm and -34.0 mV, respectively. Morphology and shape of PZQ-SLN were analysed by scanning electron microscopy revealing the presence of spherical particles with smooth surface. Differential scanning calorimetry suggested that SLN comprised a less ordered arrangement of crystals and the drug was molecularly dispersed in the lipid matrix. No supercooled melts were detected. The entrapment efficiency (EE) and loading capacity of PZQ, determined by high performance liquid chromatography, were 99.0 and 17.5, respectively. Effective incorporation of PZQ into the particles was confirmed by small angle X-ray scattering revealing the presence of a lipid lamellar structure. Stability parameters of PZQ-SLN stored at room temperature (25 ^{o}C) and at 4 ^{o}C were checked by analysing Z-Ave, ZP and the EE for a period of 60 days Results showed a relatively long-term physical stability after storage at 4 ^{o}C, without drug expulsion.

Acknowledgements: Authors wish to thank Dr. Marcelo Ornaghi Orlandi and Tarek Fernandes for SEM analysis. Laboratorio Nacional de Luz Sincrotron (LNLS) is acknowledged and especially SAXS staff support. Financial support provided by FAPESP, CNPq, CAPES, FCT.

Substituição isomórfica em compósitos do tipo óxido de ferro-carvão - estudo por XANES e EXAFS

Guimaraes, I.R.[1], Mesquita, A.M.[1], Nunes, C. A.[1], and Guerreiro, M.C.[1]

Universidade Federal de Lavras - Lavras MG Brazil

O carvão ativado é um material carbonáceo de estrutura porosa de forma microscristalina não grafítica. É caracterizado por possuir uma elevada área específica e porosidade altamente desenvolvida. Por outro lado, embora altamente viáveis em diversas aplicações tecnológicas devido, sobretudo, ao seu comportamento redox, óxidos de ferro são caracterizados por possuírem, em sua maior parte, baixa área específica. Em catálise heterogênea, área superficial e atividade catalítica estão correlacionados diretamente. Nesse contexto, teve-se como objetivo do trabalho suportar óxido de ferro (fase goethita) puro e parcialmente substituído por níquel em carvão ativado, cuja função básica foi manter a fase ativa em um estado altamente disperso. As análises por XANES e EXAFS permitiram determinar a identidade, estrutura e ambiente químico dos átomos de ferro. O sinal na região de pré-borda, com energia próxima a 7112 eV (relacionada à transição quadrupolar 1s −¿ 3d) foi pouco intenso em todas as amostras, o que é consistente com a geometria octaédrica da vizinhança do ferro. Para geometrias tetraédricas, um sinal na região de pré-borda mais intenso deveria ser observado. Para os materiais substituídos com níquel, a altura e posicionamento da pré-borda variam, o que sugere a formação de algumas estruturas octaédricas ligeiramente distorcidas, possivelmente pela presença dos íons isomórficos. Segundo Cornell e Schwertmann, vários cátions não modificam a estrutura, mas afetam o tamanho da célula unitária, o que pode ser responsável por tais distorções. Com relação à análise por EXAFS, os ajustes indicaram que as distâncias Fe-O e Fe-OH permanecem praticamente constantes mostrando que não houve variações significativas na estrutura local do Fe em substituição. Por outro lado, a altura dos picos diminui quando comparada à goethita pura, tomada como padrão. Esse fato sugere que o número de coordenação dos pares Fe-O e Fe-Fe é menor que o da amostra padrão, o que indica a formação parcial de unidades tetraédricas na estrutura com os elementos dopantes, possivelmente relacionadas à presença do níquel.

Acknowledgements: Esse trabalho foi financiado pela Fapemig, CNPq, Capes e LNLS

Parte V

Matéria Mole e Fluídos Complexos

Equivalent Aqueous Phase Modulation of Domain Segregation in Myelin Monolayers and Bilayer Vesicles

Oliveira, R.G.[1]

Universidad Nacional de Cordoba - Córdoba CO Argentina

Purified myelin can be spread as monomolecular films at the air/aqueous interface. These films were visualized by fluorescence and Brewster angle microscopy, showing phase coexistence at low and medium surface pressures (<20-30 mN/m). Beyond this threshold, the film becomes homogeneous or not, depending on the aqueous subphase composition. Pure water as well as sucrose, glycerol, dimethylsulfoxide, and dimethylformamide solutions (20% in water) produced monolayers that become homogeneous at high surface pressures; on the other hand, the presence of salts (NaCl, $CaCl_2$) in Ringers and physiological solution leads to phase domain microheterogeneity over the whole compression isotherm. These results show that surface heterogeneity is favored by the ionic milieu. The modulation of the phase-mixing behavior in monolayers is paralleled by the behavior of multilamellar vesicles as determined by small-angle and wide-angle x-ray scattering. The correspondence of the behavior of monolayers and multilayers is achieved only at high surface pressures near the equilibrium adsorption surface pressure; at lower surface pressures, the correspondence breaks down. The equilibrium surface tension on all subphases corresponds to that of the air/alkane interface (27 mN/m), independently on the surface tension of the clean subphase.

Acknowledgements: We thank HASYLAB-Deutsches Elektronen Synchrotron (DESY), Hamburg, Germany (beamline A2 at DORIS) and Laboratório Nacional de Luz Síncrotron, Campinas, Brazil (beamline SAXS2) for measurement times. This work was supported by Consejo Nacional de Investigaciones Científicas y Ténicas (CONICET), Fundación Antorchas, Fondo para la Investigación Científica y Tecnológica (FONCyT), and Secretaría de Ciencia y Tecnología, University of Córdoba (SECyT-UNC). R.G.O. is career investigator of CONICET (Argentina). R.G.O. thanks the Alexander von Humboldt Foundation for a postdoctoral research fellowship.

Thermoplastic starch and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) bionanocomposites before and after prolonged storage

Magalhães, N. F.[1], DAHMOUCHE, K[2], and Andrade, C. T.[2]

[1] Universidade Federal do Rio de Janeiro - Macae RJ Brazil
[2] Universidade Federal do Rio de Janeiro - Rio de Janeiro RJ Brazil

Glycerol-plasticized cornstarch and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) were melt-mixed at a constant 70:30 (wt/wt) ratio. One-step extrusion processings were performed in the presence of a commercial organically-modified clay. The effect of increasing clay contents on the morphologies and physical properties of the blends was investigated after processing, and compared to the neat blend, by scanning electron microscopy (SEM), X-ray diffraction (XRD) and dynamic mechanical analysis (DMA). The results indicated that increasing clay contents promoted improvements in the compatibility between the components and allowed to better understand the role of clay in compatibilization mechanism. After aging for 12 months, the blends were characterized by SEM, XRD and Small-Angle X-ray Scattering (SAXS). As revealed by all techniques, the reduced size of the PHBV dispersed phase and the decreased crystallinity of both phases promoted by clay particles were maintained, although some prejudicial effect of aging was noticed. Nevertheless, SAXS results unambiguously proved the presence of both exfoliated lamellae and a small number of clay tactoids in the aged bionanocomposites.

Acknowledgements: CNPq, FAPERJ, CAPES and LNLS

Unimolecular Micelles and Electrostatic Nanoassemblies Stemming From Hyperbranched Polyethyleneimine

Picco,A.[1], Silbestri, G.F.[2], O. Azzaroni[1], and Ceolin M.[1]

[1] Instituto de Investigaciones Fisicoquimicas Teoricas y Aplic - La Plata BA Argentina
[2] Universidad Nacional del Sur - Bahía Blanca Bueno Argentina

Hyperbranched polyethyleneimine (HPEI) was used as a building block to construct different self-assembled soft nanomaterials. This was accomplished via covalent linkage of carboxylic acids (CA) of different chain lengths to terminal amino groups of HPEI, thus leading to the formation of reverse unimolecular micelles constituted of a hydrophilic core and a hydrophobic shell. On the other hand, acid-base interactions in organic solvents between CAs and peripheral amino groups of HPEI also facilitated the formation of electrostatic assemblies with reverse micellar properties.

In this work we describe the formation of both structures as well as their characterization using diverse techniques including SAXS, NMR, IR, and fluorescence spectroscopy, among others. Unimolecular micelles were synthesized through the reaction of HPEI (Mn= 10 KDa) and acyl chlorides with different chain lengths (C8, C10, C12, C14, C16, C18). Depending on the chain length, the solvent and the temperature, a broad variety of supramacromolecular assemblies can be observed by SAXS measurements, including structured aggregation, and gelation.

Hyperbranched electrostatic assemblies were simply produced by mixing HPEI with selected carboxylic acids (C8, C10, C12, C14, C16, C18) in an appropriate solvent, which dissolves the CA, or both reactants, i.e. chloroform, toluene or THF. The formation of the assemblies was corroborated using FT-IR by monitoring the appearance of the carboxylate bands. SAXS experiments of electrostatically assembled micelles showed globular, core-shell structures, whose characteristics are similar, in many cases, to their covalent counterparts prepared using the same chain length CA shells.

Acknowledgements: CONICET, ANPCyT, UNS ,UNLP (Argentina), LNLS (Brazil), Max Plank Society (Germany), and Anton Paar (Austria).

In situ SAXS experiment during DNA and liposome complexation

Gasperini, A. A.[1], Balbino, T. A.[2], de la Torre, L. G.[2], Oliveira, C. L. P[3], and Cavalcanti, L. P.[1]

[1] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[2] Universidade Estadual de Campinas - Campinas SP Brazil
[3] Universidade de São Paulo - São Paulo - São Paulo SP Brazil

Gene therapy is an exciting research area that allows the treatment of different diseases. Basically, an engineered DNA that codes a protein is the therapeutic drug that has to be delivered to the cell nucleus. After that, the DNA transfection process allows the protein production using the cell machinery. However, the efficient delivery needs DNA protection against nucleases and interstitial fluids. In this context, the use of cationic liposome/DNA complexes is a promising strategy for non-viral gene therapy. Liposomes are lipid systems that self-aggregate in bilayers and the use of cationic lipids allows the electrostatic complexation with DNA. In this work, we used SAXS technique to study the complexation kinetics between cationic liposomes and plasmid DNA and evaluate the liposome structural modifications in the presence of DNA.

Liposomes were prepared according to [1] using as plasmid DNA vector model a modified version of pVAX1-GFP with luciferase as reporter gene [2]. The complexation was promoted in a SAXS sample holder containing a micro-channel to get access to the compartment between two mica windows where the X-ray beam could cross through [3]. We obtained *in situ* complexation using such sample holder coupled to a fed-batch reactor through a peristaltic pump. The scattering curves were recorded each 30 seconds during the cycles. The DNA was added until a certain final ratio between surface charges previously determined. We studied the form and structure factor model for the liposome bilayer to fit the scattering curves [4]. Structural information such as the bilayer electronic density profiles, number of bilayers and fluidity were determined as a function of the complexation with DNA. These differences can reflect in singular *in vitro* and *in vivo* effects.

[1] L. G. de la Torre *et al.* Colloids and Surfaces B: Biointerfaces, **73**, 175 (2009)
[2] A. R. Azzoni *et al.* The Journal of Gene Medicine, **9**, 392 (2007)
[3] L. P. Cavalcanti *et al.* Review of Scientific Instruments, **75**, 4541 (2004)
[4] J. Trevisan *et al*, in *Non-viral gene therapy* (Yuan, X.), Intech (2011)

Acknowledgements: The authors thank Dr. Adriano Azzoni (USP-SP) for the contribution with the plasmid DNA extraction. This project was financed by FAPESP, UNICAMP and LNLS. The SAXS experiments were performed at LNLS/SAXS1 beamline.

Estudo da ordem de longo alcance e propriedades termodinâmicas de multicamadas de ácidos fosfônicos pela técnica de difração de raios-x dispersiva em energia

Pauli, M. de[1], Malachias, A.[2], and Pérez, C. A.[3]

[1] Universidade Estadual de Campinas - Campinas SP Brazil
[2] Universidade Federal de Minas Gerais - Belo Horizonte MG Brazil
[3] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

Medidas de difração de raios-X foram realizadas em multicamadas auto-organizadas de ácidos fosfônicos OPA e OcPA. Esses dois sistemas apresentam ordenamento lamelar de longo alcance quando depositados em substrato plano como silício. Periodicidades distintas são observadas nos padrões de difração, apontando para o fato que diferentes formas de empacotamentos podem ser encontradas. Para estudar o comportamento termodinâmico do sistema, a temperatura foi variada a fim de observar modificações estruturais no empilhamento das multicamadas. Medidas de difração convencional permitiram introduzir modelos de empilhamento demonstrando modificações na estrutura de empilhamento em função da temperatura. Utilizando difração de raios-x dispersiva em energia que permite realizar medidas em curto intervalo de tempo mas com menor resolução analisamos a fração volumétrica presente na amostra para cada tipo de ordenamento em vários intervalos de temperatura. O padrão de ordenamento das moléculas no plano do substrato foi também investigado realizando-se medidas em geometria de transmissão de raios-x (SAXS/WAXS). Os resultados mostram uma transição entre empacotamento planar hexagonal para baixas temperaturas e empacotamento cúbico para temperaturas acima de 75C. Reunindo as informações obtidas através dessas técnicas é possível a construção de um diagrama de fase ilustrando a fração ordenada de moléculas em função da temperatura.

Acknowledgements: Os autores agradecem ao LNLS e a FAPESP processo n2009/11875-2 pelo auxílio financeiro.

Structural Investigations of Sodium Caseinate micelles in complex environments

Huck Iriart, C.[1], M. L. Herrera[2], Candal, R.[2], Oliveira, C. L. P[3], and Torriani, I.[4]

[1] Universidad de Buenos Aires - Buenos Aires - Argentina
[2] Universidad de Buenos Aires - Buenos Aires DF Argentina
[3] Universidade de São Paulo - São Paulo - São Paulo SP Brazil
[4] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

The most frequent destabilization mechanisms in Sodium Caseinate (NaCas) emulsions are creaming and flocculation. Coarse or fine emulsions with low protein content destabilize mainly by creaming. If migration mechanism is suppressed, flocculation may become the main mechanism of destabilization. Small Angle X-Ray Scattering (SAXS) technique was applied to investigate sodium caseinate micelles structure in different environments. As many natural products, Sodium Caseinate samples have large polydisperse size distribution. The experimental data was analyzed using advanced modeling approaches. The Form Factor for the Caseinate micelle subunits was described by an ellipsoidal core shell model and the structure factor was split into two contributions, one corresponding to the particle-particle interactions and another one for the long range correlation of the subunits in the supramolecular structure. For the first term the hard sphere structure factor using the Percus-Yevick approximation for closure relation was used and for the second term a fractal model was applied.

Three concentrations of sodium Caseinate (2, 5 and 7.5 %wt.) were measured in pure water, sugar solutions (20 %wt.) and in three different lipid phase emulsions containing 10 %wt. sunflower seed, olive and fish oils. Data analysis provided an average casein subunit radius of 4 nm, an average distance between the subunits of around 20nm and a fractal dimension value of around 3 for all samples. As indicated by the values of the correlation lengths for the set of studied samples, the casein aggregation is strongly affected by simple sugar additions and it is enhanced by emulsion droplets hydrophobic interaction. As will be presented, these nanoscale structural results provided by scattering experiments is consistent with macroscopic results obtained from several techniques, providing a new understanding of NaCas emulsions.

Acknowledgements: This work was supported by CONICET, ANPCyT, UBA, CNPq and FAPESP. The authors wish to thank to the Synchrotron Light National Laboratory (LNLS, Campinas, Brazil) for the use of X-ray facilities.

SAXS as a tool to understand the phase behavior of ethoxylated complex salts

Percebom, A. M.[1], Barbosa, L.R.S.[2], Itri, R.[2], and Loh, W.[1]

[1] Universidade Estadual de Campinas - Campinas SP Brazil
[2] Universidade de São Paulo - São Paulo - São Paulo SP Brazil

Complex salts formed by the cationic surfactant hexadecyltrimethylammonium (CTA+) and random copolyanions grafted with neutral hydrophilic side chains were investigated in mixtures with water at different concentrations. The structural characterization by Small Angle X-Ray Scattering (SAXS) allowed understanding the changes on the shape and size of the aggregates with increasing the concentration of complex salt. Besides, the comparison of three systems formed by different anionic copolymers showed the effect of the amount and length of the grafted side chains.

Generally, strong electrostatic attraction between polyelectrolytes and ionic surfactants of opposite charges leads to the formation of a concentrated phase rich in complex salt. However, this study involved the synthesis of complex salts formed by polyelectrolytes containing grafted neutral side chains (oligomers of ethylene oxide), and the investigated systems presented remarkably distinct phase behavior in water.

The presence of oligomers of ethylene oxide pending along the main chain of polymethacrylate enhanced the solubility of the complex salt aggregates in water, leading to formation of micelles. The longer or more numerous the hydrophilic side chains of the copolymer, the greater the solubility of the complex salt in water. The SAXS curves for these systems could be fitted using a model for core-shell cylinders or ellipses, providing parameters such as the core radius, the shell thickness and the main-axes length. Whereas, by increasing the complex salt concentration, a rich phase behavior could be observed. The systems displayed a variety of liquid crystalline phases identified from SAXS curves (e.g. cubic Pm3n, hexagonal close packing of spheres hcp and hexagonal packing of finite and infinite cylinders), which were used to calculate parameters such as the unit cell size.

Due to the possibility of characterizing the structures formed by complex salts in water at different concentrations, the phase behavior of the systems was studied and important information about the structure of the aggregates were obtained.

Acknowledgements: FAPESP is gratefully acknowledged for the PhD scholarship to A.M.P. The authors thank the Brazilian Synchrotron Laboratory, LNLS, for support and the use of the SAXS beamline.

SAXS investigations on lipid membranes under osmotic stress

RUBIM, R. L.[1], vieirav[1], Gerbelli, B. B.[1], Teixeira da Silva, E.R.[1], Oliveira, C. L. P[1], and Oliveira, E. A.[1]

Universidade de São Paulo - São Paulo - São Paulo SP Brazil

In this work we, experimentally, investigate the interactions between lipid bilayers. A structural characterization is performed by small angle x-ray scattering (SAXS) on multilamellar systems under known osmotic pressure. Changes in the composition of membranes can modify their mechanical properties and structural parameters, like the flexibility of these membranes, which plays a key role on the determination of the tridimensional organization of bilayers. The membranes are composed of soya lecithin, where the major component is DPPC (Dipalmitoylphosphatidylcholine), and fatty acids are incorporated to the membrane in different concentrations, in order to turn the membrane more fluid. The membranes are inserted in a solution of PVP [poly(vinyl-pyrrolidone) - 40000] and the polymer will apply an osmotic pressure on them. The osmotic pressure is controlled by preparing PVP solutions of desired composition and, as we know the concentration of polymer in solution, we can obtain the intensity of the osmotic pressure. SAXS experiments were done in order to determine the distance between the bilayer. From the position of the Bragg peaks, the lamellar periodicity (the thickness of the membranes plus their distance of separation) was determined. Using theoretical model for the form and structure factors we fitted those experimental data and determined the thickness of the membranes. The distance between the membranes was controlled by the osmotic pressure (P) applied to the membranes and, for a given pressure, we determine the distance between the bilayers (a) on equilibrium. The experimental curve P(a) is theoretically described by the different contributions from van der Waals, hydration and fluctuation forces. From the fitting of experimental curves, relevant parameters characterizing the strength of the different interactions are obtained, such as Hamaker and rigidity constant [2, 3]. We observe that the separation between the bilayers on equilibrium is shifted to higher values when fatty acids are incorporated to the membrane, indicating a relative increasing of repulsive interactions [2]. These findings reveal the great potential of this methodology for studies of membranes of biological interest.

[1] J. Israelachvili, Intermolecular and surface forces, 2nd edition, Academic Press, London 1991.; [2] H. Petrache, T. Zemb, L. Belloni, and V. Parsegian, PNAS, 103, 7982(2006).; [3] T. J. McIntosh, S. A. Simon, Biochemistry 25, 4058(1986).

Acknowledgements: This work was supported by CNPq and INCT-FCx.

Parte VI

Materiais Estruturais e Aplicações na Indústria

TEM, SEM, and X-ray analysis of Cu–Ni alloy nanoparticles

Carreras, A. C.[1], Cangiano, M de los A.[2], Ojeda, M.W.[2], and Ruiz, M. del C.[2]

[1] Universidad Nacional de Cordoba - Córdoba Cba Argentina
[2] Universidad Nacional de San Luis - San Luis Argentina

Cu–Ni alloys are extensively used in several metallurgical industries. The traditional methods for the synthesis of these alloys have some limitations, mainly related with manufacturing costs and with the homogeneity of the final product, which encourages the study and development of new methodologies to produce them. In our research group we have developed a new chemical route for the synthesis of Cu–Ni alloys [1,2]. The process involves four steps, including the precursor preparation by the citrate-gel method and the subsequent decomposition, calcination and reduction. In this work, the physicochemical characterization of Cu–Ni alloy nanoparticles sinthesized by the new chemical route is presented. The sample characterization was performed by means of Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS) and X-Ray Diffraction (XRD). The results of TEM and EDS analyses showed that Cu–Ni alloy nanoparticles with a good chemical homogeneity were obtained. The mean Cu/Ni atomic ratio was around 0.98. The XRD diagram showed the formation of a new phase with intermediate lattice parameter between the corresponding to pure Cu and Ni structures, and with an average grain size around 6 nm. The chemical homogeneity of the alloy obtained is discussed on the basis of the resolution of the analytical techniques used.

[1] M. de los A. Cangiano, A. C. Carreras, M. W. Ojeda and M. del C. Ruiz, A new chemical route to sythesize Cu–Ni alloy nanostructured particles. *Journal of Alloys and Compounds*, **458** (2008) 405-409.

[2] M. de los A. Cangiano, M. W. Ojeda, A. C. Carreras, J. A. González and M. del C. Ruiz, A study of the composition and microstructure of nanodispersed Cu–Ni alloy obtained by different routes from copper and nickel oxides. *Materials Characterization*, **61** (2010) 1135-1146.

Acknowledgements: We are grateful for the financial support of CONICET for this study. The measurements were performed in the LME-LNLS, from Campinas (SP), Brazil; and in the INTEQUI-UNSL, from San Luis, Argentina.

CONTROLLING SILICATE MESO-STRUCTURES USING SUCUPIRA OIL AS A NEW SWELLING AGENT

Rocha, L. A.[1], FARIA, E.H.[1], Ciuffi, K J[1], Nassar, E. J.[1], Cunha, W. R.[1], and Caiut, J. M. A.[2]

[1] Universidade de Franca - Franca SP Brazil
[2] Universidade de São Paulo - Ribeirão Preto - Ribeirão Preto SP Brazil

Since the discovery of meso-organized template materials by Mobil e Co., the study of silica based nanostructures has become a very active field of research. The synthesis procedure of mesoporous material involves the formation of organic-inorganic composites by self-assembly process. Surfactants micelles and derived structures are used as templates in the generation of mesoporous. The final materials have large specific area and pore volumes, low density, high mechanical and thermal stability, and they may have a wide range of application as catalysis, shape-selective adsorbents, capsules for controlled release of therapeutic agents, electro-optics, and other emerging nanotechnologies [1]. The pore size engineering allows the synthesis of multifunctional materials by the use of many different oils, which have been tested as swelling agents and incorporated during the micellar solution preparation in order to synthesize large pore mesoporous materials; however, most oils have some difficulties like expensive cost or low extraction yield. Oil extracted from Pterodon emarginatus seeds, widely called Sucupira oil has advantage of a high extraction yield and great availability, which allows obtain easily a large volume at low cost. The present work shows an effective natural expander to enlarge the pore size of mesoporous silica. The process was applied by using a solution containing deionized water, ammonium hydroxide, tetraethylorthosilicate (TEOS), and either cetyltrimethylammonium bromide (CTAB) or the block copolymer Pluronic P-123 as structure-directing agent. Sucupira oil has used as swelling agent in different concentrations. The effect of the swelling agent and the influence of the temperature on the structural properties of products were investigated. The obtained materials were characterized by scanning electron microscopy (SEM), small-angle X-ray scattering (SAXS) and nitrogen adsorption-desorption analysis. The results obtained show a highly ordered hexagonal, cubic and lamellar mesostructure depending of oil concentration. Furthermore, the increase of pore diameter in function of oil concentration was clearly observed by nitrogen adsorption-desorption analysis.

[1] S. B. Jung, T. J. Ha and H. H. Park, Thin Solid Films, 2007, 515, 6521-6525.

Acknowledgements: FAPESP, CAPES, CNPq and LNLS

Local Structure of $SrTi_{1-x}Fe_xO_3$ Nanocubes Analyzed by XAS Technique

da Silva, L. F.[1], Mesquita, A.[2], Moreira M. L.[3], Avansi,W.Jr.[1], Longo, E.[3], and Mastelaro, V.R.[1]

[1] Universidade de São Paulo - São Carlos - São Carlos SP Brazil
[2] Universidade Federal de São Carlos - São Carlos SP Brazil
[3] Universidade Estadual Paulista - Araraquara - Araraquara SP Brazil

Perovskite based compounds are promising materials in current science and technology because its structure are very versatile having different and useful technological applications. Among the several perovskite based compounds, more recently, the $SrTi_{1-x}Fe_xO_3$ (STFO) solid solution has attracted the attention of many researches due to its potential application as oxygen gas sensor for automotive emission control [1]. The addition of Fe_2O_3 in $SrTiO_3$ network implies in the substitution of some Ti^{4+} by Fe^{3+} ions which may create different types of defects due the difference in the Ti^{4+} and Fe^{3+} oxidation state [2]. When Fe^{3+} ion occupies the Ti^{4+} octahedral site, mobile oxygen vacancies (Vö) are formed in order to balance the electric charge and thus, the introduction of a large amount of iron creates a relatively large concentration of defects. For the first time, an efficient methodology based on the microwave assisted hydrothermal route to prepare nanostructured STFO at lower temperature (140^{o}C) and shorter treatment time (10 minutes) without the presence of any template. XANES spectra at Fe-K edge revealed that Fe ions have a mixed 2+/3+ oxidation state. XANES spectra at Ti-K edge indicated a significative displacement of Ti atoms from its centrosymmetric position and the analysis of EXAFS spectra shows that iron ions occupy substitutionally Ti^{4+} site. In addition, the increasing of iron content causes an increase of the Debye-Waller factor and a reduction on the optical gap (E_g) and in the photoluminescence intensity. FE-SEM and HR-TEM images showed that the morphology of the microsized particles is a cube-like formed by a self-assembly process of small primay nanocrystals. The Ti and Fe K-edge X-ray absorption spectra were collected at the XAFS1 and XAFS2 LNLS beam lines. HR-TEM images were collected at the C2Nano laboratory. [1] G. Jin, G. Choi, et al. **J Nanosci. Nanotechnol.** 11,*2011*,1738. [2] M. Vracar, A. Kuzmin, et al. **Phys. Rev. B.** 76,*2007*,174107.

Acknowledgements: This work was supported by CNPq (Proc. 70/2008) and FAPESP

Phase characterization of recycled Zircaloy

Martinez, L. G.[1], Pereira, L.A.T.[1], Rossi, J. L.[1], Takiishi, H.[1], Corrêa, H. P. S.[2], Orlando, M. T. D.[3], Ichikawa, R. U.[1], and X. Turrillas[4]

[1] Instituto de Pesquisas Energéticas e Nucleares - São Paulo SP Brazil
[2] Universidade Federal do Mato Grosso do Sul - Campo Grande MS Brazil
[3] Universidade Federal do Espírito Santo - Vitória ES Brazil
[4] Consejo Superior de Investigaciones Científicas - Madrid Spain

PWR reactors employ as nuclear fuel UO_2 pellets with Zircaloy clad. Brazil is autonomous in the nuclear fuel cycle, from uranium mining to enrichment and nuclear fuel manufacture. However, the industrial production of nuclear zirconium alloys does not meet the demand, leading to importation of Zircaloy for fuel manufacturing. In the fabrication of fuel elements parts, machining chips of alloys are generated. As the Zircaloy chips cannot be discarded as ordinary metallic waste, the recycling of this material is strategic in economical and environmental aspects. In this work are described two methods that are being developed to recycle Zircaloy chips. The first method the Zircaloy machining chips are melted using an electric arc furnace to obtain small laboratory ingots. The second method uses powder metallurgy technique. By this later method, the Zircaloy chips are submitted to a hydriding process and the resulting material is milled in a high-energy ball mill. The powder is cold isostatically pressed and vacuum sintered. The elemental composition of the materials obtained using both methods is being determined using X-ray fluorescence techniques and compared to the specifications of nuclear grade Zircaloy and to the composition of the starting chips. The phase composition was determined using synchrotron X-ray diffraction. The ingots were vacuum annealed and the microstructures resulting from both processing methods before and after heat treatments were characterized using optical and scanning electron microscopy. The hardness of the materials was evaluated. A methodology of chemical analysis using X-ray fluorescence spectrometry, for composition certification, was established and tested. The results showed that recycled Zircaloy presented adequate microstructure for nuclear use. The good results of the powder metallurgy method suggest the possibility of producing small parts, like cladding cap-ends, using near net shape sintering.

Acknowledgements: The authors would like to acknowledge to CNPEM/LNLS, to CNPq (contracts n 306530/2010-4 and 483686/2010-7), to Indústrias Nucleares Brasileiras - INB and to Comissão Nacional de Energia Nuclear - CNEN for a Ph.D. scholarship of L. A. T. Pereira.

Estrutura, morfologia e estabilidade térmica de fluoromicas sintéticas

Souza, D. H. S.[1], DAHMOUCHE, K[1], Andrade, C. T.[1], and Dias M. L.[1]

Universidade Federal do Rio de Janeiro - Rio de Janeiro RJ Brazil

A morfologia e estabilidade térmica de uma fluoromica sintética completamente inorgânica (Somasif ME-100) e quatro fluoromicas organofílicas foram investigadas comparativamente usando diferentes técnicas, tais como, FTIR, XRD, SAXS, GPC, SEM e TGA. Essas micas organofílicas que são intercaladas com sais de amônio contendo cadeias longas à base de oligoéteres (Somasif MEE e MPE) e de grupos alquila (Somasif MAE e MTE) apresentam, como morfologia típica, famílias de domínios de mica com dimensão lateral de até 4 μm, formado pela associação de agregados nanométricos de mica com diferentes distâncias entre as plaquetas. As micas Somasif contendo sal de amônio com grupos alquila apresentaram a maior proporção de camadas não-modificadas organicamente, enquanto que as fluoromicas modificadas contendo oligoéteres apresentaram a maior fração volumétrica de agregados com maiores distâncias interlamelares d (até 6,1 nm). Todas as fluoromicas organofílicas apresentaram degradação térmica entre 200-460 C e a mica Somasif MPE que contem cadeias de poli(propileno glicol) tem a melhor estabilidade térmica entre as organomicas.

Acknowledgements: Os autores agradecem ao CNPq, CAPES e FAPERJ pelo apoio financeiro e ao Professor Chiaki Azuma da University of the Air, Japão, pela doação das micas Somasif. Os autores também agradecem ao LNLS pela oportunidade de realizar medidas de SAXS.

Nanocompósitos de poli(ácido lático)/organofluoromica sintética: estrutura, propriedades reológicas e térmicas

Souza, D. H. S.[1], DAHMOUCHE, K[1], Andrade, C. T.[1], and Dias M. L.[1]

Universidade Federal do Rio de Janeiro - Rio de Janeiro RJ Brazil

Nanocompósitos de poli(L-ácido lático)(PLLA)/fluoromica organicamente modificada a diferentes composições foram preparados por processamento no estado fundido em um misturador interno, nas mesmas condições. Cromatografia de permeação em gel (GPC) foi utilizada para medir as massas molares do PLLA, antes e após o processamento. Os resultados indicaram que o PLLA apresentou alguma degradação durante a mistura no estado fundido. Com a adição da fluoromica organicamente modificada, uma maior redução nas massas molares do polímero foi observada. A estrutura da mica sintética e dos compósitos foi estudada por espalhamento de raios-X a baixo ângulo (SAXS), o que revelou a presença de agregados de mica de tamanho nanométrico. Medidas reológicas dinâmicas no estado fundido do PLLA e dos nanocompósitos foram realizadas na região viscoelástica linear. Um comportamento predominantemente viscoso foi obtido para as amostras do polímero, enquanto os nanocompósitos apresentaram um comportamento elástico pronunciado. A adição de mica ao PLLA também teve um efeito significativo sobre a viscosidade complexa, apresentando um aumento da pseudoplasticidade com o aumento da composição de mica. Abaixo da T_g, os resultados da análise dinâmico-mecânica mostraram uma diminuição substancial da rigidez dos nanocompósitos em relação ao PLLA sozinho, atribuída à presença de alto teor do intercalante orgânico presente na fluoromica sintética. Uma menor taxa de cristalização durante aquecimento foi detectada para os nanocompósitos em comparação ao PLLA processado sem carga.

Acknowledgements: Os autores agradecem ao CNPq, CAPES e FAPERJ pelo apoio financeiro e ao LNLS pela oportunidade de realizar medidas de SAXS.

Study of the piezoresistive properties of semiconductor oxide thin films

Cardoso, G. W. A.[1], Massi, M.[1], Fraga, M. A.[2], and Cunha, Cícero L.A.[1]

[1] Instituto Tecnológico de Aeronáutica - São José dos Campos SP Brazil
[2] Instituto de Estudos Avançados - São José dos Campos SP Brazil

The purpose of this study is to characterize the piezoresistive properties of semiconducting oxides thin films in order to develop a prototype of piezoresistive microsensors for high temperature applications. Zinc oxide (ZnO), titanium oxide (TiO_2) and nitrogen-doped titanium oxide (TiO_xN_y) thin films have been deposited by RF magnetron sputtering technique using targets of Ti (99.99%) and ZnO (99.99%) on (100) Si substrates under different experimental conditions. A set of test structures were designed to characterize the piezoresistive properties of these films. The test structures are constituted of thin-film piezoresistors in different strain gauge configurations: Wheatstone bridge (open and closed), half bridge and also the piezoresistor alone. The thin-film piezoresistors have been microfabricated using well known processes such as photolithography, metallization, lift-off and RIE (reactive ion etching). The piezoresistive measurements have been performed by cantilever deflection method to determine the variation of the electrical resistance of the strain gauge as a function of mechanical stress from room temperature up to 300 ^oC. These analyses will allow comparing the performance of strain gauges based on semiconductor oxide with of others piezoresistive materials presented in the literature, in order to identify potential applications.

Acknowledgements: CNPq for financial support

Phase characterization of recycled Zircaloy by synchrotron diffraction

Martinez, L. G.[1], Pereira, L.A.T.[1], Rossi, J. L.[1], Takiishi, H.[1], Corrêa, H. P. S.[2], Orlando, M. T. D.[3], and X. Turrillas[4]

[1] Instituto de Pesquisas Energéticas e Nucleares - São Paulo SP Brazil
[2] Universidade Federal do Mato Grosso do Sul - Campo Grande MS Brazil
[3] Universidade Federal do Espírito Santo - Vitória ES Brazil
[4] Consejo Superior de Investigaciones Científicas - Madrid Spain

Brazil is autonomous in the nuclear fuel cycle, from uranium mining, processing and enrichment to nuclear fuel manufacture. Our PWR nuclear reactors employ as nuclear fuel UO_2 pellets in Zircaloy cladding. Some other reactor core parts are also made using zirconium alloys. The Brazilian production of nuclear zirconium alloys does not meet the demand, leading to its importation for fuel manufacturing. Otherwise, in the fabrication of nuclear fuel, a quantity of machining chips are generated and, as these Zircaloy chips cannot be discarded as ordinary waste, its recycling is strategic in economical and environmental aspects. Two methods are being developed at the Instituto de Pesquisas Energéticas e Nucleares - IPEN - in order to recycle these chips. By one of the methods the Zircaloy chips are melted in an electric arc furnace to obtain ingots. By the other method the Zircaloy chips are submitted to a hydriding process and milled in a high-energy ball mill. The powder is cold isostatically pressed and vacuum sintered. The elemental composition of the materials was determined using X-ray fluorescence techniques and compared to the specifications of nuclear grade Zircaloy. The microstructures resulting from both processing methods, before and after heat treatments, were characterized using optical and electron microscopies. The phase composition was determined using synchrotron X-ray diffraction at the D10B-XPD beamline of the Brazilian Synchrotron Light Source - LNLS. The results showed that recycled Zircaloy presented adequate microstructure for nuclear use.

Acknowledgements: The authors would like to acknowledge to CNPEM/LNLS, to FINEP, to CNPq (contracts n 306530/2010-4 and 483686/2010-7), to Indústrias Nucleares Brasileiras - INB and to Comissão Nacional de Energia Nuclear - CNEN for a Ph.D. scholarship of L. A. T. Pereira.

Theoretical and experimental investigation of the disordered quaternary oxide $CoMo_{0.5}W_{0.5}O_4$

Licea, Y.[1], Eon J-G.[1], Palacio L.[2], Faro Jr., A. C.[1], and Grau-Crespo, R.[3]

[1] Universidade Federal do Rio de Janeiro - Rio de Janeiro RJ Brazil
[2] Universidade do Estado do Rio de Janeiro - Rio de Janeiro RJ Brazil
[3] University College London - London UK United Kingdom

DFT calculations, EXAFS and synchrotron-light XRD techniques have been used to determine the solid structure and thermodynamic of mixing of a trimetallic wolframite oxide. The chemical formulae $CoMo_{0.51}W_{0.49}O_4$ has been determined from Rietveld refinement of synchrotron-light XRD data. From EXAFS simulation it could be concluded that oxygen in the first W(Mo) coordination shell are distributed as in the wolframite pure phase lattice. The theoretical calculation of Gibbs free energy of mixing, using the SOD and VASP codes, predicts a thermodynamically favorable wolframite-like structure solid solution which is disordered at all temperatures of interest, with a slightly negative enthalpy of mixing. Calculation of vacancies formation energies in all oxygen different asymmetric position of a 2x2x2 super cell have shown that electrons are dislocated toward Mo atom after oxygen vacancies formation and also that these vacancies are energetically favored by Mo incorporation from x=1 to x=0 in the $CoMo_xW_{(1-x)}O_4$ wolframite phase system, concluding that no synergetic between Mo and W but a linear effect would explain its catalytic behavior on propane ODH reaction.

Acknowledgements: Y. E. Licea would like to acknowledge Nora de Leeuw for the financial support at stage in Dept. Chemistry-University College London and Carlos Paiva for his great help on Rietveld refinement. The authors would like to thank LNLS for the project approval and financial support for carrying through of the experiments (proposals on XPD and XAFS2) and Beatriz Moreno help at the XPD line.

Estudos Estruturais (XRD1-LNLS) e Morfológicos (FEG-Zeiss) de Akaganeíta [β-FeO(OH)] Suportadas em Argilas Esmectitas

Villalba, J. C.[1], Galvan, V[2], Anaissi, F. J.[1], Berezoski, S.[1], and Cavicciolli, K.[1]

[1] Universidade Estadual do Centro-Oeste - Guarpuava PR Brazil
[2] CONICET - Universidad Nacional de Córdoba - Córdoba Argentina

Neste trabalho estudou-se o efeito das argilas na formação de akaganeíta, fase beta do oxihidróxido de ferro. As imagens de MEV mostraram que as nanopartículas já são formadas num tempo de até 4 h. Refinamento de dados XRD1-LNLS revelou a formação de 10% hematita e 90% de akaganeíta.

Acknowledgements: LNLS, C2Nano, CNPq, Capes, Fundação Araucária, Finep

Luminescência excitada por raios X do $SrAl_2O_4$ dopado com Eu e Dy

Santos, C.[1], Rezende, M. V. dos S.[1], Montes, PJR[1], and Valerio, M.E.G.[1]

Universidade Federal de Sergipe - São Cristóvão SE Brazil

O desenvolvimento de uma nova rota de produção de materiais através da técnica sol-gel possibilita a produção de nanopós usando temperaturas de calcinação mais baixas e tempos menores quando comparada com outras rotas cerâmicas como, por exemplo, a reação de estado sólido. O $SrAl_2O_4$ dopado com terras raras tem atraído muita atenção devido ao seu grande potencial em aplicações práticas como material que apresenta fosforescência com longo tempo de vida. A composição $SrAl_2O_4$ apresenta duas estruturas cristalográficas, hexagonal e monoclínica, com transição reversível em $650°C$. Este trabalho tem como objetivo, a produção de pós cerâmicos de aluminato de estrôncio, na fase monoclínica, puro e dopado com terras raras para aplicações na indústria. As amostras foram analisadas através das técnicas de Difração de Raios X (DRX) e Espectroscopia de absorção de raios X (XAS). A emissão luminescente estimulada por raios X (XEOL) do $SrAl_2O_4$: Dy^{3+} foi verificada. O espectro de absorção de raios X foi realizado utilizando a linha XAFS-2 (X-ray Absorption Fine Structure) no Laboratório Nacional de Luz Síncrotron, Campinas, Brasil (LNLS). As análises de difração de raios X mostram que a fase $SrAl_2O_4$ foi obtida , mas apresenta as duas estruturas, monoclínica e hexagonal. As emissões características do Dy^{3+} foram observadas através dos espectros de fluorescência, indicando a presença do Dy na matriz do $SrAl_2O_4$. Resultados de espectroscopia de absorção de raios X mostram a absorção na borda L_3 do Dy. A emissão luminescente da amostra de $SrAl_2O_4$: Dy^{3+} também foi registrada. A intensidade total da emissão XEOL apresenta um aumento bastante significativo quando a energia do raio X aumenta, passando pela borda de absorção L_3 do Dy, em 7794eV. Após esta energia a emissão XEOL permanece praticamente constante. O Espectro XEOL apresenta uma modificação importante que é o aumento de uma banda de emissão larga em cerca de 300nm, quando a energia dos fótons de raio X aumentam passando pela borda de absorção. Estes resultados são discutidos a luz dos processos de geração e recombinação de portadores e um modelo para a emissão luminescente estimulada por raios X é apresentado. O decaimento do tempo de vida das amostras de $SrAl_2O_4$: Eu^{3+}, medido no modo single bunch, na linha de luz XAFS2/LNLS, mostrou-se cerca de 62 ns e 78 ns para as amostras com controle de resfriamento de $10°C$/min e $20°C$/min, respectivamente.

Acknowledgements: CNPq, CAPES, LNLS e Cerâmica Sergipe S/A.

Synthesis and Characterization of New Nanocomposites Reinforced with Amazonic Kaolinite

Neto, J. C. M.[1] and Malere, C.P.R[1]

Universidade Estadual de Campinas - Campinas SP Brazil

In recent years, nanocomposites with polymer matrix has attracted the attention of researchers both at university and inside the industry because of its improved properties such as thermal, mechanical, and fire retardancy when compared to pure polymers and composites. Kaolinite is a material that can be used as reinforcement for nanocomposites. Kaolinite is the most abundant of all clay minerals. Kaolinites have two types of interlayer surfaces: (SiO)6 microrings on one side, and aluminol groups on the other side in an asymmetric structure. Kaolinite mineral deposits can be formed either by metamorphic or sedimentary process. Brazil is the third largest kaolin producer in the world, with deposits in the Amazon basin greater than those already known in the rest of the world.1 In Brazil, there are deposits with an exceptionally high quality product2, and others being discovered and still under study, mainly in the State of Amazon. In this work, for the first time, nanocomposites reinforced with kaolinite from the State of Amazon in Brazil were synthesized. Kaolinite was extracted from two distinct deposits, purified, and previously treated. Nanocomposites were obtained by in situ polymerization of polystyrene. Some physical properties were measured for the characterization of the

Acknowledgements: Fundação de Amparo a Pesquisa do Estado do Amazonas (FAPEAM), Universidade do Estado do Amazonas (UEA) e a Univesidade Estadual de Campinas (UNICAMP).

Comportamiento Polimórfico de Estearinas de Girasol Alto Estéarico Alto Oleico

Rincón Cardona, J. A.[1], Huck Iriart, C.[2], Candal, R.[3], and M. L. Herrera[3]

[1] Universidad Nacional de General San Martin - San Martin Bueno Argentina
[2] Universidad de Buenos Aires - Buenos Aires - Argentina
[3] Universidad de Buenos Aires - Buenos Aires DF Argentina

El objetivo de este trabajo es estudiar las transiciones de fase de estearinas obtenidas de girasol. Una de ellas posee un 46.9% de ac. esteárico (S) y 54.6 % de SOS. La otra contiene 28.1% de S y sus triglicéridos principales son SOS (23.7%), SOO (22.3%) y OOO (22.8%). Sus puntos de fusión son 30.0^oC y 35.0^oC. La estearina blanda cristalizó en la forma α por debajo de 17^oC dando una se$\tilde{n}$al a q = 1.14 nm^{-1} y 14.90 nm^{-1}. A 5^oC, a los 12 min apareció la forma β'_2 con se$\tilde{n}$ales a q = 1.72 y 14.37, 14.30 y 16.40 nm^{-1}. Entre 12 y 23 min coexisten ambas formas α y β'_2. A temperaturas mayores a 17^oC no se detectó la forma polimórfica α y la forma β' encontrado fue la β'_1 con señales a q = 1.39, 14.6 y 16.20 nm^{-1}. La estearina dura cristalizó en la forma α a todas las temperaturas ensayadas. A 10^oC, luego de 6 min apareció la forma $\beta'2$ que fue la única detectada. A 23 ^oC, se formaron ambas formas β' a los 25 y 37 min. A 24^oC la forma predominante fue la β'_1. En este caso ambas formas β' se formaron simultáneamente a los 33 min. Luego de 79 min a 24^oC apareció la forma β con espaciamientos largos a valores de q = 1.13 y 2.26 nm^{-1} y espaciamientos cortos a valores de q = 13.7 nm^{-1}. A 25 ^oC se registró el mismo comportamiento que a 24^oC.

Acknowledgements: María L. Herrera and Roberto J. Candal are researchers of the National Research Council of Argentina (CONICET). This work was supported by CONICET through Project PIP 11220080101504, by the National Agency for the Promotion of Science and Technology (ANPCyT) through Project PICT 0060, and by the University of Buenos Aires through Project 20020100100467 The authors wish to thank to the Synchrotron Light National Laboratory (LNLS, Campinas, Brazil) for the use of X-ray facilities.

Identificação da precipitação de fases em aço inoxidável dúplex UNS S31803 envelhecido a 475°C

Melo, E. B.[1], Magnabosco, R.[2], and Moura Neto, C[1]

[1] Instituto Tecnológico de Aeronáutica - São José dos Campos SP Brazil
[2] Centro Universitário da FEI - São Bernardo do Campo SP Brazil

Os aços inoxidáveis dúplex são, frequentemente, utilizados em aplicações onde é necessária grande resistência mecânica combinada a resistência à corrosão. Entretanto, durante envelhecimento isotérmico, conformação a quente ou soldagem, pode ocorrer a precipitação de fases indesejáveis, que causam tanto redução de propriedades mecânicas quanto afetam a resistência à corrosão. As transformações entre 700°C e 900°C (formação de fase sigma) e a 475°C (formação de fase alfa linha) são as mais discutidas na literatura. Trabalhos recentes deste grupo de pesquisa[1,2] indicam a provável formação de fase alfa linha entre 300°C e 600°C, a partir da ferrita original, além de evidências de formação de nitretos de cromo e/ou fase G no mesmo intervalo de temperaturas na austenita original desses aços. O material em estudo é o aço inoxidável dúplex UNS S31803, que foi solubilizado a 1.175°C por 30 minutos, e resfriado em água. O envelhecimento a 475°C foi conduzido por tempos de até 360 horas. As amostras foram analisadas pelo emprego das técnicas de microscopia óptica, microscopia eletrônica de transmissão e medições de microdureza Vickers. As análises por microscopia eletrônica de transmissão, realizadas até o momento, comprovam a precipitação de fases tanto na ferrita quanto na austenita originais na amostra envelhecida a 475°C por 360 h (proposta 11402 - Identificação de fases G, alfa linha e nitretos em aços inoxidáveis dúplex envelhecidos). 1. MELO, E. B.; MAGNABOSCO, R.; MOURA NETO, C. Phase transformations on an UNS S31803 duplex stainless steel during aging at 650°C and its influence on pitting potentials in a 0.6M NaCl solution. 7th European Stainless Steel Conference - Science and Market - conference proceedings. Milão: AIM, 2011. 2. MELO, E. B.; MAGNABOSCO, R. Transformações de fase durante o envelhecimento isotérmico a 475 °C do aço UNS S31803. 66° Congresso Internacional Anual da ABM anais. São Paulo: ABM, 2011.

Acknowledgements: Os autores agradecem ao Conselho Nacional de Desenvolvimento Científico e Tecnológico - CNPq (141094/2011-7) pelo apoio financeiro ao presente projeto de pesquisa.

A SAXS and Swelling Study of Ureasil-Polyether Hybrid Matrix for Controlled Drug Delivery Systems

Molina, E. F.[1], Pulcinelli, S.H.[1], and Santilli, C.V.[1]

Universidade Estadual Paulista - Araraquara - Araraquara SP Brazil

Hybrid materials chemistry represents an inherent interdisciplinary field of research and development bridging together a variety of communities such as organometallics, colloids and nanoobjects, soft matter and polymers, coordination polymers including MOFs, solgel, catalysis and surfaces, clays and lamellar compounds, nanocomposites, nanoporous and mesoporous materials, biomaterials, biochemistry and engineering.[1] The hybrid materials formed by ureasil cross-linked poly(oxyalkylene) chains are ruberry, flexible, transparent, and insoluble in water.[2-4] In our work, urea-cross-linked polyether-siloxane hybrids with tunable hidrophilic/hidrophobic areas were prepared from end group functionalized poly (ethylene oxides) PEO or poly (propylene oxides) PPO and 3-(isocyanatopropyl)-triethoxysilane). The combination of the different polymer phases resulted in materials with hydrophilic and hydrophobic domains. The aim of the study was a comprehensive swelling investigation of ureasil-PEO-PPO hybrids in order to reveal differences in the swelling behaviour responsible for the diverging drug release mechanisms. The effect of the swollen shrinkage on the nanostructure of monolithic xerogels was monitored by small angle X-ray scattering (SAXS). DSC and swelling tests were performed to study the chain mobility in the polymer matrix. The controlled of swelling degrees in water at 37 C were achieved with the balance hidrophilic/hidrophobic (PEO/PPO) in the ureasil hybrids. The investigations with SAXS revealed the dependence of the distance correlation as a function of proportion of the PEO/PPO. The release rate of sodium diclophenac can be modulated by these ureasil hybrids.

Keywords: Ureasil-polyether, Swelling, Drug Delivery, SAXS.

Literature Cited: [1]C. Sanchez, P. Belleville, M. Popalld, L. Nicole, Chem. Soc. Rev., 2011, 40, 696753. [2] C. V. Santilli; L. A. Chiavacci; L. Lopes; S; H. Pulcinelli; A. G Oliveira; Chem. Mater. 2009, 21, 463-467. [3] Molina E. F.; Pulcinelli S. H.; Santilli C. V.; Blanchindin S.; Briois V.; J. Phys. Chem. B, 2010, 114, 3461-3466. [4] Molina E. F.; Santilli C. V.; Pulcinelli S. H.; Santilli C. V.; Blanchindin S.; Baudelet, F.; Briois V, Phase Transitions, 2011, 6.

Acknowledgements: This work was supported by CNPq, Capes, Fapesp

---

Combined UV-Vis-Raman-QuickXAFS and UV-Vis-SAXS study of hydrolysis and condensation of Sb-doped SnO_2 nanoparticles performed at SOLEIL Synchrotron

Caetano, B.L[1], Pulcinelli, S.H.[1], Santilli, C.V.[1], Valerie Briois[2], and Florian Meneau[2]

[1] Universidade Estadual Paulista - Araraquara - Araraquara SP Brazil
[2] Syncrotron SOLEIL - Orsay France

SnO_2 is a n-type semiconductor with a wide band gap of about 3.5 eV and with one of the highest carrier mobility among the oxides. Because of its advantageous transport properties pure and doped SnO_2 can be used as transparent electrodes, sensor for reduced gases, and material for catalysts or thick film resistors [1]. The aim of this work is to give experimental evidence of the different steps involved in the hydrolysis and condensation of Sb-doped SnO_2 nanoparticles formation and growth, by in situ and simultaneous time-resolved monitoring of UV-vis absorption and Raman spectroscopy combined with small-angle X-ray scattering (SAXS) and with X-ray absorption fine structure (XAFS). The first step deals with the hydrolysis of a mixture of ethanolic solution of $SnCl_4.5H_2O$ ([Sn] = 0.2 M) with ethanolic solution of $SbCl_3$([Sb] = 0.5 M) containing different amounts of Sb: 0, 5, 10, 15, 20, 25 and 30 at %. The water addition was done by two manners: at once and drop by drop. The time evolution of QD size for different Sb levels and different ways of water addition has shown this variation is more pronounced after the beginning of the heating step. Fourier Transforms (FT) of XAS spectra of reactions containing 15% Sb in both the ways of water addition show a first peak related to Sn-O distance at 2.07 and a second one mainly related to the Sn-Cl at 2.37 . The intensity of the peak related to the Sn-Cl decreases, while the peak corresponding to the Sn-O increases with water addition indicating the formation of nanoparticles of SnO_2.The evolution of SAXS intensity for the reaction containing 15% of Sb performed with drop by drop water addition shows an increase of the scattering intensity characteristic of the presence of large particles or aggregates, which size decreases after this initial stage. A second growth step occurs after 30 minutes (heating step) showing a new increase in peak intensity: nanoparticles are growing at the expense of the first population.

References [1] Y. Liu, E. Koep, M. Liu,Chem. Mater. (2005) 17, 3997.

Acknowledgements: The authors want to thank SOLEIL for providing beamtime at the SAMBA and SWING beamlines and for financial support of the experiments. This work was also partially supported by the FAPESP and CAPES/COFECUB cooperation program (Ph 564/07).

Estudo do grau de intumescimento em híbridos Siloxano-Poliéter contendo argila montmorilonita

Jesus, C.R.N.[1], Molina, E. F.[1], Pulcinelli, S.H.[1], and Santilli, C.V.[1]

Universidade Estadual Paulista - Araraquara - Araraquara SP Brazil

As propriedades térmicas e mecânicas de híbridos siloxano-poliéter foram investigadas em função de proporções de três diferentes tipos de argila, disponíveis comercialmente como Cloisite. Além da argila montmorilonita contendo íons Na^+ no espaçamento interlamelar ($MMTNa^+$), duas diferentes argilas modificadas organicamente estão sendo investigadas: MMT20A contendo um modificador apolar e MMT30B com modificador polar. O efeito da proporção e do tipo de argila empregada, na nanoestrutura e no intumescimento dos xerogéis monolíticos transparentes foi analisada por espalhamento de raios-X a baixo ângulo (SAXS). Em geral, as propriedades mecânicas de nanocompósitos com base na matriz siloxano-poliéter-$MMTNa^+$ são superiores que na matriz pura. As propriedades térmicas também são claramente influenciadas pela adição de argila, levando a uma diminuição no grau de cristalinidade da fase PEO. Os padrões de SAXS dos híbridos siloxano-PEO-MMT (Na^+, 20A e 30B) contendo proporção de argila de 3 e 5% m/m apresentaram dois picos de correlação localizados ao redor de qmax= 1,5 e 3,5 nm^{-1}[1]. O primeiro pico é associado a uma forte correlação espacial entre os grupos siloxanos, já o segundo é devido a existência de partículas de MMT de tamanho nanométrico dispersas na matriz híbrida[2]. A hidratação da matriz híbrida siloxano-PEO durante os experimentos de intumescimento em água a 37^oC leva a uma mudança na posição do pico localizado a qmax = 1,5 nm^{-1}. Este deslocamento na posição pode ser correlacionado com a quantidade de água retida pela amostra. A presença da MMT influencia a relação de intumescimento, indicando uma alteração na capacidade de absorção de água. Esta característica pode ser explorada para adequar a dissolução e a liberação de drogas incorporadas nesta matriz.

[1] C. V. Santilli, L. A. Chiavacci, L. Lopes, A. G. Oliveira, Chem. Mater. 21, 463 (2009). [2] W. Loyens, P. Jannasch, F. H. J. Maurer, Polymer. 46, 903 (2005).

Acknowledgements: Trabalho financiado pela CAPES,CNPq e FAPESP.

Desidrogenação do etanol em catalisadores de cobre suportado em aluminas porosas

Cassinelli, W. H.[1], Pulcinelli, S.H.[1], Martins, L.[1], and Santilli, C.V.[1]

Universidade Estadual Paulista - Araraquara - Araraquara SP Brazil

Atualmente, com as recentes regulamentações ambientais para diminuir a emissão de gases prejudiciais ao meio ambiente e a busca pela utilização de insumos químicos e combustíveis mais limpos, há um grande incentivo para o uso de fontes alternativas de energia e matérias-primas, sobretudo aquelas oriundas de fontes renováveis. Neste contexto, o etanol se destaca, pois, além de ser utilizado como uma fonte de combustível direta, este pode ser utilizado na produção de hidrogênio e outros insumos químicos de interesse industrial. Neste trabalho, estudou-se a relação entre as propriedades catalíticas, estruturais e superficiais de catalisadores de cobre suportados em alumina na reação de desidrogenação/desidroacoplamento do etanol. Os catalisadores de cobre (5, 10 e 20 % em massa) foram impregnados em uma alumina (Al) com estrutura hierárquica de poros obtida pelo método sol-gel [1] e caracterizados por fisissorção de N_2, porosimetria de mercúrio, DRS, DRX e EXAFS. Os resultados de DRS e EXAFS mostraram que espécies de cobre isoladas, obtidas nos catalisadores de 5CuAl, favorecem a formação de acetaldeído e H_2 a partir da reação de desidrogenação. Por outro lado, cristalitos de Cu com maior número de coordenação, verificados nas amostras com maior conteúdo do metal, favorecem a formação de acetato de etila e acetaldeído. Além disso, um maior recobrimento da superfície da alumina pela presença de uma maior quantidade de Cu promove uma queda na quantidade de sítios ácidos de Bronsted/Lewis, aumentando a seletividade para as reações de desidrogenação/desidroacoplamento em relação a reação de desidratação.

[1] L. Martins, M.A.A. Rosa, S.H. Pulcinelli, C.V. Santilli, Micropor. Mesopor. Mater. 132 (2010) 268-275

Acknowledgements: FAPESP, CNPq e CAPES

Caracterização microscópica das fibras de bagaço de cana, obtidas como subproduto no setor sucroalcooleiro, para aplicação em bioprocessos

Silva, V. F. N.[1] and Rocha, GJ[1]

Laboratório Nacional de Ciência e Tecnologia do Bioetanol - Campinas SP Brazil

A utilização de biomassas vegetais, em substituição aos derivados do petróleo, para a obtenção de produtos dentro da plataforma da biorefinaria é de grande interesse tanto econômico quanto ambiental. Neste contexto, a análise morfológica, juntamente com a caracterização química de materiais lignocelulósicos, é necessária para a compreensão da estrutura do complexo celulose-hemicelulose-lignina, bem como suas interações durante as reações químicas ou enzimáticas. Desta forma, a técnica de microscopia eletrônica de varredura tem sido amplamente utilizada na investigação de ultraestruturas de diversas fibras lignocelulósicas, para várias aplicações, tais como, bioetanol, materiais compósitos, etc. Neste trabalho, as fotomicrografias de MEV foram obtidas em um Microscópio Field Emission Gun JSM 6330 F, disponível no Laboratório de Microscopia Eletrônica do LNNano, a fim de se comparar as alterações na ultraestrutura da biomassa e se estudar qual a condição de pré-tratamento mais adequada para a preservação da fração celulósica. Resultados preliminares permitiram a visualização de alterações morfológicas destas biomassas vegetais após os tratamentos físico-químicos ou enzimáticos os quais são responsáveis pela difusão de reagentes durante os processos de fracionamento da biomassa. Nas próximas etapas pretende-se analisar o comportamento das fibras celulósicas, proveniente de diferentes pré-tratamentos, e então concluir até que ponto a mudança estrutural nestas fibras poderá interferir em processos de uso da celulose para obtenção de bioetanol.

Acknowledgements: LNNano/CNPEM

Espalhamento de raios X a baixo ângulo aplicado ao estudo estrutural de membranas poliméricas de troca iônica obtidas utilizando o método da enxertia induzida por radiação.

Ribeiro, G.[1], Zen, H. A.[2], Westfahl Jr., H.[3], and Lugao, A. B.[2]

[1] Universidade Federal de Itajubá - Itajubá MG Brazil
[2] Instituto de Pesquisas Energéticas e Nucleares - São Paulo SP Brazil
[3] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

Neste trabalho a morfologia dos microdomínios de membranas de troca iônica obtidas a partir do polímero poli(etileno-co-tetrafluoroetileno) (ETFE) utilizando o processo de enxertia induzida por radiação do monômero estireno na presença do agente de reticulação divinilbenzeno (DVB) foi avaliada por espalhamento de raios X a baixo ângulo (SAXS). A curva de espalhamento para o filme de ETFE comercial apresenta o pico de longo período em torno de $17\mathrm{nm}^{-1}$ que caracteriza o contraste entre a fase cristalina e a fase amorfa deste polímero. Após a enxertia do poliestireno por pré-irradiação foi observado um aumento na intensidade do espalhamento. Estes dados são consistentes com a menor densidade eletrônica do poliestireno enxertado em relação ao ETFE, e esta característica explica o aumento no contraste da densidade eletrônica entre a fase cristalina e a fase amorfa observado na curva de espalhamento do filme após o enxerto. A enxertia do poliestireno também desloca o pico de longo período para região de mais baixo ângulo, $25\mathrm{nm}^{-1}$. O processo de sulfonação da poliestireno enxertado nas membranas preparadas com ou sem DVB não altera significativamente a posição do pico de período longo, mas diminui a intensidade do espalhamento. Este fato sugere que os grupos $SO_3{}^+$ ocupam as vacâncias da fase amorfa, pois aumenta a densidade eletrônica e reduz o contraste entre a fase amorfa e a fase cristalina e, consequentemente, diminui a intensidade do espalhamento.

Acknowledgements: CNPq - 150887/2010-8

Investigação da ativação de catalisadores de Ni ou Ni-Co suportados em alumina modificados com Zn por XANES *in situ*.

Oliveira, D. C.[1]

Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

O conhecimento da estrutura da fase ativa e da superfície dos catalisadores de diversas composições para obtenção de hidrogênio é de extrema importância para controle das propriedades destes materiais. Neste trabalho pretende-se compreender a eficiência catalítica utilizando-se espectrometria de massas e caracterização por XANES *in situ* de catalisadores de alumina modificados com zinco. Os catalisadores foram preparados a partir do óxido de alumina e nitratos de zinco, níquel e cobalto. Os experimentos de XANES na borda K do Ni foram realizados durante a ativação do catalisador; a atividade na produção de hidrogênio foi acompanhada por espectrometria de massas. Os espectros de XANES resolvidos no tempo e temperatura mostraram que a redução do níquel é dependente da composição do material. Em todas as amostras observou-se a redução do NiO; a amostra de Ni suportado em alumina (AlNi) é ativada a partir de 415^{o}C durante 1h40min. A presença de Zn (AlZnNi) reduz significativamente o tempo de ativação para 1h sem alterar a temperatura inicial, enquanto a presença de Co (AlNiCo) reduz a temperatura para 338^{o}C sem alterar o tempo total. A presença de ambos os elementos (AlZnNiCo) mostra a temperatura inicial e o tempo de duração idênticos aos da amostra AlNiCo. A comparação das curvas finais mostra que a composição também leva a formação de diferentes espécies de Ni após a ativação. O espectro final da amostra AlNi sofre diminuição da linha branca indicando uma redução parcial do Ni, porém ainda é semelhante ao NiO. A presença de Zn leva a redução parcial e o espectro final das amostras AlZnNi e AlZnNiCo apresentam características de mistura de NiO e Ni metálico; a amostra AlNiCo é a mais reduzida a Ni metálico. A produção de hidrogênio foi estudada em diferentes temperaturas, entre 200-500^{o}C, sob vapor de etanol e água. As amostras modificadas por Zn (AlZnNi e AlZnNiCo) apresentam produções de hidrogênio similares em 500^{o}C e superiores às amostras não modificadas; nestas condições, os espectros de XANES indicaram uma redução parcial do Ni, indicando que a mistura Ni^0 e Ni^{2+} pode ser a responsável pela atividade do material; nas amostras não modificadas, nestas condições, observa-se apenas óxido de níquel ou níquel completamente reduzido.

Acknowledgements: ao LNLS pelo suporte nas medidas realizadas na linhas de luz XAFS1 e XAFS2.

Parte VII

Métodos e Instrumentação

SIMULAÇÃO E MODELAGEM COMPUTACIONAL DO ESPALHAMENTO A BAIXOS ÂNGULOS DE ESTRUTURAS GEOMÉTRICAS COMPLEXAS

Alves, C.[1] and Oliveira, C. L. P[1]

Universidade de São Paulo - São Paulo - São Paulo SP Brazil

A combinação de diferentes técnicas de microscopia com as técnicas de espalhamento vem sendo utilizadas em diversas aplicações na literatura. Para um sistema de partículas, randomicamente orientadas, um experimento de SAXS fornecerá como resultado uma curva unidimensional. Neste processo de promediacão tem-se a perda de uma grande quantidade de informação e por isso diz-se que a técnica de SAXS é tanto de baixa resolução quanto informação. No entanto, mesmo com esta perda de informação, é possível obter informações sobre a estrutura tridimensional de um objeto em estudo. Em diversas aplicações, tem-se indicações ou modelos, obtidos por meio de técnicas de microscopia, sobre a forma da partícula espalhadora a priori, sendo então necessário realizar o cálculo da intensidade de espalhamento teórica baseada neste modelo e eventualmente comparar com os dados experimentais afim de poder obter valores médios do modelo com grande confiabilidade. Como a obtenção de expressões analíticas ou semi-analíticas para amplitudes e intensidades de espalhamento é restrita apenas as geometrias muito simples, métodos alternativos de modelagem da curva de espalhamento são necessários. Neste trabalho utilizamos o método de elementos finitos, para construir e modelar mais de uma centena de diferentes tipos de corpos geométricos. Para tanto foi criado um banco de dados com as estruturas geométricas básicas que são então utilizadas para a construção dos modelos. Os modelos finais podem então ser construídos com, por exemplo, subunidades conhecidas como esferas, ou estruturas base mais complexas como fragmentos de DNA, proteínas, etc. A intensidade final é então calculada utilizando a fórmula de Debye. Como em muitos casos o numero de subunidades pode ser muito grande, o cálculo da intensidade foi otimizado para que possa ser feito de modo rápido. Além disso, por meio da utilização de métodos de mínimos quadrados, as intensidades calculadas podem então ser ajustadas aos dados experimentais, fornecendo os parâmetros estruturais desejados. Por meio desta abordagem é possível realizar tanto a simulação quanto e análise de dados de espalhamento, facilitando a interpretação de dados experimentais e sua respectiva correlação com dados obtidos por outras técnicas. Resultados iniciais da aplicação deste procedimento de modelagem serão apresentados e discutidos.

Acknowledgements: USP, CAPES and FAPESP

Confecção De Eletrodos Descartáveis Para Detecção Eletroquímica Em Sistemas Microfluídicos

Duarte Junior, G. F.[1], Braga, L.E.P[1], Gabriel,E.F.M[1], Garcia, P.T.[1], and Coltro, W. K. T.[1]

Universidade Federal de Goiás - Goiânia GO Brazil

O presente trabalho descreve a fabricação de eletrodos para C4D em microchips de eletroforese utilizando-se placas de circuito impresso (PCI) como fontes metálicas alternativas. Os eletrodos foram confeccionados fotolitograficamente em PCI de cobre com espessura de aproximadamente 50 μm. A geometria dos eletrodos foi definida com uma resina fotossensível à radiação UV e corroídos quimicamente por via úmida. Estudou-se também o efeito dos parâmetros geométricos (largura e espaçamento) na resposta do detector bem como a separação de cátions e ânions. Para esta finalidade, os eletrodos foram produzidos em uma configuração antiparalela com larguras e espaçamento entre 0.5 e 3.0 mm. Primeiramente realizou-se a limpeza das placas PCI para tanto utilizou-se solução de acetona e posteriormente solução de ácido Sulfúrico 10%; a qual é importante para remoção da camada de óxido formada na superfície do cobre promovendo uma melhor aderência do resiste. A aplicação do fotorresiste AZ 4210 foi realizada sob rotação de 3600 rpm por 30 s. Na etapa de corrosão utilizou-se solução de 150 g $FeCl_3$/30 mL HCl/300 mL H_20 na qual a esta se procedeu numa taxa de 12,5 μm/min. A análise estatística mostrou uma frequência ótima em torno de 400 kHz e a combinação que favorece um incremento no sinal é largura maior e espaçamento reduzido. Para a separação eletroforética uma mistura equimolar de K^+, Na^+ e Li^+ foi injetada eletrocineticamente (300 V/2 s) e separada sob potencial de 800 V e como eletrólito uma solução de MES/His 20 mmol/L. O dispositivo apresentou a detecção das três espécies e também do plug de água em aproximadamente 90 s. Uma amostra contendo Cl^- também foi injetada (-500 V/10 s) e detectada em aproximadamente 20 s sob aplicação de -1 kV; em ambos casos a detecção foi feita sob aplicação de um sinal senoidal de 500KHz e amplitude 2 V_{pp} ao eletrodo de excitação. A fabricação deste tipo de eletrodo se mostrou fácil e rápida, porém é necessário instrumentação sofisticada e sala limpa. O uso de PCI para fabricação de eletrodos mostrou-se vantajosa economicamente quando comparada a outras técnicas, sendo que o preço estimado para cada protótipo é da ordem de R$1,00.

Acknowledgements: LMF; INCTBio; CNPq

Ultra-anomalous transmission in thick asymmetrically-cut crystals

M.G. Honnicke[1], Kakuno, E. M.[2], and Huang X-R.[3]

[1] Universidade Federal de Goiás - Jataí GO Brazil
[2] Universidade Federal do Pampa - Bagé RS Brazil
[3] Argonne National Laboratory - Argonne IL United States of America

Anomalous transmission (Borrmann effect) is a well-known effect for diffraction in single crystals. In asymmetrically-cut crystals, a transmission of about 40 per cent in 4 mm thick Si crystal at low energies (10.7 keV) is theoretically expected. We developed such an experiment in XRD2 beamline at NSLS. Experimentally, we found an ultra-anomalous transmission of about 4 per cent. Even this value being small, it is much more pronounced than for a symmetrically-cut crystal (around 0.1 per cent). This low transmission, compared with the theoretical value, is probably due to the stress in the used crystals, since extinction is extremely sensitive to stress. The use of this effect in a new phase contrast imaging setup was tested and is proposed. Blurred images due to the distorted Borrmann fan were detected. Improvements in this experiment are proposed aiming its use as a compact phase contrast imaging setup for mammography purposes.

Acknowledgements: LNLS for the beamtime, CNPq and DOE. We are in debt with LORXI/UFPR for the support in preparing the crystals for this experiment.

Development of a Two-Dimensional Detector for X-Ray Experiments

Sales, E.[1], SUAIDE, A. A. P.[2], and Oliveira, C. L. P[1]

[1] Universidade de São Paulo - São Paulo - São Paulo SP Brazil
[2] Universidade de São Paulo - São Paulo - Sao Paulo SP Brazil

The detection system is one of the most important aspects of any experimental apparatus. One example are the proportional counters which, in its simplest conception, are composed of a wire (anode), placed between two plates (cathode), with a kilovolt voltage between them. When a photon passes, it ionizes the gas. The created ions are accelerated by the difference of potential, creating a well defined signal at the anode wire, permitting a precise determination the event position [1]. Several methods have been developed to determine the position of the event in a proportional detector [2]. This principle can be extrapolated to an area detector where wire planes are used both for the anode and for the cathode, placed perpendicularly in order to permit the X and Y determination. In this project we will work on the development, characterization and control of a two-dimensional multiwire gas detector that will be used for X-Rays experiments (5-8KeV). This project is been developed in collaboration with the Department of Nuclear Physics of University of São Paulo, which has experience with two-dimensional multiwire gas detectors used for heavy ions research [2]. One of the first goals will be to perform modifications in currently available detectors for X-Ray experiment. The modification of the detectors carries several implications, which corresponds to the design of an appropriate window, choice of the internal pressured gas mixture and the setup of the operation and control system [3]. For the windows, some alternatives would be Kapton ^{TM} or Mica since both materials have low X-Ray absorption and also sufficient high mechanical strength to support the pressure difference ($\sim$ 4atm), even using thin windows. Since the detector will have a reasonable large area (10x10cm or larger), the fixation and sealing of the window is an additional problem. As will be shown, several tests have been already performed both for the test of the electronics and control of the system and also the development of solutions for window fixation and sealing. [1] G. F. Knoll, Radiation Detection and Measurement, John Wiley and Sons, New York, Chicester, Brisbane, Toronto, Singapure (1979). [2] M.M de Moura et al, Nucl. Instr. and Meth. 433 (1999) 623-629A [3] A. Gabriel et al, Nucl. Instr. and Meth. 152 (1978) 191-194

Acknowledgements: We thank FAPESP and CNpQ for the finantial support and the tecnitians Celso C. Perego (Pelletron) and Tarsis M. Germano (GFCx) for their valuable support to this work.

Current and Future Instrumentation at the D09B XRF Fluorescence Beamline of the LNLS

Pérez, C. A.[1], MIGUEL, D. I.[1], Meyer, B.C.[1], and Neueschwander, R.[1]

Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

Synchrotron Radiation X-ray Fluorescence (SR-XRF) analysis is a well-established microanalytical method for quantitative determination of trace elements in several matrices. The LNLS laboratory has a dedicated XRF beamline for this purpose which is installed at the D09B (15^o) bending magnet of the LNLS storage ring. It covers an energy range from 4 to 25 keV, having the possibility of using monochromatic as well as polychromatic beam emitted from the bending magnet for sample excitation. The beamline comprises several experimental arrangements which include a high vacuum chamber aiming to improve the detection of light elements between oxygen and sulfur. Several in air hard x-ray microprobe configurations are also available for developing experiments related to microscopic x-ray fluorescence analysis.

In this work, the main experimental arrangements, currently available at the XRF beamline, will be shown. Some of latest facilities developed along the last year together with the new optical system for x-ray micro-focusing, will also be described.

Acknowledgements:

Parte VIII

Propriedades Estruturais, Eletrônicas e Magnéticas de Sólidos

A mesoscopic description of ferroelectric relaxor ceramics using high resolution synchrotron light diffraction patterns

Botero, E. R.[1] and Garcia D[2]

[1] Universidade Federal da Grande Dourados - Dourados MS Brazil
[2] Universidade Federal de São Carlos - São Carlos SP Brazil

Ferroelectric relaxor materials have been extensively studied due to their special properties, as giant electromechanical (piezoelectric) response, and become used in the ultrasonic and medical applications, as well as in telecommunications. Besides the technological interest, ferroelectric relaxor materials have a scientific interest, focused on the mechanism of polar interactions during the phase transition process, which still not completely understood for all their classes. In lead based relaxor ferroelectric systems, as the lanthanum modified lead titanate zirconte, it is well know that the dynamics of polar nanoclusters (PN) interactions, which appear for temperatures below the Burns temperature (T_B), are considered the responsible for the relaxor behavior. As well as at higher temperatures the PN may be nearly decoupled, but strong correlations are developed between neighboring PN, upon cooling, getting a maximum close to the freezing temperature (T_F). For these class of relaxor materials the nature of the PN is associated with structural disorder, more specifically compositional disorders of the B sites. In this way, the specific influences of the structural parameters, characterized by Rietveld refinement of the X-ray diffraction patterns, on the nanoclusters formation and interactions have been the aim of researches in the last decade. Although, for these cases, the concerning about a single-phase structure with low symmetry distortion, have not been presented conclusive results to describe the mean structure. In such way, in previous works we proposed an innovative refinement protocol (DPRRP), which quantifies simultaneously one paraelectric (centrosymmetric) phase and one low distortioned ferroelectric (non-centrosymmetric) phase of relaxor-like systems. The results have shown good concordances between the structural and ferroelectric properties of the analyzed systems. Although, looking for the best describing of the quantity and structural characteristics of the non-centrosymmetric phase, this work presents the study of the DPRRP applied in the high resolution XRD patterns of the PLZT ferroelectric relaxor ceramic system, obtained from Synchrotron Light. The results have shown an increase on the amount of the non-centrossymetric phase if compared with the same sample analyzed by the conventional diffratocmeter, who fits with more concordance the dielectric and ferroelectric parameters. Although for samples with low structural distortion, it was observed very similar results for the both light sources when the DPRRP were applied. The results are being analyzed for future publication.

Acknowledgements:

Synthesis, structural and morphological characterization of $Ce_{1-x}Cu_xO_2$ nanorods synthesized by a microwave-assisted hydrothermal method

Araújo, V.D.[1], de Carvalho H. B.[2], and Bernardi, M.I.B.[1]

[1] Universidade de São Paulo - São Carlos - São Carlos SP Brazil
[2] Universidade Federal de Alfenas - Alfenas MG Brazil

Ceria (CeO_2) has earned intensive interest in the past decade because it plays a vital role in emerging technologies for environmental and energy-related applications [1]. CeO_2 has found its applications in many aspects, such as fast-response gas sensors, ultraviolet ray detector, environmental-friendly pigments, and gamma radiation dosimetry [2]. It can be used as an additive to glass (24%) to protect light-sensitive materials, as a coating for corrosion protection of metals, as an oxidation catalyst, and as a counter electrode for electrochromic devices [3]. In the work presented here, nanoparticles from the system $Ce_{1-x}Cu_xO_2$ with x = 0, 0.01, 0.03, 0.05 and 0.10, were synthesized by a microwave-assisted hydrothermal method. The microwave-assisted hydrothermal method combines the advantages of both hydrothermal and microwave-irradiation techniques such as very short reaction time, production of small particles with a narrow size distribution and high purity which might be attributed to fast and homogeneous nucleation of the mixture [4]. The samples were characterized by X-ray diffraction, scanning electron microscopy with field-emission gun (SEM-FEG) and X-ray absorption near edge spectroscopy in the Ce L_{III} edge. X-ray diffraction measurements detected the presence of cubic CeO_2 for all synthesized samples. Secondary phases were observed for the powders with 10% Cu. The SEM-FEG images revealed that the samples are constituted of nanorods with size between 10 nm in diameter and 100 nm in length. XANES spectra revealed the presence of Ce^{4+} and Ce^{3+} species; the incorporation of Cu in the ceria matrix leads to an energy shift in the peak related to Ce Ce^{3+} species. The microwave-assisted method reveals to be an efficient synthesis route for $Ce_{1-x}Cu_xO_2$ nanoparticles.

[1] C. Sun et al. J. Phys. Chem. B. 110 (2006) 13445.
[2] Y. Li et al. Phys. E. 41 (2009) 1550.
[3] H. Wang et al. Phys. Chem. Chem. Phys. 4 (2002) 3794.
[4] F. Gao et al. J. Nanosci.Nanotechnol. 6 (2006) 3812.

Acknowledgements: The authors are grateful to FAPESP, CAPES and INCTMN-CNPq for financial support.

Effect of Pd on the structural properties and reduction behaviour in gadolinia-doped ceria nanopowders

Muñoz, F.F.[1], Baker, R.T.[2], and Fuentes, R. O.[1]

[1] Consejo Nacional de Investigaciones Científicas y Técnicas - Buenos Aires Argentina
[2] University of St Andrews - St Andrews UK United Kingdom

In the present work, 1 wt% and 5 wt% Pd/GDC nanopowders were prepared by two different methods: a) cation complexation (CC) and b) incipient wetness impregnation (WI) onto GDC nanopowders. All samples were characterized by XRD, X-ray absorption near-edge spectroscopy (XANES) and scanning and high resolution transmission electron microscopy (SEM and HRTEM). In order to study the oxidation state of Pd in samples without and with reducing treatments, XANES experiments at the Pd L_3-edge were carried out. In situ Ce L_3-edge XANES experiments were carried out under reducing conditions in order to investigate the reduction behaviour of these materials. The Pd/CeO_2-based nanopowders exhibited the cubic phase (Fm3m space group), with an average crystallite size about 12 nm and a specific surface area of 30 m^2g^{-1}. Elemental analysis showed that Ce:Gd:Pd ratios appeared to be approximately constant across space, suggesting compositional homogeneity in the samples. XANES results indicated that the extent of reduction of these materials is low and that the Ce^{4+} state is in the majority over the reduced Ce^{3+} state.

Acknowledgements: This work has been supported by: the Brazilian Synchrotron Light Laboratory (LNLS, Brazil), under proposals D04A - SXS-11749 and D04B - XAFS1-11748; the Agencia Nacional de Promoción Científica y Tecnológica (Argentina, PICT 2007 No. 01152); PIDDEF No. 0011/11/CITEDEF. The TEM was performed at the Electron Microscopy Facility, University of St Andrews.

Síntese e Caracterização de Nanocolunas de ZnO

Rodrigues, A[1], BOITA, Jocenir.[1], KILIAN, A. S.[1], Alves, M.C.M.[1], and Morais, J.[1]

Universidade Federal do Rio Grande do Sul - Porto Alegre RS Brazil

O óxido de zinco (ZnO) é um importante semicondutor do grupo II-IV que possui uma banda de energia proibida de 3,3 eV. O interesse em obter nanoestruturas de ZnO tem sido crescente nos últimos anos, tanto nas pesquisas científicas básicas como também visando sua aplicação industrial [1]. Recentemente dispositivos utilizando ZnO nanoestruturados, tais como lasers, sensores, diodos emissores de luz, tem sido produzidos. Estes dispositivos apresentam melhores propriedades do que aqueles fabricados com o ZnO na forma massiva (bulk) [2, 3]. Tendo em vista que a morfologia possui grande influência na determinação das propriedades físicas, têm-se produzido nanoestruturas com diversas formas, tais como: nanofios, nanotubos, nanoanéis, nanoflores, etc. No presente trabalho serão apresentados estudos da produção e caracterização de filmes de ZnO. Os filmes foram depositados sobre substratos de aço inoxidável e cobre, utilizando o método hidrotérmico. Na caracterização das amostras empregamos a DRX (Difração de Raios X) para obter a estrutura cristalina dos filmes, enquanto que MEV (Microscopia Eletrônica de Varredura) e MET (Microscopia Eletrônica de Transmissão) forneceram detalhes da morfologia das nanoestruturas. No LNLS foram realizadas medidas de XPS (Espectroscopia de Fotoelétrons induzidos por Raios X) e XAS (X-ray absorption Spectroscopy). Os resultados de XPS permitiram sondar o ambiente químico dos elementos presentes na superfície das amostras. XAS foi empregado para obter a estrutura atômica ao redor do Zn em função das condições de síntese. Como resultado obtivemos filmes contendo nanocolunas de ZnO, altamente orientadas na direção (002) contendo ligações do tipo Zn-OH na sua superfície.

Referências

1. Mousavi, S. H. Haratizadeh, H. Kitai, A. H; Materials Letters 65, 2470-2472 (2011).
2. Sipr, O. Rocca, F; Journal of Physics: Condensed Matter 23, 315501 (2011).
3. Wang, Z, et al. Applied Surface Science 255, 4705-4710 (2009).

Acknowledgements: agradecemos ao apoio do CNPq, CAPES e LNLS.

Local structure of $Pb(Fe_{1/2}Nb_{1/2})O_3$ and $Pb(Fe_{2/3}W_{1/3})_{1-x}Ti_xO_3$ multiferroic materials probed by X-ray absorption spectroscopy

Mesquita, A.[1], Fraygola, B.M.[1], Mastelaro, V.R.[2], and Eiras, J.A[1]

[1] Universidade Federal de São Carlos - São Carlos SP Brazil
[2] Universidade de São Paulo - São Carlos - São Carlos SP Brazil

Among the multiferroic materials, a large number of Pb-based perovskites present the formula $Pb(B_1B_2)O_3$ with excellent dielectric, electromechanical and pyroelectric properties, make these and their solid solutions suitable for high performance materials with potential applications as sensors and actuators. The $Pb(Fe_{1/2}Nb_{1/2})O_3$ (PFN) and $Pb(Fe_{2/3}W_{1/3})_{1-x}Ti_xO_3$ (PFW-PT) are multiferroic compounds from this kind of materials showing ferroelectric to paraelectric phase transitions and paramagnetic to G-type antiferromagnetic respectively. These materials have attracted the attention of many researchers because it can be used in multilayer ceramic, capacitors and other electronic devices due to its high dielectric constant, by presenting a diffuse phase transition and low sintering temperature. Although the long distance structure and magnetic/electric properties of these compounds have been characterized by numerous researchers in order to better understand the processes of phase transition and electrical behavior of these compounds, few studies were conducted to verify the existence of a correlation between these properties and local order and electronic structure of materials. Thus, the aim of this study is probe the local structure of PFN and PFW-PT materials by X-ray absorption spectroscopy at Fe K-edge and W L_{III}-edge. XANES spectra at Fe K-edge show that the state of oxidation presents different as a function of the temperature, with a minimum value of +2.7 0.1 in certain temperature as the temperature increases. In addition, it is not well established in the literature whether PFN composition undergoes a transition from a tetragonal ferroelectric phases to a rhombohedral or a monoclinic phase as the temperature decreases. Our EXAFS measurements at Fe K-edge for this material have shown that the local structure in lower temperatures is compatible to a monoclinic structure.Moreover, EXAFS measurements at Fe K-edge for PFW compound are relative to a rhombohedral structure in lower temperatures. This result is in agreement to the ferroelectric hysteresis loops, which show a typical behavior of ferroelectric material, although the structure for PFW compound has been described as a cubic phase.

Acknowledgements: This study was supported by FAPESP and CNPq funding agencies

Polylactide/Clay Nanocomposites: A Fresh Look into the In Situ Polymerization Process

Silvino, A. C.[1], DAHMOUCHE, K[1], de Souza, K. S.[1], and Dias M. L.[1]

Universidade Federal do Rio de Janeiro - Rio de Janeiro RJ Brazil

In the present work Polylactide (PLA) based nanocomposites were produced by using a catalyst comprising tin centers supported within the layers of an organo-modified clay. The catalyst was characterized by atomic absorption spectrophotometry and Fourier transform infrared spectroscopy (FTIR). FTIR was also employed for conversion analysis of PLA following the method established by Braun *et al* [1]. Using the peak at 935 cm^{-1} (COO lactide ring breathing mode) to determine monomer concentration and the peak at 1454 cm^{-1} (CH_3 bending mode) for normalization, was possible to conclude that the reactions reach around 95 % of conversion within 3 hours of polymerization. The morphology of the nanocomposites was studied by WAXD and SAXS. The WAXD provided direct evidence of clay exfoliation in the polylactide matrix through the total absence of the diffraction peak characteristic of the organo-modified silicate at low 2θ angles. The disappearance of the basal peak suggests the formation of an exfoliated structure. In order to confirm this trend, the size distribution of clay aggregates in the polylactide matrices was quantitatively determined by SAXS applying the stacked-disk model [2]. The populations of the clay aggregates in the polylactide matrices calculated employing the aforementioned procedure showed that the proportion of aggregates with thickness around 20 or less was greater than 99 % confirming the high degree of delamination of the silicate in the polylactide nanocomposites even at high concentration of clay (>10 wt %). The DSC analyses have shown that the amount of clay does not affect significantly the glass transition and the melting temperatures in the PLA/clay nanocomposites. However, the crystallization temperature is gradually shifted toward a higher temperature with increasing silicate content. This indicates that the organoclay content affects the crystallinity of the PLA matrix. These results are discussed in details in an accepted JAPS manuscript [3].

References

[1] B. Braun, J. R. Dorgan, and S. F. Dec. *Macromolecules*, 39, (2006), 9302. [2] H. J. M. Hanley, D. D. Muzny, and B. D. Butler, *Langmuir* 13, (1997), 20, 5276. [3] A. C. Silvino, K. S. De Souza, K. Dahmouche and M. L. Dias, (2011), *Journal of Applied Polymer Science*, (accepted manuscript).

Acknowledgements: CNPq, CAPES, LNLS (Campinas - Brazil), PEMM/COPPE/UFRJ and Prof. Emerson Oliveira da Silva for his help in the FTIR discussion.

Caracterización estructural de sistemas $\mathrm{Nd}_y\mathrm{Fe}_{(86-y-x)}$ B_{14} Ti_x: Un estudio con espectroscopia XAFS (Fe-K, Nd-$\mathrm{L}_{II,III}$)

Lede, E. J.[1], Pagnola, M.P.[2], Saccone, F. D.[2], and Pampillo, L. G.[2]

[1] Universidad de Buenos Aires - Buenos Aires Argentina
[2] Universidad de Buenos Aires - Buenos Aires CapFe Argentina

Los imanes permanentes han despertado gran interés industrial debido a su alta densidad de flujo, su campo coercitivo y su producto energético máximo. Un hito en los 90 fue el desarrollo de imanes nanocoposite. Imanes de Nd-Fe-B han seguido un proceso de desarrollo continuo en áreas de tecnología de fabricación y composición química mejorando sus propiedades magnéticas. La esencia está en su estructura de fases magnéticas con un fuerte acoplamiento de intercambio: $\mathrm{Nd_2Fe_{14}B}$ (dura) y α-Fe, $\mathrm{Fe_2B}$ o $\mathrm{Fe_3B}$ (blandas). Imanes de alto rendimiento pueden obtenerse por sinterización de polvos, permitiendo mayor libertad en la forma del producto final. Las materias primas son producidas por técnicas de solidificación rápida, y convertidas en polvo por molienda mecánica. La incorporación de aditivos (Ti, Cr, Nb, Mo, etc.) retarda la formación de núcleos y crecimiento de granos de α-Fe, promoviendo la cristalización de $\mathrm{Nd_2Fe_{14}B}$ y la precipitación de fases intergranulares no magnéticas homogéneamente distribuidas [1]. El ordenamiento de corto rango para estos aditivos y el mecanismo de control sobre la nanostructura final, son procesos aún no bien comprendidos. Para el presente trabajo se emplearon muestras sintetizadas por esta vía [2]. Aquí presentamos los resultados obtenidos mediante XAFS en los bordes de absorción : Fe-K y Nd-$\mathrm{L}_{II,III}$. Para el tratamiento de los datos XANES, se empleó Análisis de Componentes Principales . Se determinaron 2 fases conteniendo Nd y 3 con Fe. Mediante Iterative Transformation Factor Análisis se obtuvieron las fases puras y sus concentraciones relativas en función del tenor de aditivo (Ti). Esto permitió investigar la formación de las distintas fases nanocristalizadas durante la evolución del sistema en función de la concentración del dopaje con Ti. Se observaron variaciones notables en la intensidad de la línea blanca en los espectros Nd-$\mathrm{L}_{II,III}$-XANES y marcadas diferencias en la región del pre-borde cercano en Fe-K-XANES. Esto indica una transferencia de estados disponibles en la estructura electrónica de sub-bandas de Fe y Nd, lo que se corresponde con las diferentes respuestas en saturación y anisotropía magnética [2].

[1] R. Ishii, T. Miyoshi, H. Kanekiyo, S. Hirosawa, J. of Magn. and Magn. Mater. 312 410-413. (2007). [2] Spyra, M., Derewnicka, D., and Leonowicz, M.. Phys. Status Solidi A 207, No. 5, 1170-1173 (2010).

Acknowledgements: Los autores agradecen al Laboratorio Nacional de Luz de Sincrotrón por el financiamiento parcial de proyecto.

Morphology of Conducting Bacterial Cellulose Nanocomposites with Polianiline - A SAXS study

Marins, J. A.[1], Soares, B.G.[1], and DAHMOUCHE, K[1]

Universidade Federal do Rio de Janeiro - Rio de Janeiro RJ Brazil

In situ polymerization of aniline with bacterial cellulose provides composites with potentially useful properties [1]. This work has been done to study how the content of dodecylbenzenylsulfonic acid used in polyaniline synthesis affects the structure and properties of bacterial cellulose-polyaniline composites. The composites have been characterized trough attenuation reflectance Fourier transformed infrared spectroscopy, wide-angle-X-ray scattering, small angle X ray scattering, emission field scanning electron microscopy, thermo-gravimetric analysis and electrical impedance analysis. The increase of DBSA content leads to the fracture of the cellulose matrix structure and to the increase of the crystalline character of PAni. The small angle X ray scattering results, shows that a low DBSA concentration (PAniBC3) the nanostructure of the composites consists of spatially correlated PAni nano-domains in the cellulose, forming larger secondary aggregates presenting a rough surface (slope of the Porods region of the aggregates around 3.6). By increasing PAni content (PAniBC2) the shoulder observed at high q-values due to spatial correlation between domains is more pronounced. This feature occurs probably because the more efficient polymerization and crystallization of PAni promoted by DBSA causes shrinkage of the cellulose chains located around and between the PAni primary domains. In the spectrum of the composite containing the highest PAni content (PAniBC1) the spatial correlation between PAni domains disappears and the slope at low q-values decreases up to around 3, consistent with the fracture of the cellulose with the excess of DBSA. This also explains the observed reduction of electrical conductivity for this material. Conductivity relative to the untreated bacterial cellulose is strongly increased, and an inverse relationship of conductivity to dielectric, and hence capacitance is observed. This preliminary work showed the possibility to incorporate conducting PAni in bacterial cellulose and that a chemical interaction exists between both polymers, allowing interpenetration at nanometer scale. In this sense these preliminary study is promising aiming the future obtainment, of nano-composites of bacterial cellulose-PAni presenting adequate electrical and mechanical properties for optical and electrical displays.

Keywords: Bacterial cellulose, polyaniline and SAXS.

1. Marins J.A et al. Cellulose, DOI: 10.1007/s10570-011-9565-4

Acknowledgements: Work supported by CNPq, FINEP and FAPERJ.

Estudo da Correlação entre Propriedades Estruturais e Magnéticas em Cerâmicas Magnéticas de $Zn_{1-x}Mn_xO$

Sabioni, A.C.S.[1], de Carvalho H. B.[2], Ferraz, W. B.[3], Carabalho, M. M[2], Iikawa, F.[4], Neves, P. P.[2], and Mesquita, A.[5]

[1] Universidade Federal de Ouro Preto - Ouro Preto MG Brazil
[2] Universidade Federal de Alfenas - Alfenas MG Brazil
[3] Centro de Desenvolvimento Tecnologia Nuclear - Belo Horizonte MG Brazil
[4] Universidade Estadual de Campinas - Campinas SP Brazil
[5] Universidade Federal de São Carlos - São Carlos SP Brazil

Os avanços teóricos e o forte envolvimento do magnetismo em todos os ramos do desenvolvimento tecnológico fazem desta disciplina uma das mais relevantes do ponto de vista científico. Hoje em dia, uma das áreas de maior de aplicação do magnetismo é a spintrônica, a eletrônica baseada no spin de portadores de carga. Esta área tem atraído grande interesse, motivados pelo desenvolvimento de novos dispositivos com novas funcionalidades e especificidades técnicas superiores as obtidas na eletrônica convencional. Neste cenário, o desenvolvimento de materiais semicondutores magnéticos, particularmente os óxidos magnéticos diluídos, ganha destaque, uma vez que esta família de materiais apresenta comportamento ferromagnético à temperatura ambiente e pode ser facilmente integrada aos dispositivos eletrônicos.
Neste trabalho apresentamos os resultados da caracterização estrutural de amostras cerâmicas do tipo $Zn_{1-x}Mn_xO$ com concentrações atômicas de Mn de 1, 3, e 5%. Misturas dos pós de ZnO e MnO foram homogeneizadas, mecanicamente, e, a seguir, compactadas na forma de pastilhas sob pressão de 60 MPa. As pastilhas verdes foram sinterizadas na faixa de temperaturas de 1300 C a 1400 C, durante quatro horas, em atmosfera dinâmica de oxigênio. A determinação da estrutura de longo alcance se deu através de Difração de Raios X (DRX) e refinamento Rietveld. Espectroscopia de Espalhamento RAMAN foi utilizada para avaliar a desordem estrutural provocada pela incorporação do dopante à matriz de ZnO. A microestrutura e a distribuição de composição foram também caracterizadas por Microscopia Eletrônica de Varredura (MEV) e EDS (Energy Dispersive X-Ray Spectrometer). A ordem local foi estudada por meio de técnicas de absorção de raios X (EXAFS e XANES). Palavras chave: spintrônica, óxido magnético diluídos, estrutura e propriedades magnéticas.

Acknowledgements: Os autores são gratos às agências de financiamento CAPES, FAPEMIG, CNPq e FAPESP pelo apoio financeiro e ao LNLS pelo tempo de medida nas linhas EXAFS.

Phase stability and structural distortions of nanostructured iron-cobaltite mixed conductor

Baqué, L.[1], Napolitano, F. R.[2], Soldati, A.L.[2], A. Caneiro[3], and Serquis, A[2]

[1] Universidad Nacional del Comahue - Neuquén Argentina
[2] Centro Atômico de Bariloche - S. C. de Bariloche Argentina
[3] Centro Atômico de Bariloche - La Plata AC Argentina

Mixed conductors oxides such as $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-d}$ are good candidates for intermediate-temperature solid oxide fuel cells cathodes. Our previous studies showed that the electrochemical performance is largely improved when using cathodes prepared with nanosized $La_{0.4}Sr_{0.6}Co_{0.8}Fe_{0.2}O_{3-d}$ (LSCF) powders (i.e. crystallite sizes 20-30 nm). However, an irreversibility increase in the polarization resistance occurs after measurements under reductive atmospheres in the 500-700 C range, which seemed to be related to the presence of some unidentified lattice distortions or an additional phase that could not be identified by conventional laboratory X-ray powder diffraction (XPD). In this work, nanocrystalline LSCFO powders were prepared by two different chemical methods. In-situ experiments were carried out using the D10BXPD beamline at LNLS under different atmospheres (pure He or synthetic air) between 20 and 600 C. In addition, some samples were prepared ex-situ under Ar and O2 and studied by transmission electron microscope (TEM) and laboratory XPD. The formation of phases with oxygen vacancy ordering was observed for first time in the studied composition. The XPD data indicate that only a portion of the sample is transformed while the rest keeps the original phase. These results are in agreement with TEM observations that show the coexistence of two phases in the same grain. All these changes can be reverted with heat treatments under oxygen or air atmospheres.

Acknowledgements: This work has been supported by the LNLS under proposals D10B - XPD-8219 and D10B - XPD 9892 and the ANPCyT project PICT-PAE 2288. D. Lamas and L. Suescum is acknowledged for useful discussions.

Speciation of metals in a nanostructured iron-cobaltite Mixed Conductor used for SOFC design

Soldati, A.L.[1], Baqué, L.[2], Napolitano, F. R.[1], and Serquis, A[1]

[1] Centro Atômico de Bariloche - S. C. de Bariloche Argentina
[2] Universidad Nacional del Comahue - Neuquén Argentina

Nanocrystalline Cobalt-ferrite powders with composition $La_{0.4}Sr_{0.6}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (LSCF) are being investigated as eficient cathode materials for solid oxide fuel cell devices. In this case, we compare two LSCF powders obtained by two different chemical methods called Acetate and HMTA [1]. XRD and TEM analyses showed in both samples the formation of a new phase under reductive conditions (Ar at 500 C), which coexists with that characteristic of the oxidated state. We used XANES to determine whether or not the formation of this new phase implies a chemical change, i.e. in the oxidation state of the transition metals (Fe and Co). XANES spectra were taken at room temperature from 200 eV below to 800 eV above the metal s K absorption edge using a Si(111) monochromator crystal. We observed intensity shifts in the metals K-edge features of samples treated in a reductive atmosphere. These differences might be explained by a change in the valece of the Co and Fe atoms to slightly lower formal oxidation states. In addition, the spectral features of re-oxidized samples did not differ significantly from the untreated samples, supporting the reversibility of this transformation. This behavior was observed in the Acetate as well as in the HTMA samples and can be attributed to intrinsic microstructural defects (size and strain) related to these synthesis routes.
[1] Baque L. et al., Electrochem.Comm. 10, 1905 (2008).

Acknowledgements: This work has been supported by the LNLS under proposal D04B-XAFS1-9932, the Argentinean project PICT-PAE 2288 and the PRH074 Agencia-CONICET. L. Andrini and D. Lamas are acknowledged for useful discussions.

Structural characterization and phase transition of cobalt doped titanates

Napolitano, F. R.[1], Baque, L.[2], Soldati, A.L.[1], Acuña, L. M.[3], Lamas, D. G.[2], and Serquis, A[1]

[1] Centro Atômico de Bariloche - S. C. de Bariloche Argentina
[2] Universidad Nacional del Comahue - Neuquén Argentina
[3] Consejo Nacional de Investigaciones Científicas y Técnicas - Buenos Aires Argentina

Lanthanum strontium titanates (LST) based oxides are good candidates to be utilized as symmetrical fuel cells (SFC) electrode materials because their good mixed conductivity (electronic and ionic) and electrocatalytic activity for both oxygen reduction and hydrogen oxidation reactions. However, it has been reported that the structure of this compound is strongly dependent on synthesis conditions leading to an apparent lack of reproducibility. In this work, structural characterization of $La_{0.4}Sr_{0.6}Ti_{1-y}Co_yO_{3+\delta}$ $(0.0 \leq y \leq 0.5)$ by powder X-ray diffraction at room temperature is reported.

In addition, a first study of these properties (y = 0.3 sample) at 750 C under oxidizing (synthetic air) and reductive $(5\%H2/95\%He)$ atmospheres is reported. A phase transition was found between room temperature and 750 C in oxidizing atmosphere, changing from rhomboedral to cubic structure. Also, a cubic structure with a strong lattice parameter shift was observed when atmosphere was switched from oxidizing to reductive conditions at 750 C.

High temperature structural characterization at these atmospheres is required to understand electrochemical properties of SFC electrodes under working conditions.

Acknowledgements: This work has been supported by the LNLS under proposals D10B - XPD-11737.

Synthesis and characterization of vanadium-doped TiO_2nanostructures prepared by hydrothermal method

Avansi, W.[1], Mendonça, V. R.[2], Ribeiro, C.[3], and Longo, E.[4]

[1] Universidade de São Paulo - São Carlos - São Carlos SP Brazil
[2] Universidade Federal de São Carlos - São Carlos SP Brazil
[3] Empresa Brasileira de Pesquisas Agropecuárias - São Carlos SP Brazil
[4] Universidade Estadual Paulista - Araraquara - Araraquara SP Brazil

Over the last decades, TiO_2 nanostructured have been extensively studied as photocatalysts . However, this application is limited to UV light irradiation because the light absorption edge of pure TiO_2 is less than 380 nm. Nevertheless, some papers reported that the shift of the absorption band gap of TiO_2 to the visible region of the solar spectrum can be significantly achieved by doping the TiO_2 materials [1, 2]. In this sense, the main objective of this work is study the synthesis of vanadium-doped TiO_2 nanostructures obtained by an environmental friendly hydrothermal method. In order to obtain samples with different amount of V in TiO_2 nanostructures, an appropriate amount of peroxovanadate and peroxytitanate solutions were mixed and then placed into a micro-controlled hydrothermal cell. Titanium and vanadium peroxide were prepared according to described by Ribeiro et al [3] and Avansi et al [4]. The temperature and treatment time was set at 200^{0}C and 4 hours, respectively. The influence of the vanadium load on the structural characteristics of the V-TiO_2 nanostructures was studied by X-ray diffraction, X-ray Absorption Near Edge Structure (XANES) and Transmission Electron Microscopy (TEM) techniques. For all samples with different amount of V only anatase crystalline phase could be identified by XRD patterns. An analysis of the V-K edge XANES spectra showed that the oxidation state of vanadium atoms in the samples containing different amount of V was predominantly V4+. TEM images shows that with increasing the V content, a morphology evolution, from anisotropic to isotropic nanostructures could be observed.

[1] R. Akbarzadeh, S. B. Umbarkar, R. S. Sonawane, S. Takle, M. K. Dongare, Applied Catalysis a-General, 374, 103. [2] G. B. Soares, B. Bravin, C. M. P. Vaz, C. Ribeiro, Applied Catalysis B-Environmental, 106, 287. [3] C. Ribeiro, C. M. Barrado, E. R. Camargo, E. Longo, E. R. Leite, Chemistry-a European Journal 2009, 15, 2217. [4] W. Avansi, C. Ribeiro, E. R. Leite, V. R. Mastelaro, Crystal Growth Design 2009, 9, 3626.

Acknowledgements: The authors gratefully acknowledge the financial support of the Brazilian research funding agencies FAPESP and CNPq. XANES measurements and HRTEM microscopy facilities were provided by LNLS-Campinas, SP, Brazil

Studies on the Magnetic-ion-rich Nanoscale Inclusions Formed by Spinodal Decomposition in Diluted Magnetic Oxides

Rhodes, F.P.[1], Sabioni, A.C.S.[1], de Carvalho H. B.[2], Ferraz, W. B.[3], Carabalho, M. M[2], Neves, P. P.[2], Mesquita, A.[4], and Iikawa, F.[5]

[1] Universidade Federal de Ouro Preto - Ouro Preto MG Brazil
[2] Universidade Federal de Alfenas - Alfenas MG Brazil
[3] Centro de Desenvolvimento Tecnologia Nuclear - Belo Horizonte MG Brazil
[4] Universidade Federal de São Carlos - São Carlos SP Brazil
[5] Universidade Estadual de Campinas - Campinas SP Brazil

Nanoscale enrichments resulting from spinodal decomposition have been proposed to contribute to the interesting magnetic properties of diluted magnetic oxides such as cobalt-doped ZnO ($Zn_{1-x}Co_xO$), but little is known experimentally about the electronic structures or physical properties of such enrichments. High-temperature ferromagnetism is frequently reported for this class of materials, but its origins are still under debate. Recently, attention has been drawn to the possibility that the ferromagnetism of many DMOs might be associated with spinodal decomposition [1], in which isostructural dopant-rich nanoscale domains embedded within a dopant-poor host matrix show cooperative magnetization and hysteresis. Spinodal decomposition alone does not appear to generate ferromagnetism in $Zn_{1-x}Co_xO$ [2], but it is conceivable that it could be a necessary-but-not-sufficient condition, e.g., with donor defects also required for high-TC ferromagnetism. Difficulties arise in the investigation of spinodal decomposition in $Zn_{1-x}Co_xO$ because of the similar local electronic and geometric environments of Co^{2+} and Zn^{2+} in the wurtzite lattice. Experimentally verifying the Co-rich inlusion hypothesis thus requires methods that reliably detect those inclusions and demonstrate their correlation with the observed ferromagnetism.

[1] Sato, K.; Katayama-Yoshida, H.; Dederichs, P. H. Jpn. J. Appl. Phys. 44, L948-L951 (2005).
[2] M. A. White, S. T. Ochsenbein, and D. R. Gamelin, Chem. Mater. 20, 7107 (2008).

Acknowledgements: The authors are grateful to FAPESP, CAPES and CNPq for financial support.

Síntese e Caracterização estrutural do semicondutor magnético diluído $Ti_{1-x}Co_xO_3$

Souza, T. E.[1], Alves,D.M.[1], Doriguetto, A.C.[1], de Carvalho H. B.[1], and Neves P.P[1]

Universidade Federal de Alfenas - Alfenas MG Brazil

Óxidos semicondutores magnéticos diluídos (SMDs) possuem grande potencial para serem empregados em dispositivos de spintrônica [1,2], uma nova tecnologia na qual os benefícios da carga e do spin do elétron se unem em um único dispositivo (microeletrônica). O dióxido de titânio (TiO_2)dopado com metais de transição (Co, Fe, Ni etc.) faz parte dessa classe de material. Embora muitos resultados experimentais e correspondentes modelos teóricos tenham sido apresentados nos últimos anos, a natureza das propriedades ferromagnéticas observadas no sistema é ainda questão de debate, pois resultados distintos são frequentemente obtidos. Outro aspecto importante é o método de preparo do material, é conhecido que as propriedades desses óxidos são bastante afetadas pelas rotas de síntese. Dentro desse contexto, o presente trabalho teve como principais objetivos: a obtenção de amostras de TiO_2na fase anatase pura com incorporação de íons de Co2+ via método dos precursores poliméricos em concentrações molares de 3, 6, 9 e 12 %(% em mol) e o estudo de suas características estruturais. As amostras foram submetidas a tratamento térmico à 450^oC por 2 horas em atmosfera ambiente. As fases cristalinas foram identificadas por difração de raios X (DRX). Espectroscopia de espalhamento Raman e Absorção de raios X (XAS) foram empregadas para investigar as características estruturais das composições. Os experimentos de XAS foram realizados no Laboratório Nacional de Luz Síncrotron (modo transmissão, linha de XAS), espectros coletados nas bordas k do Ti e do Co. Os resultados de DRX e Raman mostraram que as amostras cristalizaram na fase anatase sem formação de fases espúrias. As medidas de XAS (XANES/EXAFS) confirmaram a inserção dos íons Co (2+) no sítio do Ti da rede cristalina. A próxima etapa do trabalho será a caracterização das propriedades magnéticas das amostras.

Palavras chaves: $TiO_2 : Co$, ferromagnético, difração de raios X, Raman, absorção de raios X

[1]KASUYA, T.; YANASE, A.; Rev. Mod. Phys. 40, 684 (1968); MAUGER, A.; GODART, C., Phys. Rep. 141, 51 (1986).

[2] WOLF, S. A.; et al. Science, v. 294, p. 1488 (2001).

Acknowledgements: FAPEMIG, CAPES, CNPq e LNLS pelo apoio financeiro e ao laboratório de cristalografia da Unifal-MG pelas medidas de DRX.

X-ray Multiple Diffraction Phenomenon in the Evaluation of small structural changes in a new single crystal used as optical bandpass filters

C. M. R. Remedios[1], Melo, G. S.[1], Moreira, S. G. C.[1], Cardoso, L.P.[2], and de Menezes, A. S.[3]

[1] Universidade Federal do Pará - Belém PA Brazil
[2] Universidade Estadual de Campinas - Campinas SP Brazil
[3] Universidade Federal do Maranhão - Imperatriz MA Brazil

The X-ray multiple diffraction using synchrotron radiation has been applied to study manganese ions incorporated into Nickel sulfate hexahydrate (NSH) crystal lattice. NSH crystal has been used in optics. The NSH crystal has high transmission efficiency and narrow spectrum bandwidth at 250 and 500 nm. A light transmission spectrum with these characteristics is similar to an optical filter. Unfortunately, this material loses stability at a relatively low temperature, 73°C. Some researchers have attempted to solve this problem - NHS crystals have been grown doped with several kinds of ionic complexes The presence of dopants into a crystal lattice can modify the physical properties of these materials for technological applications. In this paper we present the structural characterization of crystals of Mn doped NSH. They were grown by slow evaporation from supersaturated aqueous solutions. High-resolution Renninger Scans of NSH crystals were carried out at XRD1 station of the Brazilian Synchrotron radiation facility (LNLS). Wavelengths of $\lambda = 1.63267$ and 1.48059 were used in the Mn doped NSH study. A three-axes Huber goniometer was used in order to provide Renninger scans. The (008) primary reflection was chosen for these experiments. The results show that the crystals symmetries are practically the same regardless of the incorporation of manganese ions. Accurate calculation of the unit-cell parameters revels that there is relative dilation of the lattice parameters following Mn dopant. The results have also demonstrated that reflection phases are sensitive to presence of dopant ions in the lattice of NSH. Variations in the peak profiles were observed from pure to doped samples, and these variations correlated with shifts in the structure factor phases, triplet phases. It can be evidence of structural changes. Experimental profiles of the three-beam cases $(204)(\bar{2}04)(008)$ and $(024)(0\bar{2}4)(008)$ in the NSH and NMnSH samples are very different. Structural changes causing the phase shifts are discussed.

Acknowledgements: This work was supproted by CNPq and LNLS

STUDY OF STRUCTURAL AND MAGNETIC PROPERTIES OF Co_3O_4 NANOPARTICLES

Lima, R. J. S.[1], Moura, K. O.[1], Pedra, P. P.[1], Duque J.G.S.[1], and Meneses, C. T.[1]

Universidade Federal de Sergipe - São Cristóvão SE Brazil

In the last years several nanostructured magnetic materials have been extensively explored both from the point of view of fundamental physical and applications [1-3]. Studies on the magnetic properties in nanosized particles have shown significant change in your properties when yours sizes is enough reduced. In this work antiferromagnetic Co_3O_4 nanoparticles were synthesized by the coprecipitation method. With the addition of the sucrose as chelating agent (sucrose) the size of the particles was reduced of 54nm for 19nm. The Co_3O_4 nanoparticles exhibit a cubic spinel structure identified for X-ray diffraction (XRD) and confirmed by Rietveld refinement. Scanning Electron Microscopy (SEM) images exhibit a spherical-like morphology and confirm the decrease of the particle size observed by XRD. The magnetic measurements as function of temperature using a superconducting quatum interference device (SQUID) show a large surface anisotropy for samples obtained with addition of sucrose accompanied by an exchange Bias effect indicating also the existence of a weak ferromagnetism. A decreasing of the Néel temperature from the bulk (and others nanostructes-type) was observed, which can be associated with finite-size effect a the nanoparticles shape.

REFERENCES [1] Q. A. Pankhurst et al., J. Phys. D 36, R167 (2003). [2] Sun S., Murray C. B., Weller D., Folks L. and Moser A., Science 287 (2000) 1989. [3] Dobson J., Nat. Nanotechnol., 3 (2008) 139.

Acknowledgements: The authors are grateful for access to the facilities of Laboratório Nacional de Luz Sincrotron (LNLS) for the use of Laboratório de Microscopia Eletrônica micrographs and the Brazilian agency CNPq for financial support.

Caracterização Estrutural de Fases Amorfas de $Fe[Co(CN)_6]$ Obtidas em Alta Pressão

ROVANI, Pablo Roberto[1], Pereira, A. S.[1], De Lima, J.C.[2], Catafesta, J.[1], and Perottoni, C. A.[3]

[1] Universidade Federal do Rio Grande do Sul - Porto Alegre RS Brazil
[2] Universidade Federal de Santa Catarina - Florianópolis SC Brazil
[3] Universidade de Caxias do Sul - Caxias do Sul RS Brazil

O composto $Fe[Co(CN)_6]$ possui uma estrutura que pode ser descrita como um arranjo tridimensional de unidades octaedrais $Fe(NC)_6$ e $Co(CN)_6$, conectadas por ligações metal-cianeto-metal. Essa estrutura altamente flexível dá lugar a comportamentos não usuais, quando o material é submetido a variações de temperatura e/ou pressão. $Fe[Co(CN)_6]$ possui um coeficiente de expansão térmica isotrópica negativa em uma ampla faixa de temperatura [$-1,47 \times 10^{-6} K^{-1}$, entre 4,2K e 300K, S. Margadona, K. Prassides, A. M. Fitch. J. Am. Chem. Soc. 2004; 126: 15390]. Por outro lado, esse material sofre um processo de amorfização quando submetido a pressões acima de 10 GPa à temperatura ambiente [J. Catafesta, J. Haines, J. E. Zorzi, A. S. Pereira, C. A. Perottoni. Phys. Rev. B 77, 064104, 2008. J. Catafesta, A. S. Pereira, C. A. Perottoni, J. Haines, F. Garcia. Proceedings of the Joint AIRAPT22 & HPCJ50 International Conference on High Pressure Science and Technology. 2009. Tokyo, 374]. Para estudar o mecanismo associado ao processo de amorfização sob pressão e sua possível correlação com o comportamento térmico anômalo, foi realizado um estudo sobre as alterações estruturais induzidas em amostras de $Fe[Co(CN)_6]$ recuperadas após processamento em altas pressões (7.7 GPa) e temperaturas ($T < 400^oC$). Esse estudo identificou: (a) a indução de uma alta deformação da estrutura de partida em amostras processadas a baixas temperaturas; (b) a amorfização completa da fase de partida a 200^oC e a decomposição com oxidação para $T > 250^oC$; (c) a amorfização a 250^oC, para uma forma distinta da observada a 200^oC, se a amostra é desidratada previamente ao processamento em alta pressão. O conjunto de resultados sugere uma amorfização induzida por altas pressões associada a um processo de decomposição cineticamente impedido[J. Catafesta, A. S. Pereira, C. A. Perottoni, Proceedings of the 49^{th} EHPRG Conference. 2011. Budapest]. Neste trabalho, a natureza estrutural das fases amorfas produzidas em alta pressão foi investigada por difração de raios X realizada na linha XRD1 do LNLS, usando diferentes comprimentos de onda, visando aproveitar a variação dos fatores de espalhamento atômicos dos átomos de Fe e Co. Dessa forma, considerando padrões de espalhamento obtidos para comprimentos de onda antes e após a borda de absorção desses elementos, foram obtidas as Funções de Distribuição Radial Diferenciais que permitiram uma comparação entre os ambientes químicos em torno dos átomos de Fe e Co.

Acknowledgements:

Local and periodic symmetry approach of BaZrHfO3 using sincrotron radiation: The convolution of theoretical and experimental insights.

Moreira M. L.[1], Andrés, J.[2], Mastelaro, V.R.[3], Varela, J.A.[1], and Longo, E.[1]

[1] Universidade Estadual Paulista - Araraquara - Araraquara SP Brazil
[2] Universitat Jaume I - Castelló de la Plana Spain
[3] Universidade de São Paulo - São Carlos - São Carlos SP Brazil

The input task of hafnium as a substitution element into barium zirconate cubic lattice was preformed through microwave-assisted hydrothermal method. A low temperature at relative short times as 140C and 160 min respectively, was employed to ensure the features of a friendly synthesis. Regardless of hafnium concentration, all diffraction patterns remain reporting a single cubic phase identified as barium zirconate compound, even at high concentration of hafnium. Scanning and transmission electronic microscopy revealed the mesocrystalline nature of self-assembled BZHO nanoparticles under dacaoctahedral shape. Furthermore, X ray absorption spectroscopy (XAS) over k and L-edge of zirconium, K-edge of hafnium and K-edge of oxygen, found local symmetry breaks associated with specific ordering degree. The K-edges is very sensitive to overlapping of 4d 2p orbital regarding the Zr-O bond and/or 5d 2p, regarding Hf-O bound. ab initio theoretical approach was used to available the main electronic features like band structure and density of states of high doped BZO host lattice, via super-cell conduction under DFT methodology. The theoretical insight also allows the correlation between simulated and experimental induced Raman modes.

Acknowledgements: This work is supported by FAPESP/CEPID 98/14324-8., CNPq, and national institute INCTMN. The authors acknowledges to Ministerio de Educación y Cultura(project CTQ2009-14541-C02) of the Spanish Government, PROMETEO program (PROMETEO/2009/053) of the Generalitat Valenciana, and Programa de Cooperación Científica con Iberoamerica (Brasil), Ministerio de Educación (PHB2009-0065-PC), Thanks for Luz Sincrotron National Laboratory (LNLS) user facilities.

Structural and electrical properties of ultra-thin films of VO_x electrodeposited on Si

I. L. Graff[1] and Cezar, A. B.[1]

Universidade Federal do Paraná - Curitiba PR Brazil

Vanadium oxides, especially V_2O_5 and VO_2, are very interesting compounds both from the fundamental and applied points of view. V_2O_5 for instance, has been used as electrode material in Li-based batteries due to its capability of intercalating Li in its structure[1] and as a catalyst for the selective reduction of NO_x[2] and oxidation of *o*-xylene[3]. VO_2 on the other hand, is a very promising material for a number of applications, including the so called intelligent windows, ultra-fast optical switches, gas sensors, varistors, etc[4]. Such a range of applications comes from the fact that VO_2 undergoes a sharp metal-insulator transition (MIT), simultaneously accompanied by a structural phase transition from a high-temperature rutile-type (R) phase to a low-temperature monoclinic (M_1) phase, around 340 K[5].

We present a new method to obtain VO_2 thin films grown on Si(001) substrates by an electrodeposition technique[6]. The phase of interest was obtained by drying and annealing the $V_2O_{5-\delta}\cdot nH_2O$ xerogel precursor deposit at 773 K. The effective formation of the monoclinic VO_2 phase, after annealing, is strongly dependent on the time of storage under atmospheric conditions. The VO_2 films so obtained have [011]-preferred orientation and undergo a metal-insulator transition. The resistance change as function of temperature is characterized by a broad hysteresis where two transition temperatures can be identified, $T_1 \approx 328$ K and $T_2 \approx 350$ K.

1 S.-L. Chou *et al.*, *Chem. Mater.* **20**, 7044 (2008).
2 L. Casagrande *et al.*, *Appl. Catal. B* **22**, 63 (1999).
3 K. V. Narayana *et al.*, *Appl. Catal. A* **11**, 167 (1999).
4 B.-J. Kim *et al.*, *IEEE Electron Dev. Lett.* **31(1)**, 14 (2010).
5 F. J. Morin, *Phys. Rev. Lett.* **3**, 34 (1959).
6 A. B. Cezar *et al.*, *Electrochem. Solid State Lett.* **14(3)**, D23 (2011).

Acknowledgements: The authors acknowledge the support of CNPq, CAPES, Fundação Arauária, and LNLS.

Estudio electrónico, estructural y magnético de nanopartículas de Pt_3Co y Pt_3Co/Au

M. Mizrahi[1], Giovanetti, L. J.[1], Beron, F.[2], Ramallo-López, J. M.[3], Pirota, K. R.[4], E. V. Shevchenko[5], and Requejo, F. G.[3]

[1] Universidad Nacional de La Plata - La Plata Bs.As Argentina
[2] Universidade Estadual de Campinas - Campinas SP Brazil
[3] Universidad Nacional de La Plata - La PLata B.A. Argentina
[4] Consejo Superior de Investigaciones Científicas - Madrid Spain
[5] Lawrence Berkeley National Laboratory - Berkeley CA United States of America

Diferentes materiales ensamblados en una única nanopartícula (NP) brindan un camino para obtener sistemas que presenten nuevas propiedades físicas y químicas. Este tipo de compuestos son sintetizados generalmente partiendo de NP's de un determinado material para posteriormente usarlas como semillas de nucleación del resto de los constituyentes [1]. La combinación de materiales magnéticos y de alto contraste a los rayos X, son una vía prometedora hacia el diseño de agentes duales que permiten tanto la detección por resonancia magnética y por rayos-X [2]. En este trabajo se estudiaron NP's de Pt_3Co y Pt_3Co/Au suspendidas en diferentes solventes. La caracterización se realizó empleando microscopia electrónica (TEM), absorción de rayos-X (XAS), dispersión de rayos-X a bajo ángulo (SAXS), medidas magnéticas globales (MM) y medidas de dicroísmo circular magnético (XMCD). Los resultados de microscopía muestran partículas esféricas con una baja dispersión de tamaños para el sistema Pt_3Co, mientras que se observa la formación de estructuras tipo dumbell con el agregado de Au. De los resultados de las medidas magnéticas se observa que todas las muestras presentan un comportamiento superparamagnético a RT con una temperatura de bloqueo que disminuye con el agregado de Au a las NP's. Las medidas de XMCD muestran que existe una transferencia de momento magnético de los átomos de Co a los de Pt.

[1] Ver como ejemplo: M. Casavola, et. al., Nano Lett. 2007,7, 1386.; R. Buonsanti, et al., J. Am. Chem. Soc. 2006, 128, 16 953; J. Gao, et al., J. Am. Chem. Soc. 2007, 129, 1428; D. V. Talapin, et al., J. Phys. Chem. C 2007, 111, 14 049.

[2] J.-H. Lee, et al., J. Cheon, Nat. Med. 2006,13, 95.

Acknowledgements: Este trabajo ha sido financiado por el Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) y por el Laboratorio Nacional del Luz Sincrotrón (LNLS).

Study of optical and structural properties of Eu^{3+} doped in $BaTiO_3$ nanocrystals

Macario, L. R.[1], Mazzo, T M[1], Avansi,W.Jr.[2], Rosa, I. L. V.[3], Siu Li, M.[2], Mastelaro, V.R.[2], and Longo, E.[1]

[1] Universidade Estadual Paulista - Araraquara - Araraquara SP Brazil
[2] Universidade de São Paulo - São Carlos - São Carlos SP Brazil
[3] Universidade Federal de São Carlos - São Carlos SP Brazil

Eu^{3+}-doped $BaTiO_3$ (BT:Eu^{3+}) nanocrystals were synthesized by a microwave assisted hydrothermal method (HAM) in few minutes in order to study the synthesis, optical properties and structural properties of these powders. The photoluminescence properties and decay times of the BT:Eu^{3+} nanocrystalline powders have been investigated as a function of the dopant concentration and used to reveal the strong influence of europium on the barium titanate nanostructure. The behavior of the Eu^{3+} lattice modifier was followed in a long-range order by X-ray diffraction (XRD) and the structure was supported by the Ti K-edge X-ray absorption near-edge structure (XANES). Fourier transform Raman (FT-Raman) spectroscopy was used to analyze the short-range order and ultra violetvisible (UVVis) measurements suggested the presence of Eu^{3+} in the barium titanate lattice and the intermediary energy levels in the band gap of $BaTiO_3$ powders heat treated at 140^{o}C.

Acknowledgements: The authors thank the financial support of the Brazilian research financing institutions: FAPESP, CAPES, CNPq and to Laboratório Nacional de Luz Síncrotron (LNLS).

Study of the influence of reduction agents in the Eu reduction in the $BaAl_2O_4$ host

Rezende, M. V. dos S.[1], Montes, PJR[1], and Valerio, M.E.G.[1]

Universidade Federal de Sergipe - São Cristóvão SE Brazil

Rare-earth-doped aluminates serve as an important class of phosphor for commercial applications, especially in the areas of safety improvement and energy saving. Strontium aluminates ($SrAl_2O_4$:Eu^{2+}, Dy^{3+}) and barium aluminates ($BaAl_2O_4$:Eu^{2+}, Dy^{3+}) represent a class of materials that may exhibit long lasting phosphorescence and luminescence when doped with trivalent and divalent rare-earth ions. Most aluminates are activated by Eu^{2+} ions, and to obtain the rare earth with this valence the trivalent rare earth oxide is usually used as the starting material. To reduce the rare earth from Eu^{3+}-Eu^{2+} it is necessary to use particular schemes in the production of the rare earth containing sample. Many such schemes have been used and developed. The most common scheme is to use N_2/H_2 or H_2, or CO_2 or CO as reducing agents when the rare earth containing sample is calcined. In this work, the DXAS technique (Dispersive X-ray Absorption Spectroscopy) is used to follow the XANES spectrum of the Eu ions during the calcinations program in different atmospheres.. Analysis of the reduction dynamics can give information of the synthesis process and DXAS technique can be used to follow it. The pre-calcined samples of Eu-doped BaAl2O4 were prepared at 600 C via a sol-gel proteic route. DXAS spectra were obtained as a function of temperature excited at the LIII edge of Eu ions during the synthesis. The 5H2+He, CO+He, Synthetic air, N2 gases were used as reduction agents during the synthesis. DXAS spectra exhibit changes of absorption edge position associated to the LIII edge of the Eu ions during heating and cooling of samples. The ratio of absorption edge Eu^{3+}-Eu^{2+} was investigated to verify the efficiency of reduction agents in the stability of Eu2+ ion in the matrix. Eu2O3 was used as reference sample. The results show that He2+H2 gas are the best atmosphere to stabilize the Eu ion the 2+ valence. For all the other atmospheres, the reduction of Eu occur at the calcinations temperature (1100C), but the process is reversible upon cooling down to room temperature.

Acknowledgements: This work was supproted by CAPES, CNPq, FINEP and LNLS. MVSR acknowledge the PhD grant from CNPq

Estudo estrutural (DRX) e morfológico (MEV) de argilas Bentonitas modificadas com Cobalto coloidal

MARIANI, F. Q.[1] and Anaissi, F. J.[1]

Universidade Estadual do Centro-Oeste - Guarpuava PR Brazil

As atuais tecnologias, de um modo geral, solicitam materiais com combinação de propriedades que não são encontradas nos materiais convencionais. As combinações de componentes inorgânicos e argilas em escala nanométrica constituem uma alternativa para a produção de novos materiais multifuncionais, conhecidos como materiais mistos nanomodificados (MM), com uma larga faixa de aplicações potenciais. Neste trabalho foram utilizados quatro argilas esmectitas (Sódica Importada, Chocolate, Brasgel e Verde Lodo) modificadas com cobalto coloidal [CoO(OH)], gerando materiais mistos nanoestruturados, denominados de SICo, ChCo, BrCo e VLCo. Os materiais de partida e mistos tiveram sua composição química determinada por espectrometria de energia dispersiva (EDS). Para caracterização morfológica e estrutural foram utilizadas as técnicas de microscopia eletrônica de varredura (MEV) e difratometria de raios X (DRX). Pelos resultados de MEV foi possível notar uma maior quantidade de metais na superfície dos MMs se comparados com as argilas puras. Por EDS foi possível estimar a composição dos MMs que mostraram a interação do cobalto coloidal com as argilas. O DRX comprova a intercalação do cobalto coloidal entre as lamelas da argila devido deslocamento do pico d001 para as argilas SI e BR ao contrário das argilas cálcicas VL e CH, todos os materiais mistos apresentaram picos referentes à montmorilonita, quarzto de baixa cristalinidade, ilita, caulinita e óxihidróxido de cobalto. Mapas isolineares construídos a partir de um software podem ser muito úteis na identificação de alterações nos espectrogramas, as regiões do cobalto coloidal estão bem destacadas frente às regiões das argilas nos materiais mistos.

Acknowledgements: LNLS, CAPES, Fundação Araucária, FINEP, CNPQ e UNICENTRO.

Investigação estrutural de vidros aluminato de cálcio com pouca sílica dopados com íons das terras raras.

Peixoto, S. M. B.[1], dos Santos, D. R.[1], Novo, L. C[1], Medina, A.N.[2], and Sampaio, J. A.[1]

[1] Universidade Estadual Norte Fluminense - Campos dos Goytacazes RJ Brazil
[2] Universidade Estadual de Maringá - Maringá PR Brazil

O vidro aluminato de cálcio é um vidro óxido que possui uma boa transmitância na região do infravermelho. Estudos recentes indicaram que esse vidro apresenta propriedades mecânicas, óticas e térmicas adequadas para ser aplicado na fabricação de componentes óticos para a fotônica, quando dopado com íons das terras raras e preparado em atmosfera controlada. Contudo, o aumento da concentração de íons dopantes na matriz do vidro aluminato de cálcio causa uma redução da eficiência quântica de fluorescência do vidro. Neste estudo, investigou-se o ambiente químico dos íons dopantes do vidro aluminato de cálcio utilizando a Espectroscopia de Absorção de Raios X (XAS) e verificou-se através da técnica de Espalhamento de Raios X a Baixo Ângulo (SAXS) se houve a formação de agregados de íons dopantes durante a preparação do vidro. As medidas de XAS foram realizadas no modo de fluorescência em torno da borda L_III dos dopantes Ce e Nd na linha XAFS2. Já as medidas de SAXS de vidros dopados com diferentes concentrações de Nd, Ce, Er e Yb foram realizadas, em temperatura ambiente, na linhas de luz SAXS2 do LNLS (Campinas-SP). A análise da região de Espectroscopia de Alta Resolução da Borda de Absorção de Raios X (XANES) do espectro de absorção mostrou que o estado de valência do Ce mudou de 4+ para 3+ durante a preparação dos vidros. A causa da redução do cério é atribuída ao grande número de átomos de oxigênio que estão ao redor dos átomos de cério no vidro. As simulações da região de Espectroscopia de Estrutura Fina de Absorção de Raios X (EXAFS) do espectro de absorção indicaram que os primeiros vizinhos do Ce são 8 átomos de O localizados em $R \approx (2{,}34 \pm 0{,}01)$, também foi visto que o Ce está coordenado com 12 átomos de Ce em $R \approx (3{,}83 \pm 0{,}01)$. Para o Nd, foi encontrado que seus primeiros vizinhos são 4 átomos de O localizados em $R \approx (2{,}42 \pm 0{,}01)$. Nas análises das curvas de espalhamento de raios X a baixo ângulo não foi encontrado nenhum indício da presença de agregados de íons das terras raras nos vidros aluminato de cálcio.

Acknowledgements: CAPES, FAPERJ e LNLS

CoNi catalysts for reforming reactions of ethanol

Braga, A. H.[1], Ferreira, A.P.[1], Santos, J.B.O.[1], and Bueno, J.M.C.[1]

Universidade Federal de São Carlos - São Carlos SP Brazil

The search of new energy sources, that may be clean and alternatives to oil, has shown that hydrogen is promising, because its use generates water as waste. The ethanol reforming process appears to be interesting for H_2 production. These reactions need catalysts. Ni is referred to be an active and low cost catalyst, although it suffers deactivation by carbon deposition and yields large amounts of methane, which is undesirable. Co catalysts products less methane, even deactivate by carbon deposition. Thus, we proceeded with addition of Co to Ni catalyst supported on $MgAl_2O_4$. Samples were synthesized by conventional impregnation with nitrate of the respective metals onto a $MgAl_2O_2$ obtained by a sol-gel route with mass content of 15% of Ni (15Ni), 7.5% of Ni and 7.5% of Co (7.5Co7.5Ni), and 15% of Co (15Co). These samples were used in the oxidative reforming of ethanol reaction, with a molar ratio $H_2O/EtOH/O_2$of 3/1/0,5. XANES spectra were collected in the Ni (8333 eV) and Co (7709 eV) edges, during the reduction of the catalyst, on H_2 flow (activation step) at 750C; and during the reaction at 500C and 550C. The analysis of the white line showed up that the CoNi catalyst is reduced at lower temperatures than the single Ni and Co ones. 15Ni and 15Co samples showed similar profile in reaction: oxidize (to CoO and NiO) and reduce again (Co^0 and Ni^0). Instead of Co has shown the same profile in the sample CoNi, Ni remained partially oxidized on stream. DRX patterns of 15Co and 15Ni samples exhibited Co_3O_4 and NiO species and no NiO phase for the fresh CoNi catalyst. These results suggest the formation of a spinel $NiCo_2O_4$ phase, once reduced can form a CoNi alloy. This can explain some electronic changes in the CoNi sample. The catalytic evaluation result in similar EtOH conversion, 100% in these temperatures. Product distribution revealed that the CH_4, selectivity followed the order: 15Ni ¿ 7.5Co7.5Ni ¿ 15Co. However, thermogravimetric analysis of the spent catalyst showed no carbon deposition on bimetallic sample, despite severe formation on Co and Ni ones. So Co addition in this proportion is effective in lowering CH_4,selectivity and prevents the C deposition, which is desirable for reforming catalysts. Eventhough, new experiments are needed to explain this effect.

Acknowledgements: DEQ-UFSCar, LNLS, CNPq, Petrobras

Effect of TM doping on Structural and Magnetic properties TM-doped CuO

Pedra, P. P.[1], Duque J.G.S.[1], and Meneses, C. T.[1]

Universidade Federal de Sergipe - São Cristóvão SE Brazil

CuO is a Mott-Hubbard insulator with a gap of the charge-transfer type and is um quasi-one-dimensional antiferromagnet above the treedimensional phase transition temperature at $T_{N1} = 229K$ and $T_{N2} = 213K$ [1]. Recently, Zheng et al. have observed the T_N suppression of CuO doped with a non-magnetic Li^{+1} ion [2]. It is well known that this kind of doping create one hole in the valence band because the charge difference between Cu^{+2} and Li^{+1} ions. Magnetic order was shifted to around $100K$ at concentrations larger than 16% his suppression is believed to be due the different electronic structure of the Li^{+2} ion related Cu^{+2}. To test the role of the electronic structure in the magnetic ordering of CuO we have used the co-precipitation method to synthesize polycrystalline M-doped CuO samples (M= Ni^{+2}, Fe^{+3}, Zn^{+2} and Al^{+2}) [3]. The magnetic and structural properties of $Cu_{1-x}M_xO$ samples have been investigated as function of doping concentrations(x). X-ray powder diffraction (XRD) carried out in $Cu_{1-x}M_xO$ (x= 0.01, 0.05 and 0.10) samples show the formation of single phase with structure isomorphous to that semiconductor host (CuO). Magnetization measurement as function of temperature show that T_N is suppressed from $213K$ (CuO) to $70K$ in the Fe-doped sample with concentration around $x = 0,06$. Surprisingly, for Ni-doped samples, T_N seem to be unaffected by the TM substitution. To understand magnetization results were performed X-ray Diffraction (XRD) and X-ray absorption (XAS) analysis in regions near to magnetic transitions temperature (T_N). The XAS results for M ions K-edge show not larger modifications in the XANES profile. Therefore, the XANES results in the TM $L_{2,3}$-edge and O K-edge show significant modifications depending of the doping ion. (CNPq)

References:

[1] J. Zaanen, *Phys. Rev. Letters*, **55**, 418, 1985.
[2] X. G. Zheng et al, *Phys. Review B* **67**, 094610, 2004.
[3] C. T. Meneses et al, *J. Non-Cryst. Solids* **354** (2008) 4830.

Acknowledgements: This work was supported by CNPq funding agency. The authors also are grateful to the LNLS by facilities access to XPD, XAFS and SGM beamlines.

Estudo estrutural (XRD1-LNLS) e morfológico (MEV-LV) de Argilas Bentonitas

MARIANI, F. Q.[1], Villalba, J. C.[1], Castro, E.G.[1], and Anaissi, F. J.[1]

Universidade Estadual do Centro-Oeste - Guarpuava PR Brazil

Neste trabalho foram estudadas quatro argilas esmectitas (Sódica Importada, Chocolate, Brasgel e Verde Lodo) para posterior modificação com cobalto coloidal [CoO(OH)], com intúito de gerar novos materiais mistos nanoestruturados. As argilas tiveram suas composições químicas determinadas por espectrometria de energia dispersiva (EDS). Para caracterização morfológica e estrutural foram utilizadas as técnicas de MEV-LV e XRD1-LNLS. O DRX mostra que o pico d001 para as argilas sódicas SI, BR e cálcicas VL, CH apresentam distâncias 2θ condizentes com as encontradas na literatura, apresentam ainda picos referentes à montmorilonita, quarzto de baixa cristalinidade, ilita e caulinita.

Acknowledgements: LNLS, C2Nano, Capes, CNPq, Finep, Fundação Araucária e Unicentro.

ADP:Mn Piezoelectric coefficients obtained by X-ray multiple diffraction

GOMES,E.J.L.[1], Moreira, S. G. C.[1], de Menezes, A. S.[2], Cardoso, L.P.[3], and C. M. R. Remedios[1]

[1] Universidade Federal do Pará - Belém PA Brazil
[2] Universidade Federal do Maranhão - Imperatriz MA Brazil
[3] Universidade Estadual de Campinas - Campinas SP Brazil

Piezoelectric constants may be determined directly by X-ray multiple diffraction (XRMD) measurement in a piezoelectric crystal by a static electric field. XRMD occurs when two or more set of crystallographic planes satisfy Braggs law at the same time for a certain incident X-ray beam. A set of planes called primary reflection and another set of planes which is called secondary reflection. A straightforward approach to obtain this phenomenon is first to adjust a primary reflection to the exact Bragg condition. Second, the crystal is rotated around an axis perpendicular to the primary planes satisfying Braggs law, called phi-rotation. For a certain angle, a different secondary reflection also diffracts the incident X-ray beam. As result, one obtains the Renninger scan (RS) that consists of a plot of the primary intensity versus phi with several peaks, which are associated with the interference between the waves diffracted by the primary and secondary reflections. This obtained pattern is known to contain structural information such as lattice parameters, symmetry and crystal quality. Avanci at *ali* determined the piezoelectric coefficients of mNA and MBNAP organic nonlinear optical materials (2000 Phys. Rev. B 61 6507). In this work Ammonium and Potassium Phosphate (ADP) crystals doped with manganese ions (ADP:Mn) have been grown and their piezoelectric proprieties have been studied as a function of dopant concentration by X-ray multiple diffraction. It should be pointed out that the values obtained for ADP:Mn d_{36} and d_{25} piezoelectric coefficients are higher than that of the well known pure ADP values. In preliminary results, we have observed a reduction in the bridge length (H-O distance) in ADP:Mn. It is known that reduction in the bridge length (H-O) enhances the d_{36} ADP piezoelectric coefficients (McMahon *et al.*, 1990).

Acknowledgements: This work was supported by CNPQ and LNLS.

X-ray diffraction of MOFs with controlled environment at LNLS

Díaz, B.[1] and Marques, L.[1]

Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

Metal organic frameworks (MOFs) are a large family of materials, formed by an inorganic cluster and an organic ligand. Many of them have porous structures with large surface areas and adsorption capacities. These properties can be tailored choosing different combinations of metal cluster and organic ligand, aiming a particular application in the fields of gas storage, gas separation, etc. Some MOFs show the breathing property, which consists in marked structural changes accompanying adsorption/desorption of some molecular species. Hence, a technique where both adsorption and structural properties can be assessed at the same time is crucial for their characterization. In this work, we show several examples of in-situ MOFs x-ray diffraction studies carried out in controlled environment of gas pressure and temperature. Several setups were developed in order to control sample temperature and pressure in relatively wide ranges. Some of the MOFs studied show the breathing property, with the characteristics structural changes upon adsorption/desorption of molecular species in their pores.

Acknowledgements: This work was supported by LNLS.

Experimental observation of graphene-type behavior of multilayer epitaxial graphene grown on C-face 4H-SiC

Goncalves, A. M. B.; Goncalves, Alem-Mar B.[1], Mendes-de-Sá, T. G.[1], Lacerda, R. G.[1], and Magalhaes-Paniago, R.[1]

Universidade Federal de Minas Gerais - Belo Horizonte MG Brazil

A systematic study of the growth of epitaxial graphene on C-face of 4H-SiC at 1775C in Ar atmosphere as a function of time was performed. Raman spectroscopy and X-ray diffraction were measured to study the evolution of structure as function of growth time. The Raman signal of multilayer graphene starts to appear after 30 minutes of growth and increases with time. For the longest time studied (60 minutes) the spectrum is similar to that of an exfoliated monolayer graphene. X-ray diffraction reveals that multilayer graphene has two different (001) interplanar spacing that become well differentiated with increasing time. XRD, in grazing incidence mode, proves the existence of rotational misorientation, observed by diffraction of (100) and (110) planes. The misorientation evolves from three well defined rotation angles to complete rotational disorder. A comprehensive structural scenario of the evolution of epitaxial graphene on SiC(0001) will be presented.

Acknowledgements: This wok was supported by CNPq, FAPEMIG, ABTLuS and Instituto Nanocarbono.

In situ XRD Studies of the Carburization Process of Tungsten Carbides Catalysts

Rodella, C. B.[1], Amanda A. Leitão[1], Nathana C. B. Silva[1], Moya, S. F.[2], and Silva, V. T.[3]

[1] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[2] Instituto de Quimica de Sao Carlos - São Carlos SP Brazil
[3] Universidade Federal do Rio de Janeiro - Rio de Janeiro RJ Brazil

Tungsten carbide supported on carbon has great potential for one-pot biomass transformation, opening up new possibilities for increasing the sustainable production of fuels and chemicals by using a less expensive catalyst compared to Pt, Pd, Rh and Ru. The transition metal carbides are obtained when carbon atoms are incorporated into the metal interstitial sites. The carbides phase formation can be affected by several experimental parameters such as C and H ratio, heating rates and addition of promoters, but generally the W_2C phase is formed around 650^0C and the WC above 800^0C. In this work in situ X-ray diffraction measurement was applied to study the phase transition during the carburization process of tungsten carbides under flow of the 1%H_2, 5%CH_4 and 96%He gas mixture. In addition, the promoting effect of the Ni in the structural changes of the samples was evaluated as a function of the Ni loading. The in situ XRD studies were performed at XRD1 and XRD2 beamlines at LNLS and using one-dimensional Mythen detector. The results showed that it was possible to promote the carburization to form W_2C and WC phases using low concentration of H_2 and CH_4. The phase transition sequence in the non-promoted sample is WO_3,W_xO_y,WO_2,W, but the formation of the W_2C, WC_{1-x} and WC phase occurs at the same temperature (860^0C). On the other hand, in the Ni-promoted samples the carbides phase is formed at lower temperatures and the carburization mechanism sample seems to be different from the non-promoted ones. In the Ni-promoted samples the tungsten oxide reduction happens at the same time of the carbide formation. The W_2C is predominant and a small amount of WC_{1-x} and WC phases is formed. The milder carburization conditions applied to in situ XRD analysis were successfully transferred to the carburization reactor and the catalysts performed will be tested in cellulose conversion reaction.

Acknowledgements: LNLS, XRD group and CTBE

Effects of Temperature and Chemical Environment in the Electronic Properties of Pt/C and PtRu/C Electrocatalysts

Ticianelli, E. A.[1], Lopes, P.P.[1], Paganin, V. A.[1], and Flávio, R. N.[2]

[1] Universidade de São Paulo - São Carlos - São Carlos SP Brazil
[2] Instituto de Quimica de Sao Carlos - São Carlos SP Brazil

Bi-metallic Pt alloys have been the subject of intensive investigations as electrocatalysts for low temperature fuel cell reactions, such as the hydrogen oxidation reaction (HOR) in the presence of CO. Besides changes in the reaction mechanism, modifications induced by a second metallic element (typically Ru and Mo) include changes in the Pt electronic structure, which may affect the adsorption characteristics of the Pt atoms. In situ X-ray absorption spectroscopy (XAS) measurements have been used to probe these catalyst electronic changes, but the correlations of this phenomenon with the alloy composition and the understanding of the role of temperature and of the external chemical environment have been not so often discussed. This work presents results of in situ XAS investigations of Pt/C and PtRu/C electrocatalysts, working under the polymer electrolyte fuel cell experimental conditions. The XAS spectra were collected at three distinct temperatures (313, 328 and 353 K), with the catalysts exposed to different gases and fluxes (Argon, Nitrogen, Hydrogen, and CO) at a constant applied potential (100 mV vs. RHE). Together with the XAS experiments, CO stripping voltammetry and HOR polarization measurements were conducted at the same experimental conditions, as described above. The results evidence a decrease of the vacancy of the Pt 5d electronic states with the increase of temperature, in accordance with the Fermi-Dirac distribution theory. This phenomenon explains the small contribution of the electronic effect in the CO tolerance properties of PtRu/C electrocatalysts at high temperatures, as indicated by the polarization measurements. There is an increase of the Pt 5d band occupancy when the catalysts are exposed to hydrogen in comparison to argon, and this is more pronounced for Pt/C than for PtRu/C, probably because the PtRu atoms are reduced during the exposition to H_2. In contrast, the presence of CO leads to an emptying of the Pt 5d band, probably due to the Pt-CO back-bonding, which involves electron donation from Pt to CO. There is no significant temperature effect on the Pt 5d band occupancy for both Pt/C and PtRu/C when exposed to CO. This result corroborates the lower CO coverage observed at higher temperatures, as evidenced by the CO stripping voltammetry and single cell polarization data.

Acknowledgements: The authors thank FAPESP, CNPq, CAPES for financial supports, and Brazilian Synchrotron Light Laboratory (LNLS) for the XAS measurements.

Structural study of 1D metal oxide nanostructure by synchrotron X-ray powder diffraction

Xavier, A. M.[1], Carvalho, V. A. N.[2], Ferreira, F. F.[1], and Souza, F. L.[2]

[1] Universidade Federal do ABC - Santo André SP Brazil
[2] Fundação Universidade Federal do ABC - Santo André SP Brazil

In the previous work we have discussed the successful methodology to fabricate 1D thin films, to be applied in photoelectrochemical cells (PEC), of different metal oxides at low temperature (range of 90-95 C) and short time [1, 2]. Here we reported the effect of different temperatures on structural and morphological properties of 1D ZnO, SnO2 and Fe2O3 powders. The formation of 1D nanostructured powder materials was observed by HRTEM. For all temperatures studied we clearly observed the changes on the distance between atomic planes of the 1D nanostructure, however, no significant changes happened on the nanostructure formation when high temperatures of heat treatment were used. The structural properties, studied by means of synchrotron X-ray powder diffraction data collected at the X-ray Powder Diffraction (D10B-XPD) beamline [3] of the Brazilian Synchrotron Light Laboratory (LNLS, Campinas, SP), revealed that the iron oxide samples at room temperature are mainly composed by β-FeOOH. As the temperature increases a gradual phase transition from β-FeOOH to α-Fe2O3 takes place. The thermodynamically stable crystal structure of tin oxide, usually, named as cassiterite was identified, and for zinc oxide the wurtzite phase was indexed using the JCPDS data base. Finally, a complete discussion about structural and morphological parameters was done including the impact of these results on the final application.

[1] L. Vayssieres, N. Beerman, S. Lindquist e A. Hagfeldt, Chem. Mat. 13, 233-235 (2001). [2] V. A. N. Carvalho, R. A. S. Luz, B. H. Lima, E. R. Leite, F. N. Crespilho, F. L. Souza, Energy, submitted (2011). [3] F. F. Ferreira, E. Granado, W. Carvalho Jr., S. W. Kycia, D. Bruno, R. Droppa Jr., J. Synchrotron Radiat., 13, 43 (2006).

Acknowledgements: Work supported by FAPESP (2010/02464-6), CAPES, CNPq, Instituto Nacional em Eletrônica Orgânica (INEO), and NanoBioMed-Brasil Network (CAPES). Thanks are due to LNLS for beamtime.

Investigation of phase evolution of vertically oriented iron oxide film by synchrotron X-ray absorption near edge structure (XANES)

Carvalho, V. A. N.[1], Xavier, A. M.[2], Criado, D.[2], and Souza, F. L.[1]

[1] Fundação Universidade Federal do ABC - Santo André SP Brazil
[2] Universidade Federal do ABC - Santo André SP Brazil

Hydrothermal synthesis of iron oxide 1D nanorods arrays has been scope of study and great results have been reported in literature [1, 2], even though its mechanism of formation and growth of nanostrucutres is not yet fully understood. Here we showed an evidence of the formation of iron oxide nanorod governed by oriented attachment mechanism, synthesized via hydrothermal method using fluorine tin oxide glass substrate as template of undimensional nanostructure growth. In addition, the phase evolution from β-FeOOH to α-Fe2O3 phases reached by heat treament was accompanied by means of synchrotron X-ray absorption near edge strutucture (XANES) data collected at XAFS2 beamline of Brazilian Synchrotron Light Laboratory (LNLS, Campinas, SP). The spectra were collected in the 7100 7160 eV range with 0.2 eV steps at the Fe-K edge using fluorescence mode for film sample. All the spectra were normalized, and the Fe and α-Fe2O3 (hematite) spectra were included for better comparison. All the samples present a small pre-edge at about 7115 eV, except for metallic Fe, which presents a much higher pre-edge. We can conclude that the as-prepared sample does not correspond to pure α-Fe2O3, and it has the contribution of another material, in this case probably α-FeOOH, which has an absorption edge and pre-edge similar to α-Fe2O3, but presents a maximum at a lower energy. Finally, we found that the samples need to be heat treated in temperature higher than 500o C, in order to obtain iron oxide in pure hematite phase. It is generally know that the hematite phase present a good potential to be applied as photoanode material for light-induced water splitting.

[1] L. Vayssieres, N. Beerman, S. Lindquist e A. Hagfeldt, Chem. Mat. 13, 233-235 (2001). [2] V. A. N. Carvalho, R. A. S. Luz, B. H. Lima, E. R. Leite, F. N. Crespilho, F. L. Souza, Energy, submitted (2011).

Acknowledgements: Work supported by FAPESP (2010/02464-6), CAPES, CNPq, Instituto Nacional em Eletrônica Orgânica (INEO), and NanoBioMed-Brasil Network (CAPES). Thanks are due to LNLS for beamtime.

Avaliação das transformações térmicas na estrutura porosa de espumas de alumina a partir do monitoramento *in situ* por SAXS

Passos, A. R.[1], Martins, L.[1], Pulcinelli, S.H.[1], and Santilli, C.V.[1]

Universidade Estadual Paulista - Araraquara - Araraquara SP Brazil

Espumas de alumina com estrutura hierárquica de poros foram obtidas por um procedimento de síntese de etapa única, baseado no uso de micelas de tensoativos e de emulsões como direcionadores da estrutura de poros. Os materiais obtidos apresentam estrutura bem definida de meso e macroporos. As aluminas apresentam elevada estabilidade térmica em relação a estrutura porosa. A distribuição de tamanho de poros foi mantida após calcinação até 1000 C. Informações sobre a evolução da nanoestrutura durante o processo de calcinação foram obtidas por SAXS. Um forno foi acoplado a linha de SAXS e foram realizadas medidas in situ durante o aquecimento até 800 C. Foi observado um aumento acentuado na intensidade espalhada com o aumento da temperatura em torno de 300 C, ou seja, na região de eliminação do tensoativo. Abaixo e acima desta região de temperatura as curvas são praticamente invariantes, evidenciando que os eventos observados por SAXS são associados, principalmente, ao contraste de densidade de elétrons entre a parede de alumina e os poros moldados pelo tensoativo. Para encontrar um modelo geométrico de partícula que seja consistente com o espalhamento das amostras foram aplicadas as aproximações de Guinier para esferas, cilindros e plaquetas. Os dados se ajustaram melhor ao modelo da aproximação de Guinier para plaquetas. Com o aumento da temperatura esse arranjo não é mantido e a inclinação da reta se torna praticamente infinita. Isso indica que a espessura ficou muito maior que o raio, e provavelmente ocorreu a sinterização dessa estrutura. O empilhamento dessas plaquetas forma mesoporos de formatos cilíndricos e piramidais. Quando as amostras são tratadas a 300 C apresentam maior quantidade de mesoporos piramidais, formados pelo empilhamento de plaquetas de faces não paralelas. Com o aumento da temperatura de calcinação as plaquetas se tornam paralelas favorecendo a coalescência e a quantidade desses poros diminui; porém os poros com formatos cilíndricos permanecem e se tornam predominantes. Esses mesoporos cilíndricos e piramidais formam as paredes dos macroporos de seção circular. O estudo das mudanças ocorridas *in situ* durante a calcinação e os resultados decorrentes do conjunto de outras técnicas de caracterização, permitiram desvendar em detalhes a estrutura hierárquica de poros das espumas de alumina.

Acknowledgements: Ao suporte técnico do LNLS e financeiro da FAPESP, CAPES e CNPq.

Fast piezoelectric response observed by pump and probe X ray diffraction measurements.

C.S.B. Dias[1], Faria, G. A.[1], Tasca, K. R.[1], Vescovi, R. F.[1], and Giles, C.[1]

Universidade Estadual de Campinas - Campinas SP Brazil

Aiming to introduce pump and probe X ray diffraction measurements at LNLS we have performed a feasibility study of implementing this type of experiment during the single bunch period of 2011. We have used a gating method using the fast response of a pixel detector Pilatus (pixel apparatus for the SLS) 100K and Mythen (microstrip system for time resolved experiments) detector. In this way we were able to isolate a single pulse of X-rays from the LNLS ring operated in single bunch mode with the same frequency of our pump pulse that consisted of a 300V electric pulse with 1ns length delivered by a pulse generator from Kentech Instruments.

With this instrumentation we had an unique setup proper for the study of a ferroelectric systems allowing the investigation of the ferroelectric response of a lithium niobate (LiNbO3) single crystal under the effect of a pulsed electric field of the order of $3\frac{kV}{cm}$ by means of a capacitor composed of two layers of aluminium deposited on each side of the single crystal slab.

The crystal was oriented in the c-axis direction and set to diffract close to 90 degrees Bragg angle in order to achieve the high resolution regime. By measuring the two theta angle and the rocking curve width of the Bragg peak with and without an electric pulse synchronized to the x-ray pulse we could follow the deformation on the c-axis of the crystal.

This measurement was repeated at different time delays between the electric pulse and the x-ray pulse at the sample position. The gating signal sent to the pixel detector and the gating signal sent to the pulse generator were synchronized and their time delay was controlled by a digital delay generator (DG535 - Stanford Research Systems) set to achieve a delay resolution of $1ns$.

The repetition rate was $\sim 1kHz$, which means that only one X ray pulse over $\sim$ 3200 from the single bunch mode passing through the bending magnet was detected and ensuring the total relaxation of the sample ($\sim 1ms$). The exposure time was of the order of $50s$, resulting in integration of over a fifty thousand X ray pulses to create single measurements. Preliminary analysis of the data shows that the crystal responded to the electric pulse losing its crystal quality and recovering to their initial state after $10ns$. This methodology opens the way for pump and probe experiments for the study of rapid electric response of ferroelectric single crystals using X-rays at the LNLS.

Acknowledgements:

Characterization of pharmaceutical polymorphs by means of X-ray powder diffraction

Ferreira, F. F.[1], Paiva-Santos,C.O.[2], and Antonio, S.G.[2]

[1] Universidade Federal do ABC - Santo André SP Brazil
[2] Universidade Estadual Paulista - Araraquara - Araraquara SP Brazil

X-ray powder diffraction (XRPD) is one of the most employed techniques used in the characterization of materials and it is routinely utilized in the identification of crystalline phases. A large variety of polycrystalline pharmaceuticals can be simultaneously identified and their quantification can be obtained by the Rietveld method [1]. Polymorphs may be defined as different crystalline forms of a compound with the same primary chemical structure. The use of synchrotron sources to perform XRPD experiments increases significantly the amount of structural information obtained when compared to conventional sources due to its high intensity and high collimation of the X-ray beam, as well as its improved instrumental angular resolution. In this work, several results obtained with the use of high-resolution X-ray powder diffraction data, collected at the X-ray Powder Diffraction (D10B-XPD) [2] beamline of the Brazilian Synchrotron Light Laboratory (LNLS, Campinas, SP) will be discussed making a correlation between results obtained in a conventional source, showing that the high instrumental resolution is of great concern to the correct characterization/quantification of pharmaceutical polycrystalline phases. In particular, the crystal structure of isotibolone, an impurity found in tibolone, a drug used for hormone reposition of post-menopause women, due to some inadequate tibolone synthesis or as a result of degradation during drug storage, which was recently determined by our group, will be discussed. The X-ray powder diffraction technique has been confirmed as an excellent alternative to the single crystal method for the structure determination of organic compounds.

[1] Rietveld, H. M. J. Appl. Cryst., 2(2), 65-71 (1969). [2] Ferreira, F. F., Granado, E., Carvalho Jr., W., Kycia, S. W., Bruno, D., Droppa Jr., R, J. Synchrotron Radiat., 13(1), 46-53 (2006).

Acknowledgements: The author thanks the financial support provided by FAPESP (2008/10537-3), CNPq (309811/2009) and LNLS by beam time.

Correlating structural parameters with phase separation behavior in mixed valence Manganites

G. G. Eslava[1], Bernardo, P. L.[1], Ghivelder, L.[1], A.G.Leyva[2], M. Quintero[3], and F. Parisi[3]

[1] Universidade Federal do Rio de Janeiro - Rio de Janeiro RJ Brazil
[2] Comisión Nacional de Energia Atómica - Buenos Aires B.A. Argentina
[3] Centro Atómico Constituyentes, Comisión Nacional de - San Martín Provi Argentina

Previous studies of the prototype manganite compound $La_{0.225}Pr_{0.4}Ca_{0.375}MnO_3$ shows a phase separation state at low temperatures, where an antiferromagnetic charge-ordered insulating phase (AFM/CO) coexists with a ferromagnetic metallic state (FMM). The mixture of 3+ rare earth cations and 2+ alkaline earth metals in the A site leads to the so called mixed valence manganites of the form $AA'MnO_3$, where the Mn cation appears in a mixture of Mn^{3+} and Mn^{4+}, depending on the stiochiometry. This mixture gives rise to a double exchange (DE) interaction responsible for a ferromagnetic behavior. Theoretical works showed that the hopping amplitude in the DE mechanism has a dependence with the Mn–O–Mn bond angle, a crucial parameter in determining the electron mobility and the magnetic transition temperature. A way to systematically vary that angle is by doping the system with a large A cation, like Sr^{2+}, increasing the A-site mean radius, while the Mn3+/Mn4+ ratio remains constant. To carry out this study samples with the general formula $La_{0.225}Pr_{0.4}(Ca_{1-x}Sr_x)_{0.375}MnO_3$, with $0.0 \leq x \leq 1.0$, were synthesized using the liquid mix technique. Magnetization measurements showed that for low concentration samples ($x \leq 0.10$) the system exhibits coexistence of FMM and AFM/CO phases. The inverse magnetic susceptibility as function of temperature shows a linear behavior into the paramagnetic phase, from which a Curie-Weiss analysis was made. The effective magnetic moment was calculated and all the Curie-Weiss temperatures were found positive, in agreement with ferromagnetic interactions. High resolution X-ray diffraction was measured at the LNLS laboratory. The measurements were made in the low concentration samples varying the 2θ angle in steps of 0.005 degrees, in the range of 10 to 100 degrees and with x-ray energy of 9.00 keV at room temperature. The data was analyzed by the Rietvled refinement technique (Fullprof program), allowing to accurately find the atomic positions and thus determining the $Mn - O - Mn$ bond angle. All samples have single structural phase, with an orthorhombic symmetry belonging to Pnma space group. It was confirmed the existence of a correlation between the Curie Weiss temperature and the bond angle mentioned above, as functions of the concentration of the Sr^{2+} cation. In summary, high resolution x-ray powder diffraction proved to be an important tool to provide additional insights in to the nature of the phase separated state in manganites.

Acknowledgements:

A influência do solvente na síntese hidrotérmica de nanopartículas magnéticas

Andrade, F. C.[1], Carneiro, N. M.[1], Sigoli, F.A.[1], and MAZALI, I. O.[1]

Universidade Estadual de Campinas - Campinas SP Brazil

Nanopartículas magnéticas de óxidos de ferro têm sido extensivamente estudadas por apresentarem aplicações em diferentes áreas tais como catálise, armazenamento de informações, ferrofluidos além de importantes aplicações na área médica, como carregadores de fármacos e agentes de contraste em diagnósticos por ressonância magnética[1]. Neste trabalho foram sintetizadas nanopartículas magnéticas esféricas de óxido de ferro por reação hidrotérmica a partir do cloreto de ferro(III) como precursor, acetato de sódio, que age na estabilização eletrostática das nanopartículas, polietilenoglicol (PEG), atuando na estabilização por efeito estérico[2] e água ou etilenoglicol (EG) como solvente. O sistema foi mantido em autoclave a 200 ^{0}C por 6 horas. Para a amostra obtida tendo a água como solvente, os resultados de difratometria de raios X (XRD) indicam a obtenção da fase hematita (α-Fe_2O_3). No espectro vibracional de absorção no infravermelho observa-se o desdobramento da banda entre 400-500 cm^{-1} atribuída ao estiramento Fe-O característico da hematita. As imagens de microscopia eletrônica de varredura (SEM) revelam que foram obtidas nanopartículas com morfologia esférica de 60 nm, em média, e com distribuição estreita de tamanho. Medidas de magnetização realizadas à temperatura ambiente mostram o comportamento ferromagnético do material. Nanopartículas de magnetita (Fe_3O_4) foram obtidas substituindo-se a água por EG no procedimento experimental. Por SEM observa-se que as partículas apresentam morfologia esférica com diâmetro médio da ordem de 800 nm. As partículas apresentam comportamento superparamagnético à temperatura ambiente, característico de nanopartículas de magnetita de até 100 nm, corroborando com as imagens de SEM que mostram uma superfície rugosa sugerindo que o sistema é constituído por aglomerados de partículas menores. Tal comportamento pode ser explicado se considerarmos que o sistema é constituído de monodomínios de nanopartículas de magnetita como demonstram os dados de tamanho de cristalito, igual a 20 nm, determinados por XRD. Os resultados obtidos sugerem que o EG atua como agente redutor na síntese de nanopartículas de magnetita, uma vez que, na síntese em solução aquosa, não ocorre a redução dos íons ferro(III) resultando na fase hematita. Referências [1]J. H.Li et al, Materials Chemistry and Physics, v. 113, p. 140-144, 2009. [2]Hong Deng et al, Angew. Chem. Int., v. 44, p. 2782-2785, 2005.

Acknowledgements: Ao CNPq, CAPES e FAPES pelo apoio financeiro e ao LNLS-LME pela utilização do SEM-FEG (Proposta 11276).

Estudos por NEXAFS, nos modos fluorescência de raios-X (FlRX) e rendimento eletrônico (TEY), de biomoléculas contendo enxofre: Cisteina, Cistina e Insulina.

Simões, G.[1], Rodrigues, F. N.[2], Cardoso, S.C.[1], Silva, T.M.[2], Vicentin, F.C.[3], and de Souza, G.G.B.[1]

[1] Universidade Federal do Rio de Janeiro - Rio de Janeiro RJ Brazil
[2] Instituto Federal de Educação, Ciencia e Tecnologia do Rio d - Rio de Janeiro RJ Brazil
[3] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

Importantes compostos biológicos como aminoácidos e proteínas são muitas vezes submetidos a elevadas cargas de radiações ionizantes. Modificações estruturais causadas por estas radiações (radiation damage) são freqüentes na área biomédica (radiologia) e em trabalhos de difração de raios-X, por exemplo. O conhecimento dos processos básicos de absorção de radiações na região de raios-X por biocompostos é consequentemente relevante para a compreensão destes fenômenos e para a proteção radiológica de seres vivos. Espectros de fotoabsorção na região de Raios-X (NEXAFS) apresentam, além de um elevado caráter elemento-específico, forte dependência da ambientação química à qual estão sujeitos os átomos componentes da amostra em observação. Desta forma, podem fornecer informações relevantes sobre o estado de oxidação destes átomos e sobre a estrutura eletrônica da amostra. Neste trabalho foram obtidos espectros de alguns biocompostos contendo enxofre (cistina, cisteína e insulina), em fase sólida, através das técnicas de fluorescência de raios-X e NEXAFS, na borda S 1s. Compostos contendo átomos de enxofre são particularmente interessantes para a aplicação da técnica de NEXAFS pelo fato deste elemento possuir vasto leque de gráus de oxidação, estendendo-se de -2 a +6. As medidas de NEXAFS foram efetuadas nos modos rendimento eletrônico (TEY) e Fluorescência, na linha SXS. Buscou-se desta forma analisar o estado químico dos átomos de enxofre de compostos dispostos na superfície (modo TEY) ou no interior (modo fluorescência) das amostras. Parte dos estudos efetuados no LNLS, relacionados com danos causados por radiações em biomoléculas, foi apresentada em recente conferência internacional(1). (1). G Simões, FN Rodrigues, LB da Silva, GGB de Souza, Core-level photoabsorption, photoionization and gás emission in sulfur-containing biomolecules subjected to ionizing radiation. 37th Internaitonal Conference on Vacuum Ultraviolet and X-Ray Physics. Vancouver, Canadá, July 11-16. 2010;

Acknowledgements: LNLS, CNPq, FAPERJ

Magnetic structure of R_2CoGa_8 (with R=Gd, Tb and Dy) series investigated by X-Ray Resonant Magnetic Scattering

Mardegan, J. R. L.[1], C. Adriano[1], Faria, G. A.[1], C.S.B. Dias[1], Pagliuso, P.G.[1], and Giles, C.[1]

Universidade Estadual de Campinas - Campinas SP Brazil

In this work we have investigated at low temperatures the magnetic structure of R_2CoGa_8 (with R=Gd, Tb and Dy) intermetallic compounds using X-ray resonant magnetic scattering (XRMS) with linearly polarized X-ray at the L_2 and L_3 absorption edges of the rare earth elements.

These compounds showed a commensurate antiferromagnetic spin structure with a magnetic propagation vector type $\tau = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and its order antiferromagnetically (Néel temperature) around 21 K, 28 K and 15 K for R=Gd, Tb and Dy, respectively. Our measurements of magnetic susceptibility showed an anisotropy in the paramagnetic state and the magnetization easy axis along *c*-axis for Tb- and Dy-based compounds. However for the Gd_2CoGa_8 compound we did not observe anisotropy above the Néel temperature and the magnetization easy axis was found along *a*-axis.

To determine the magnetic structure of these compounds we have performed measurements of several magnetic Bragg peaks and compared with simulated intensities. The calculated intensities were obtained using a dipolar resonant scattering cross section. Five magnetic peaks with a magnetic propagation vector type $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ were analyzed and compared with intensities for different models and directions of the magnetic moments. The magnetic structure found showed the direction of magnetic moment in the *ab*-plane for the Gd-based compound and parallel to *c*-axis for the Tb- and Dy-based compounds. This difference between the directions of the moment follow the trend already studied for the R_nMIn_{3n+2} in which the non-S Tb and Dy compounds where the spins interacts more strongly with the crystal field is more susceptible to align in the *c*-direction. For the Gd compound where the weak crystalline electrical field effects are small the spins align in the *ab*-plane similarly to what is observed in the Gd_2IrIn_8.

Finally for the three compounds, the critical exponent β found to Gd_2CoGa_8 compound suggests a 3D Ising model and to R=Tb and Dy, the β value suggests a 3D Heisenberg model.

Acknowledgements: This work was supported by FAPESP (SP-Brazil), CNPq (Brazil) and CAPES (Brazil). The authors would like to thank the LNLS for the technical support and the beam time.

Síntese e caracterização de nanoanéis magnéticos para o tratamento do câncer por hipertermia

Wender, H.[1], Garcia, F.[1], and Cardoso, M.B.[1]

Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

Nos últimos anos, nanoestruturas de óxido de ferro têm sido propostas para o tratamento do câncer por hipertermia magnética [1-3]. Estudos recentes mostram que estes nanomateriais podem, sob ação de um campo magnético alternado, liberar calor diretamente na célula tumoral, resultando na apoptose celular e diminuindo assim, os efeitos colaterais devido ao superaquecimento das células e tecidos normais geralmente encontrados na hipertermia convencional [1]. Para este objetivo, nanoanéis (NAs) compostos de diferentes óxidos de ferro, mais especificamente, Fe_3O_4 (magnetita), α-Fe_2O_3 (hematita) e FeO (goetita), foram sintetizados quimicamente e caracterizados mediante o uso de técnicas como espalhamento de raios-X a baixos ângulos (SAXS), difração de raios-X (XRD), espectroscopia por absorção de raios-X próximo da borda (XANES), microscopia eletrônica de transmissão (TEM) e microscopia eletrônica de varredura (SEM). Conforme verificado por SEM e TEM, os NAs apresentaram aproximadamente 100 nm de altura e 100 e 50 nm de diâmetro externo e interno, respectivamente, formando uma estrutura similar a um cilindro de baixa razão de aspecto. Estes cristais de hematita inicialmente obtidos foram reduzidos em atmosfera de H_2 até total transformação em magnetita a 420^oC e em goetita a 600^oC, conforme verificado por medidas *in situ* de XANES na borda K do Fe, XRD e TEM. As propriedades magnéticas destas nanoestruturas estão atualmente em fase de investigação. Estudos preliminares mostram um comportamento ferromagnético, no entanto, com a presença de um estado de vórtice, dependendo da morfologia dos anéis. Assim, estes materiais mostram-se promissores para a hipertermia magnética por apresentarem altos valores de magnetização de saturação com coercividades quase nulas.

Referêcias

[1] A. K. Gupta, and M. Gupta, Biomaterials 26, 3995 (2005).
[2] W. C. Dewey et al., Radiology 123, 463 (1977).
[3] S. Mornet et al., J. Mater. Chem. 14, 2161 (2004).

Acknowledgements: Ao LNNano pelo uso dos microscópios eletrônicos TEM-HR e SEM-FEG e às linhas de luz DXAS e SAXS1.

A Study on the Correlation Between Structural and Magnetic Properties of TM-doped ZnO Nanoparticles

Silva, R. T.[1], Araújo, V.D.[2], Bernardi, M.I.B.[2], and de Carvalho H. B.[1]

[1] Universidade Federal de Alfenas - Alfenas MG Brazil
[2] Universidade de São Paulo - São Carlos - São Carlos SP Brazil

Nanostructured TM-doped ZnO systems were synthesized via microwave-assisted hydrothermal route with different Co molar concentrations of 1, 3 and 5%. The microwave-assisted hydrothermal method combines the advantages of both hydrothermal and microwave-irradiation techniques such as very short reaction time, production of small particles with a narrow size distribution and high purity which might be attributed to fast and homogeneous nucleation of the mixture. The crystal structures of the samples were characterized using x-ray diffraction (XRD). The microstructure and composition distributions were characterized by scanning electron microscopy (SEM) and energy dispersive x-ray (EDS) measurements. RAMAN scattering was used to study of the incorporation of dopants and the resulting lattice disorder of the host lattice. Co K-edge x-ray absorption near-edge structure (XANES) and extended x-ray absorption fine structure (EXAFS) was used to determine the valence state and to evaluate the environment of Co in the ZnO lattice. Changes in the density of defects were estimated by RAMAN and Photoluminescence (PL) measurements. Magnetic characterizations were performed using a superconducting quantum interference device (SQUID) magnetometer.

Acknowledgements: The authors are grateful to FAPEMIG, FAPESP and CNPq for financial support.

Parte IX

Superfícies, Interfaces e Nanossistemas

Synthesis and self-assembly of carbohydrate-clicked rod-coil amphiphiles

DAL-BÓ, A. G.[1], Giacomelli, F. C.[2], and Soldi, V.[3]

[1] Universidade Federal do Rio Grande do Sul - Porto Alegre RS Brazil
[2] Universidade Federal do ABC - Santo André SP Brazil
[3] Universidade Federal de Santa Catarina - Florianópolis SC Brazil

This work describes the synthesis and self-assembly of carbohydrate-clicked rod-coil amphiphilic systems. Copper-catalyzed Huisgen cycloaddition was efficiently employed to functionalize the hydrophilic extremity of PEG-b-tetra(p-phenylene) conjugates by lactose and N-acetyl-glucosamine ligands. The resulting amphiphilic systems spontaneously self-assembled into nanoparticles when dissolved in aqueous media as evidenced by Dynamic Light Scattering (DLS), Transmission Electron Microscopy (TEM) and Small-Angle X-ray scattering (SAXS). Formation of highly regular micelles having a mean diameter of 10 nm was observed for systems containing a PEG 900 core while a decrease of the hydrophilic moiety of the amphiphile (resulting from the use of PEG 600 instead of PEG 900) led to the formation of vesicles with broader size distribution. The presence of the carbohydrate residues on the surface of the micelles and their ability to establish specific interactions with Wheat Germ Agglutinin (WGA) and Peanut Agglutinin (PNA) was further attested by light scattering measurements, thus confirming attractive applications of such sugar micelles in biosensor devices.

Acknowledgements: We acknowledge the financial support from CNRS and CAPES-COFECUB (project 620/08). The ESRF and LNLS are acknowledged for supply the beam time (Proposals 02 01 784 and 9967 respectively). The technical assistance of Cyrille Rochas during the experiments at ESRF is greatly acknowledged. F.C.G. acknowledges FAPESP (Grant 2010/06348-0). Stéphanie Boullanger is acknowledged for the mass spectrometry analyses.

Synthesis and Self-assembled carbohydrate-based micelles for lectin targeting

DAL-BÓ, A. G.[1], Giacomelli, F. C.[2], Soldi, V.[3], Fort S.[4], and Borsali R[5]

[1] Universidade Federal do Rio Grande do Sul - Porto Alegre RS Brazil
[2] Universidade Federal do ABC - Santo André SP Brazil
[3] Universidade Federal de Santa Catarina - Florianópolis SC Brazil
[4] Université Jouseph Fourier - Saint Martin d'Hères FR France
[5] Centre National de la Recherche Scientifique - Paris cedex 16 France

Biocompatible low-polydispersity micelles designed for lectin targeting have been prepared by spontaneous self-assembly in water of macromolecular glycosylated amphiphiles. Propargyl-b-lactoside and N-acetyl-b-D-glucosaminide were conjugated by copper-catalyzed Huisgen cycloaddition to azide-terminated PEG 900 stearate. Upon dissolution in water, the resulting amphiphiles immediately self-assemble into highly regular micelles having a mean diameter of 10 nm. Dynamic Light Scattering (DLS), Transmission Electron Microscopy (TEM) and Small-Angle X-ray Scattering (SAXS) were used to investigate the structure of the self-assembled saccharidic amphiphiles micelles. The presence of the carbohydrate epitopes on the surface of the micelles and their bioavailability for lectin targeting were also demonstrated by light scattering measurements. Specific interaction of the GlcNac and Lac residues with Wheat Germ Agglutinin (WGA) and Peanut Agglutinin (PNA) respectively, unveils potential applications of such carbohydrate-derived surfactants as simple and site-specific vectorization systems for drug delivery.

Acknowledgements: We acknowledge the financial support from the CNRS and CAPES-COFECUB (project 620/08). The ESRF is acknowledged for supply of beam time (Proposal 02 01 784). The technical assistance of C. Rochas during the experiments at ESRF is greatly acknowledged. F.C.G. acknowledges FAPESP (grant 2010/06348-0). Stephanie Boullanger is acknowledged for the mass spectrometry analyses.

Commissioning an in situ x-ray characterization system for ultra-thin films grown by atomic layer deposition

Ferreira, S. O.[1] and Malachias, A.[2]

[1] Universidade Federal de Viçosa - Viçosa MG Brazil
[2] Universidade Federal de Minas Gerais - Belo Horizonte MG Brazil

Atomic layer deposition (ALD) has been established as one of the most important techniques for fabrication of ultra-thin films. The main advantages of the technique are a very accurate thickness control, the use of low deposition temperatures, excellent film conformability and easy scale-up. Besides such characteristics, ALD can be applied to the synthesis of a great variety of materials such as oxides, nitrides, metals and also organic and hybrid organic-inorganic composites. Although this technique is already being broadly used in the micro-electronic semiconductor industry, there are many open questions about the growth dynamics during the ALD process, which can only be accessed by in-situ characterization techniques. In this work we will describe an atomic layer deposition setup to be installed at the XRD-2 beam line at the Brazilian National Synchrotron Facility which will allow for in-situ growth monitoring using x-ray techniques such as grazing incidence x-ray small angle scattering, x-ray reflectivity and x-ray diffraction. The experimental set-up is based on a commercial thermal ALD system and the construction a new growth chamber using a graphite dome to be adapted in the beamline goniometer. The in-situ built chamber will allow for growth at temperatures up to 400^oC. Results of the ex-situ growth of Al_2O_3 and TiO_2 layers on Si using the modified growth chamber will be presented together with the first tests of in-situ characterization of Al2O3 on Safire substrates by grazing incidence x-ray diffraction.

Acknowledgements: This work has been supported by FAPESP and LNLS.

Photoresist analysis with synchrotron radiation and electron impact using time-of-flight mass spectrometry

Borges, B.G.A.L.[1], Rocco, M.L.M.[1], and Carlos R. A. Lima[2]

[1] Universidade Federal do Rio de Janeiro - Rio de Janeiro RJ Brazil
[2] Universidade Federal de Juiz de Fora - Juiz de Fora MG Brazil

Positive photoresists are widely used in lithographic process in microelectronics and in optics for the fabrication of relief components. The positive photoresists react in such a way that regions exposed to ultraviolet light dissolve more rapidly during the development process. The most popular positive photoresist is composed of the photoactive compound (PAC) denominated diazonaphthoquinone (DNQ) and the matrix material that is a thick resin called novolak. With the aim of identifying molecular modifications in positive photoresists unexposed and previously exposed to ultraviolet light the electron (ESID) and photon (PSID) stimulated ion desorption techniques coupled to time-of-flight mass spectrometry were employed in the study of the AZ-1518 positive photoresist. Mass spectra were obtained for different energies of the electron beam and at the S 1s edge showing specific changes related to the photochemical decomposition of the photoresist, which reinforces the applicability of these techniques to investigate and characterize structural changes in photosensitive materials.

Acknowledgements: Research partially supported by LNLS National Synchrotron Light Laboratory, Brazil. The authors would like to acknowledge CNPq, CAPES, and FAPERJ for financial support.

X rays absorption fine structure in nominally undoped and Li doped ZnO nanowires

Zapata, C.[1], C.E. Rodríguez Torres[2], Simonelli, G.[1], Villafuerte M.[3], and S. P. Heluani[3]

[1] Universidad Nacional de Tucuman -Facultad de Ciencias Exact - San Miguel de Tucumán Tucum Argentina
[2] Universidad Nacional de La Plata - La Plata Bs.As Argentina
[3] Universidad Nacional de tucuman - facultad de ciencias exact - Tucuman Argentina

Between the wide band gap semiconductors ZnO display a lot of potential technological applications in various fields such as spintronics, light-emitting diode, UV detector, laser diode and biomaterials. However, for practical spintronic and optoelectronic application reproducible doping p-type ZnO is required. Although there are a few reports of Li-doped p-type ZnO in films [1, 2], explanation of the p-character still unclear and, in addition, the stability of p materials is doubtful. Here we report X rays absorption fine structure measurements in nominally undoped and Li doped ZnO nanowires (ZOLNw). The nanowires have been grown on sapphire and Si/SiO2 substrates by the simple carbothermal reaction-assisted thermal evaporation of ZnO. The structures were studied by scanning electron microscopy and energy dispersive X-ray analysis. XANES spectra of ZOLNw do not show changes of the edge energy or their shape, meaning that Zn oxidation does not depend on Li doping. On the other side, XAFS results in undoped materials support the hypothesis that the origin of green luminescence in ZnO naowires is the oxygen vacancies.

[1]S.H. Jeong, B.N. Park, S.-B. Lee, J.-H. Boo, Thin Solid Films 516 (2008) 5586 5589.

[2] X H Wang et al 2006 Semicond. Sci. Technol. 21 494

Acknowledgements: This work was partially supported by Laboratorio Nacional de Luz Sincrotron, Campinas-Brasil; by CIUNT under Grants 26/E439 and 26/E478 and by ANPCyT-FSTics02

Chemical and Morphological Characterization of Zr/Ti/Nb Tri-layered Films Deposited on Si(111) and Stainless Steel Substrates

Tallarico, D.A.[1], Gobbi, A. L.[2], Paulin Filho, P.I.[1], A. Galtayries[3], and Nascente, P. A. P.[1]

[1] Universidade Federal de São Carlos - São Carlos SP Brazil
[2] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[3] Ecole Nationale Supérieure de Chimie de Paris - Paris France

Titanium is a metal commonly used in medical implants, due to its interesting properties, such as high mechanical strength, good corrosion resistance in extreme conditions, and excellent thermal stability. Ti-6Al-4V is one of the main biomaterial alloys employed as implants, but the release of Al and V ions is associated to health problems and adverse tissue reactions. A new class of Ti alloys employs Zr for solid-solution hardening and Nb as β phase stabilizer. The Ti-Nb-Zr alloys have mechanical and corrosion resistance characteristics which make them suitable for use as implants. Tri-layered films of Ti-Nb-Zr were deposited on both Si(111) and stainless steel substrates using a DC magnetron sputtering equipment, under an argon atmosphere. The films were deposited in the following manner: a 100 nm thick layer of Nb was deposited on a Si(111) substrate, then a 200 nm layer of Ti was deposited on top of Nb/Si, and lastly a 50 nm layer of Zr was deposited on top of Ti/Nb/Si. A similar Zr/Ti/Nb film was also grown on stainless steel substrate. The chemical composition and morphology of the films were analyzed by means of X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (ToF-SIMS), and atomic force microscopy (AFM). The XPS results for the Zr/Ti/Nb layers deposited on Si(111) presented a predominance of ZrO_2 on the surface, and Nb_2O_5 and a small quantity of TiO_2. For the layers deposited on stainless steel, only ZrO_2 and a small amount of niobium oxide were detected. The ToF-SIMS results indicated the formation a three-layered film on Si(111), with each metal in a distinct layer and a well-defined interface between the layers, while the deposition on the stainless steel substrate caused slight intermixing at the Nb/Ti and Ti/Zr interfaces. AFM images showed that the Zr/Ti/Nb tri-layer films presented nanostructured grains and low roughness, with the film deposited on stainless steel having the roughest surface.

Acknowledgements: This work received financial support from FAPESP (proposal 2009/17055-7), CAPES, CNPq, and LNLS (proposals LMF-8912 and LMF-10475).

Evolução estrutural de nanopartículas $Pt_{0.3}Pd_{0.7}$ sob condições reacionais

BOITA, Jocenir.[1], Bernardi, F[1], Alves, M.C.M.[1], and Morais, J.[1]

Universidade Federal do Rio Grande do Sul - Porto Alegre RS Brazil

Nanopartículas (NPs) bimetálicas de Pt-Pd tem sido amplamente investigadas devido a suas aplicações em catálise, em particular seu uso nas reações de hidrodesulfurização (HDS) e de hidrogenação de aromáticos (HYD). O sistema bimetálico apresenta propriedades eletrônicas e estruturais distintas se comparadas àquelas do sistema monometálico, as quais dependem da concentração relativa dos metais e da distribuição atômica. Tais parâmetros, se devidamente controlados, podem ser ajustados para se obter sistemas com melhor atividade e seletividade catalítica. Os catalisadores a base de ligas Pt-Pd empregados em reações de HDS e HYD geralmente são suportados, por SiO_2 ou Al_2O_3, existindo poucos estudos na literatura de NPs isoladas (não-suportadas). Neste trabalho utilizamos a espectroscopia de absorção de raios X (XAS) realizada *in situ*, para monitorarmos a evolução estrutural de NPs isoladas $Pt_{0.3}Pd_{0.7}$ enquanto as mesmas eram submetidas a diferentes condições reacionais. As medidas de XAS *in situ* foram realizadas na borda L_3 da Pt, nas linhas de luz XAFS-1 e DXAS do LNLS. Com os experimentos na linha DXAS, no modo dispersivo, medimos os espectros de XANES com resolução temporal. Inicialmente as NPs foram ativadas sob uma atmosfera de H_2 e He (300° C), e posteriormente sulfetadas com H_2S a 300° C. Em trabalhos recentes (Bernardi et al., 2011; Bernardi et al., 2010; Bernardi et al., 2009) mostramos que tais tratamentos térmicos induzem um rearranjo atômico nas NPs, resultando em uma estrutura caroço-casca (core-shell), que apresenta um caroço rico em Pt e uma casca rica em Pd. Tais trabalhos também mostraram que o grau de sulfetação (quantidade de ligações metal-S) aumenta diretamente com a concentração de Pd. No presente estudo, após as duas etapas descritas acima, as NPs foram novamente reduzidas sob uma atmosfera de H_2 e He a fim de estudarmos a estabilidade química das ligações metal-S. Mostraremos as mudanças ao redor dos átomos de Pt induzidas por todos os tratamentos, e em função do tempo de reação.

Acknowledgements: Agradecemos ao apoio dado pelo CNPq, CAPES, LNLS (propostas DXAS - 8150 e XAFS1 - 8766).

Growth and Characterization of Thin Films of Titanium, Zirconium, and Niobium Oxides Deposited on Si(111)

Tallarico, D.A.[1], Gobbi, A. L.[2], Paulin Filho, P.I.[1], maia da costa, M. E. H.[3], A. Galtayries[4], and Nascente, P. A. P.[1]

[1] Universidade Federal de São Carlos - São Carlos SP Brazil
[2] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[3] PUC - Rio de Janeiro - Rio de Janeiro RJ Brazil
[4] Ecole Nationale Supérieure de Chimie de Paris - Paris France

Commercially pure Ti and Ti-6Al-4V are the most commonly used biomaterials for implants; however, the toxicity of vanadium and the association of aluminum with neurological disorders have raised concerns for biological applications. Thus, a new class of Ti alloys has been developed, and Zr and Nb are among the most suitable alloying elements due to the fact that the Ti-Zr-Nb alloys present interesting properties, such as high mechanical strength, good corrosion resistance in extreme conditions, and excellent thermal stability. However, these Ti-based alloys do not simulate the chemical, surface, mechanical, or grain size distribution found in physiological bone; thus, nanostructured oxide biomaterials are a good alternative for the production of implant devices since the particles generated by these implants are less harmful to the human body than particles generated by metallic implants. In this study, thin films of Ti, Zr, and Nb oxides were deposited by magnetron sputtering on Si(111) substrates and their chemical composition, morphology, and structure were characterized by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), atomic force microscopy (AFM), and nanoindentation. The thin films of Ti, Nb, and Zr oxides were produced under partial O_2 atmosphere, and only $\mathrm{Ti}O_2$, Nb_2O_5 and $\mathrm{Zr}O_2$ were identified by XPS. The XRD analysis indicated the formation of small grains having the following structures: rutile (for the $\mathrm{Ti}O_2$ films), hexagonal (for the Nb_2O_5 films), and tetragonal and monoclinic (for the $\mathrm{Zr}O_2$ films). AFM images showed that the oxidized Ti, Nb, and Zr films had nanostructured grains and low roughness. The moduli of elasticity for the oxides were: 150 GPa ($\mathrm{Ti}O_2$), 90 GPa (Nb_2O_5), and 140 GPa ($\mathrm{Zr}O_2$). These results indicate that the films are suitable for biomedical applications.

Acknowledgements: This work received financial support from FAPESP (proposal 2009/17055-7), CAPES, CNPq, and LNLS (proposals LMF-8912 and LMF-10475).

Study of depth-dependent local structures in thin films by grazing-incidence X-ray absorption spectroscopy

Rodríguez Torres, C. E.[1], S. P. Heluani[2], and A.M. Mudarra Navarro[1]

[1] Universidad Nacional de La Plata - La Plata Bs.As Argentina
[2] Universidad Nacional de tucuman - facultad de ciencias exact - Tucuman Argentina

Nowadays many different industrial technologies require knowledge of surface, near surface and interface properties of bulk materials, thin films and multilayered structures on a nanometric scale. In this regard, a clear understanding of the macroscopic properties requires a substantial knowledge of their dependence on layer thickness and the complex microstructural effects frequently localized at the interface film/substrate or at the surface of the film. Such effects can be studied using experimental techniques able to peer selectively into the depth of the films.

The versatility of geometries and detection schemes enables the association of X-ray Absorption Spectroscopy (XAS) to advanced experimental setups, providing the material science with a renewed original insight. Grazing incidence (GI) XAS is already used worldwide and its sensitivity in probing in-depth properties by tuning the grazing incidence is becoming a reliable issue. As the sampling depth is strongly dependent on the incident angle, near the critical angle for total reflection, GIXAS is used under controlled incidence to get information about the local order depth profiles in samples with different thicknesses.

Here we present results combining XAS with resolved GI, using setups available at the XRF fluorescence beamline of the Brazilian Synchrotron Light National Laboratory (LNLS) located in Campinas, SP (Brazil), to clarify the thickness-dependent magnetic properties of nanometric oxide films such as Co doped SnO_2 and Zn ferrites $ZnFe_2O_4$. Partial results in Zn ferrites was recently published by our group in [1].

[1] Evidence of defect-induced ferromagnetism in $ZnFe_2O_4$ thin films. C. E. Rodríguez Torres, F. Golmar, M. Ziese, P. Esquinazi, S. P. Heluani. Phys. Rev. B 84, 064404 (2011).

Acknowledgements:

A Dispersive XANES and XRD Investigation of the Reducibility and Crystallization Processes of Iron Oxides Promoted by Gold

Jimenez-Lam, Sergio A.[1], Gomez S.A.[2], Fuentes, G. A.[2], Handy, B. E.[3], Cardenas-Galindo, M. G.[3], and Fierro-Gonzalez, J. C.[1]

[1] Instituto Tecnologico de Celaya - Celaya GTO Mexico
[2] Universidad Autonoma Metropolitana - Mexico City Mexico
[3] Universidad Autonoma de San Luis Potosi - San Luis Potosi SLP Mexico

Supported gold catalysts are typically more active for oxidation reactions when the supports are reducible metal oxides (e.g., Fe2O3, CeO2, etc.) than when they are non-reducible metal oxides (e.g., gamma-Al2O3, MgO, etc.). This observation has led some authors to conclude that redox processes taking place at the gold-support interface might play an important role in the catalysis. H2-temperature-programmed reduction (H2-TPR) has been used to investigate the influence of gold on the reducibility of transition metal oxide supports. However, for some iron oxide-supported gold samples it has been observed that H2-TPR peaks attributed to the reduction of Fe3+ and Au3+ overlap, complicating the interpretation of the data. In this work we used dispersive X-ray absorption near edge structure (XANES) at the Au-LIII and Fe-K edges as iron oxide-supported gold samples were treated in flowing H2 at increasing temperature. We combined the XANES data with X-ray diffraction (XRD) results and demonstrated that the onset of reduction of Fe3+ and the crystallization of the support occurred at lower temperature in samples containing gold than in samples of the bare iron oxide. We propose that the reduction process could be promoted by the activation of hydrogen on reduced gold sites.

Related work: Jimenez-Lam, S.A. et al. Influence of Supported Gold on the Dynamics of Reduction and Crystallization of Iron Oxides: A Dispersive XANES Spectroscopy and XRD Study. J. Phys. Chem. C 2011, submitted.

Acknowledgements: We thank the staff at beamline D06A-DXAS at the Brazilian Synchrotron Light Laboratory. This research was supported by Consejo Nacional de Ciencia y Tecnología (Ciencia Básica, Convenio: 61856) and Fondos Mixtos Guanajuato (2007).

Effect of functionalization of montmorillonite on epoxy/montmorillonite nanocomposite

Silva, A.A.[1], Soares, B.G.[1], and DAHMOUCHE, K[1]

Universidade Federal do Rio de Janeiro - Rio de Janeiro RJ Brazil

In this work sodium montmorillonite (Na-MMT) was functionalized with N-(2-aminoethyl)-3-aminopropyltrimethoxysilane and the corresponding silylated clay was used to modify epoxy matrix cured with triethylenetetramine. The grafting/intercalation of the aminosilane inside the clay galleries were followed by infrared spectroscopy, X-ray diffraction, thermogravimetric analysis and ^{29}Si cross-polarization magic-angle-spinning nuclear magnetic-resonance (CP/MAS NMR) spectroscopy. Epoxy-based nanocomposites were prepared with different amounts of silylated clay or commercial organoclay, Cloisite 30B, whose intercalating agent consists of a methyl, tallow, bis-2-hydroxyethyl quaternary ammonium salt. The degree of intercalation/ exfoliation was estimated by X-ray diffraction experiments and confirmed by small angle X-ray scattering. Nanocomposites prepared with silylated clay displayed no peak in both XRD and SAXS curves whereas those prepared with Cloisite 30B exhibited a clear interference peak corresponding to an interlayer spacing d001 of 4.1 nm. The former also presented a better dispersion, with a high proportion of tactoids smaller than 2 nm, as estimated by SAXS. From the results of dynamic mechanical analysis it was observed that most of the nanocomposites display higher storage modulus mainly at temperatures above the glass transition temperature. The glass transition temperature is similar or higher than the neat epoxy network for nanocomposites containing 1 wt% of silylated clay or higher.

Acknowledgements: CNPq, CAPES, FAPERJ and LNLS

Development of Silver Clusters in Hybrid Organic-Inorganic Sol-Gel Materials for Biocide Coatings

Procaccini, R.A.[1], Cere, S[1], and Pellice, S. A.[1]

Instituto de investigación en ciencia y tecnología de materi - Mar del Plata BA
Argentina

A silver doped hybrid organicinorganic solgel coating was developed through the hydrolytic condensation of tetraethoxysilane (TEOS) and glycidoxypropyltrimethoxysilane (GPTMS) or methyl-triethoxysilane (MTES). Silver nitrate was added as the supplier of Ag+ ions, which have a potential effect as a biocide component. Synthesis of precursor sol and the evolution of silver clusters in the whole process were analyzed through Attenuated Total Reflectance Fourier Transformed Infrared spectroscopy (ATR-FTIR) and UVvisible spectroscopy. A high thermal sensitivity of sub-nanometric silver particles was determined by Small Angle X-ray Scattering (SAXS) carrying to formation of higher agglomerates or silver nanoparticles. Lixiviation tests show long-term and gradual silver releasing without worsening of the structural integrity of coatings.

Complete results were recently published at: Surface and Coatings Technology 205, 5464-5469, 2011.

Acknowledgements: This work has been supported by the Brazilian Synchrotron Light Laboratory (LNLS) / Brazilian Biosciences National Laboratory (LNBio) under proposal D11A - SAXS1 10004. Also the Argentine National Agency for Scientific and Technological Promotion (ANPCyT) and the Argentine National Council of Scientific and Technical Researches (CONICET) are gratefully acknowledged.

Surface functionalisation of polypropylene by inner-shell monochromatic irradiation with mild oxygen flux

Rajajeyaganthan.R[1], Kessler, F.[1], and Weibel, D. E. or Weibel, D.[1]

Universidade Federal do Rio Grande do Sul - Porto Alegre RS Brazil

NEXAFS spectroscopy is an ideal technique for probing the molecular orientation of organic polymer materials [1] because of sharp core level excitation for carbon, nitrogen, oxygen and fluorine occur in the soft X-ray region. Core level electron transition to unoccupied valence orbital of π^*, σ^* and Rydberg orbitals are characteristic features of NEXAFS spectroscopy. Polymers, in particular, are sensitive to radiation damage caused by X-ray [2]. Based on this, we successfully surface functionalized polypropylene (PP) by inner-shell monochromatic irradiation with mild flow of oxygen in SGM beamline, Campinas, LNLS. Monochromatic radiation of different energy 282.3eV, 287.8eV, 292.5eV, 299.8eV and 309.3eV are shined with mild flow of oxygen on PP thin films prepared by spin casting. C 1s NEXAFS spectra collected at 90 degree angle after irradiation confirms that the energy 299.8eV (corresponding to C-C σ^* transition) showed significant energy shift when compared to all other spectra of different irradiated monochromatic radiation energy. The resulted C 1s NEXAFS spectra for 299.8eV irradiation is then curve fitted using BGuass fit by 6 Gaussian peaks with energy 287.3eV, 287.8eV, 288.3eV, 289.1eV,$\sim$292.5eV and $\sim$299.5eV for transition in C 1S spectra and inflection point of error function step fixed at 289.7eV. The appearance of new peak at 288.6eV (corresponding to C=O π^* transition) with full width half maximum of 1.0 confirms the surface modification of PP. Monochromatic irradiation of 299.8eV is then carried out for different times of 1 min, 5 min, 15 min, 25 min and 35 min. The curve fitted C 1s NEXAFS spectra confirms the increase of C=O group on the PP surface with increase in irradiation time. The results showed that mainly 299.8eV irradiation, corresponding to C-C σ^* transition, led to very important changes to the chemical composition on PP surface. Other monochromatic excitation energies led to less efficient surface chemical composition changes. Similar selectivity in bond dissociation efficiency was already observed in thin polystyrene films [3]. [1]O.Dhez, H.Ade, S.G.Urquhart, Journal of Electron Spectroscopy and Related Phenomena 128 (2003) 85-96. [2] T.Coffey, S.G.Urquhart, H.Ade, Journal of Electron Spectroscopy and Related Phenomena 122 (2002) 65-78. [3] D.E. Weibel, F.Kessler, G.V.S Mota, Polymer Chemistry 1 (2010) 645-649.

Acknowledgements: Agradecimentos: Pesquisa realizada com apoio do Laboratório Nacional de Luz Síncrotron e CNPq. Os autores gostariam de agradecer a assistência técnica do LNLS, especialmente o grupo de espectroscopia VUV e Raios X moles.

Structural and XAS studies of calcium aluminosilicates synthesized by a new hybrid route

Teixeira, V. C.[1] and Valerio, M.E.G.[1]

Universidade Federal de Sergipe - São Cristóvão SE Brazil

This work aimed the synthesis and structural characterization of $Ca_2Al_2SiO_7$ system by a new hybrid route, which combines the proteic sol-gel method with the solid state synthesis. In this synthesis route, coconut water (*Cocos nucifera*) is used as starting soluble solvents (calcium and aluminum nitrates) and silicon dioxide is mixture in the previous solution, which is dried, becoming a xerogel. The xerogel is calcined and the ceramic powder is obtained. In order to determine the best synthesis conditions, thermal analysis techniques and powder x-ray diffraction (DRX) were used. According to the (DTA) analysis, an exothermic peak at 930^oC indicates the formation of crystalline phases in the material. In the calcination program it was observed, at temperatures lower than 1300^oC, the formation of different intermediate oxides. These oxides were formed after the firing of the organic part of the starting solution, following a standard proteic sol-gel method. The process continues, as the temperature of calcinations process increased, and the diffusion and reaction of the intermediate oxide phases resulted in a single phase of calcium aluminosilicate at 1300^oC. These results were confirmed by XRD analysis. The crystallite size was evaluated using the Scherrers equation, and the results indicated that the calcined powders are in the nanometric scale. HR-TEM analysis confirmed this result, that shows too this system has a small lattice microstrain, because interplanar distances are very regular. This result indicates that is possible to combine two different methodologies to obtain ceramic nanopowders. XANES studies confirmed the valence of the dopants ions. The dopants used in this work were Ce^{3+} and Mn^{2+}.

Acknowledgements: Work supported by CNEN and CNPq. The authors are grateful to the CETENE Centro de Tecnologias Estrategicas do Nordeste for the HR-TEM images and LNLS for XAS measurements.

Luminescence of system $Ca_2Al_2SiO_7$ doped by transition metals

Teixeira, V. C.[1] and Valerio, M.E.G.[1]

Universidade Federal de Sergipe - São Cristóvão SE Brazil

The $Ca_2Al_2SiO_7$ (CAS) is a good matrix to produce luminescent phosphor or scintillator. The synthesis of the pure and doped $Ca_2Al_2SiO_7$ system was done by a new hybrid route, which combines the proteic sol-gel method with the solid state synthesis. In this route, coconut water (Cocos nucifera) was used as a starting solvent for the soluble reactants (nitrates) and silicon oxide was added in suspension to the starting dissolved salts. The dopants, Ce^{3+}, and Mn^{2+}, were added in replacement to Ca in stoichiometric proportions. The aims of this work were to obtain de ceramic nanopowders and to study the structural and optical properties. The structural analysis was done by DTA/TG, XRD and HR-TEM. DTA/TG results indicated an exothermic peak around 950^oC which is related to CAS crystallization. This was confirmed by XRD. HR-TEM micrographs showed that: i- the nanoparticles have average size around 13nm; ii- they have spherical morphology and low microstrain iii- they are single crystals showing the typical inter planar distances of the CAS phase. The optical properties were analyzed by PL and RL techniques. The PL curves are very similar to the RL ones, but the main difference in these measurements is: the RL spectra were obtained by X-ray excitation, with energy photons from Si K edge (1,8keV) to 8,0keV, that is above Ce LIII edge, while the PL one was acquire with UV photons (3,5eV). In these processes typical transitions of dopants are observed. The pure sample presented intrinsic luminescence when excited on K edge of matrix elements. The luminescent lifetime decay of RL was measured to all samples at single bunch mode in the SXS and XAFS2 beamlines from LNLS/Brazil. The results indicated a short lifetime and a great participation of the matrix in mechanism of lifetime decay.

Acknowledgements: Work supported by CNEN, CNPq, INCT-INAMI, CETENE and LNLS.

Caracterização por difração de raios X com angulo rasante da superfície do titânio tratado com ondas ultrassônicas

Balestra, R. M.[1], Andrade, M. C.[2], and Verly, J[2]

[1] Instituto Nacional de Tecnologia - Rio de Janeiro RJ Brazil
[2] Universidade do Estado do Rio de Janeiro - Rio de Janeiro RJ Brazil

O tratamento superficial do titânio é fundamental para ativar a superficie e promover a nucleação e o crecimento de fosfato de cálcio na superfície do titânio. Este revestimento de fosfato de cálcio no titânio torna o implante bioativo, evita a formação de tecido fibroso na superfície do metal e acelera a osteointegração, o que proporciona um menor tempo de recuperação e com isto pode garantir o sucesso da cirurgia. O tratamento com hidróxido de sódio em condições hidrotérmica é realizado na literatura para formar uma camada de gel após o tratamento térmico. Neste trabalho foi visto que o uso de um ultrassom facilita e diminui o tempo para realizar o processo de tratamento da superfície. Foi possível observar a formação de rutilo na superfície tratada em todos os tempos de aplicação das ondas ultrassônicas. Os difratogramas de raios X também mostraram a importancia da temperatura do tratamento térmico, já que em 200C não mostrou rutilo na superfície antes do processo de revestimento, o que dificulta a formação de fosfato de cálcio em menor tempo. Os difratogramas com angulos rasantes apresentaram boa definição dos picos de rutilo após o tratamento térmico a 600C, entretanto na temperatura de 200C não ocorreu a formação de rutilo, o que dificulta a cristalização do fosfato de cálcio, já que os espectros na região de infravermelho mostra a formação de fosfatos na superfície do titânio.

Acknowledgements: Os autores agradecem ao CNPq, à FAPERJ, ao INT e ao LNLS

Crystal structure and local atomic order of $La_{0.6}Sr_{0.4}Co_{1-y}Fe_yO_{3-\delta}$ nanotubes

Mejía-Gómez, A.[1], Acuña, L. M.[1], Vigna, M. B.[2], Sacanell, J.[3], A.G.Leyva[3], and Lamas, D. G.[2]

[1] Consejo Nacional de Investigaciones Científicas y Técnicas - Buenos Aires Argentina
[2] Universidad Nacional del Comahue - Neuquén Argentina
[3] Comisión Nacional de Energia Atómica - Buenos Aires B.A. Argentina

Perovskite-type mixed oxides are of great interest as cathodes for intermediate-temperature solid-oxide fuel cells. It has been found that nanostructures of these compositions have enhanced electrocatalytic properties for oxygen reduction reaction.

In this work, we have studied the evolution of the crystal structure and the local atomic order of $La_{0.6}Sr_{0.4}Co_{1-y}Fe_yO_{3-\delta}$ (LSCFO) nanotubes as functions of Fe concentration (y = 0.2; 0.5 and 0.8). LSCFO nanotubes were synthesized using porous polycarbonate filters by a microwave treatment of a nitrate solution of the desired cations, followed by calcination at 900-1000°C for one hour. The as-synthesized material is a conjunct of tubes of submicrometric diameter formed by LSCFO nanoparticles. The geometry of the nanotubes depends on the pore size of the filters, as confirmed by scanning electron microscopy. The crystallographic features of these nanotubes were analyzed by synchrotron X-ray powder diffraction and EXAFS. These experiences were performed in the D10B-XPD and D08B-XAFS2 beamlines of the National Synchrotron Light Laboratory (LNLS, Brazil).

Acknowledgements: This work was supported by LNLS (Brazil, proposals XAFS1-9886 and XPD-10152), ANPCyT (Argentina, PICT 2007 No. 01152 and PICT-PAE 2007 No. 2288), CNPq (Brasil, PROSUL Program, Project 490580/2008-4) and CLAF.

Synthesis and characterization of polysilsesquioxane functionalized with mercaptan to electrorheological fluids

Marins, J. A.[1], DAHMOUCHE, K[1], and Soares, B.G.[1]

Universidade Federal do Rio de Janeiro - Rio de Janeiro RJ Brazil

There are many methods to prepared inorganic-organic polymeric hybrids, such as co-polymerization, post-treatment of organic polymers and sol-gel process [1-2]. Polysilsesquioxane functionalized with mercaptan (POSS-SH) was prepared by sol-gel process to obtain the POSS-SH particles was made a mixture of deionizer water (3.0 mol) and isopropyl alcohol (0.3 mol). This solution has the pH fitted to 1 with chloride acid solution to 0.1 N. Soon afterwards, 0.15 mol of 3- mercaptopropyltrimethoxysilane and 0.15 mol of TEOS were added to mixture with pH controlled. The reaction was kept to 60 ^{o}C/8h under agitation; the gel was dried to 80 ^{o}C/12h. WAXS of POSS-SH showed three different peaks were observed at 2θ (d) values, 7.1^o (1.15 nm), 22.1^o (0.40 nm) and 24.5^o (0.35 nm) indicating the presence POSS molecules were formed such as reported Cordes et al [3]. In the spectrum FTIR the large band between 3750 and 3000 cm^{-1} is related to OH of silanol group or water, at 1135 and 1029 cm^{-1} corresponds to Si-O-Si linear and cyclic deformation stretching respectively, at 800 cm^{-1} is related to Si-O-Si asymmetric vibration of siloxane network and at 460 cm^{-1} corresponds to Si-O bond deflection [4]. The weak peak at 2556 cm^{-1} corresponds to aliphatic mercaptans and in region 700-600 cm^{-1} is related C-S linkage. The size particles presented r = 2.5 nm, it was determined by SAXS using Beuacage Equation. POSS-SH was synthesized by sol-gel process for ER fluids. Thus a new electrorheological fluid of POSS functionalized with mercaptan groups particles in silicone oil has been investigated.

Keywords: polysilsesquioxane functionalized with mercaptan, sol-gel and SAXS.

1 - SANCHEZ, C. et al. Comptes Rendus Chimie, v. 13, n. 1-2, p. 3-39, 2010.

2 - MONTICELLI, O. et al. Macromolecules , v. 42, n. 17, p. 6614-6623, 2009.

3 - CORDES, D. B. et al. Chemical Reviews , v. 110, n. 4, p. 2081-2173, 2010.

4 - SAMBANDAM, S. et al. Journal of Power Sources, v. 170, n. 2, p. 259-267, 2007.

Acknowledgements: Work supported by CNPq, FINEP and FAPERJ.

SAXS STUDY FERROFLUIDS STRUCTURE

M. B. Fernández van Raap[1], Mendoza Zélis P.[1], Coral, D.F.[1], T.E.Torres[2], G.F. Goya[3], and F.H.Sánchez[1]

[1] Universidad Nacional de La Plata - La Plata Bs.As Argentina
[2] Universidad de Zaragoza - Zaragoza Spain
[3] Universidade de São Paulo - São Paulo - São Paulo SP Brazil

Stable ferrofluids were studied by Small Angle X Ray Scattering (SAXS) at Brazilian Synchrotron Light Laboratory (LNLS) / Brazilian Biosciences National Laboratory (LNBio) under proposal D11A - SAXS1 9293. These systems consist of $CoFe_2O_3$ nanoparticles (NP) with mean sizes in the range from 4 to 7 nm coated with 2 nm of oleic acid and resuspended in hexane. The core-shell type magnetic nanoparticles of different sizes were prepared by thermal decomposition of iron-acetylacetonate $(acac)_3$ and cobalt-acetylacetonate $(acac)_2$ as organic precursors and solvents having different boiling temperatures (538, 573, 593 and 638 K) in order to control the final particle size [1]. Nanoparticles self organized due to Van der Waals and dipole-dipole interactions between the magnetic cores. This effect is reflected in the SAXS pattern, and was taken into account modeling the SAXS pattern with a spherically symmetric form factor of the NP convoluted with a log-norm distribution and modulated whit a monodispersed structure factor [2]. Mean core radii, polydispersity, degree of aggregation and topology of size aggregates are determined. Polydispersity of aggregates was not introduced into the model, but the coexistence of clustered particles with unaggregated ones was considered thought a slight modification of the mentioned fitting function. The so determined aggregation degree range from 0 to 40 The results indicate that samples present low primary particle polydispersity, but in the tested size scale some of them self organized forming clusters displaying a chain like tendency and other more compact structures. NP size and polydispersity are in very good agreement with TEM results.

[1]. Goya, G.F., Lima, E., Arelaro, A.D., Torres, T., Rechenberg, H.R., Rossi, L., Marquina, C. Magnetic Hyperthermia with $CoFe_2O_3$ nanoparticles: the influence of particle size on energy absorption. IEEE Trans. on Magn, 44 (11) 2008.

[2]. Sorensem C.M., Wang, G.M. Size distribution effect on the power law regime of the structure factor of fractal aggregates. Phys. Rev. E. Vol. 60 (6). 1999.

Acknowledgements: This work was supported by CONICET, Argentina (PIP 6011), PICT 12-14526 (ANPCyT, Argentina) and RN3M.

Crystal structure, local atomic order and metastable phases of $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ nanopowders for intermediate-temperature solid-oxide fuel cells

Acuña, L. M.[1] and Lamas, D. G.[2]

[1] Consejo Nacional de Investigaciones Científicas y Técnicas - Buenos Aires Argentina
[2] Universidad Nacional del Comahue - Neuquén Argentina

One of the most important challenges of Solid-Oxide Fuel Cells (SOFCs) technology is the reduction of the operating temperature. A great effort is dedicated to the research and development of new electrodes (cathodes and anodes) of high electrocatalytic activity and high ionic conductivity for application in intermediate-temperature SOFCs (IT-SOFCs).

Within the new materials under investigation, mixed ionic-electronic conducting oxides (MIECs) with perovskite-type crystal structure are of great interest due to their excellent performance. For example, $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ (LSC) is one of the best candidates for IT-SOFC cathodes due to their high ionic conductivity. This compound exhibits a rhombohedral crystal structure at room temperature, which transforms to the ideal cubic perovskite (*Pm3m* space group), of high electrochemical performance for the oxygen reduction reaction, at temperatures above 400°C. The micro/nanostructure of the cathode also plays an important role. In recent works, we have demonstrated that nanostructured LSC cathodes exhibit better electric properties than microstructured ones. This high performance is related to the enhanced ionic diffusivity of the nanostructured cathodes.

In the present work, we will present our study on the influence of the average crystallite size on the crystal structure and local atomic order of LSC nanopowders synthesized by wet chemical methods. These materials were studied by X-ray Powder Diffraction and X-ray Absorption Spectroscopy at the D10B-XPD and D04B-XAFS1 beamlines of the LNLS, respectively. We will show that materials with small average crystallite size (of about 25 nm) can retain the high-performance cubic phase at room temperature, probably due to the influence of the surface Gibbs energy. In addition, we will analyze the changes in the concentration of oxygen vacancies and in the atomic local order as functions of crystallite size and discuss their influence on the electrochemical performance of LSC cathodes.

Acknowledgements: This work has been supported by LNLS (under proposals D10B-XPD-11900 and D04B-XAFS1-11744), Agencia Nacional de Promoción Científica y Tecnológica (Argentina), CONICET (Argentina), CNPq (Brazil, PROSUL Program) and CLAF.

ESTUDO DA FORMAçãO DE MICROEMULSõES COMO PROMISSOR SISTEMA DE LIBERAçãO TRANSDÉMICA PARA NIFEDIPINA COMO MODELO DE FÁRMACO LIPOFÍLICO

Nunes, R.S.[1], Brito, M.B.[1], Mota, F.M.[2], Santos, M.R.V.[2], Lira, A.A.M.[2], and Sarmento, V.H.V.[2]

[1] Universidade Federal de Sergipe - São Cristovão SE Brazil
[2] Universidade Federal de Sergipe - São Cristóvão SE Brazil

Foi construído um diagrama de fase pseudo-ternário à 25C com o objetivo de obter um sistema de liberação transdérmica para a nifedipina do tipo microemulsões (ME). Foi utilizado como tensoativo o Tween 80, co-tensoativo o álcool etílico, e como fase oleosa óleo essencial de laranja (OEL). Determinações reológicas, microscopia de luz polarizada, avaliação de tamanho por espalhamento dinâmico de luz (DLS), espalhamento de raio-X a baixo ângulo (SAXS), e condutividade elétrica foram utilizados para caracterizar os sistemas como ME contendo ou não a nifedipina. Os experimentos de permeação para avaliação do efeito transdérmico, foram realizados em células de difusão do tipo Franz. 2 mL das ME saturada com o fármaco, solução tampão fosfato saturada com o fármaco (controle1) e solução tampão fosfato contendo 1% de OEL saturada com o fármaco (controle2) foram colocados no compartimento doador. Após os intervalos de tempo, 1 mL da solução receptora foi coletada sendo reposta imediatamente. A nifedipina foi quantificada por cromatografia líquida de alta eficiência, na região do ultravioleta. Todos os sistemas estudados apresentaram-se isotrópicos. O tamanho médio variou de acordo com o sentido de fase O/A ou A/O, em uma faixa de 11,72 a 32,03nm. O comportamento reológico mostrou que as amostras se comportaram como líquido Newtoniano típico de dispersões líquidas compostas de gotículas coloidais. As curvas de SAXS apresentaram picos simétricos a baixas e altas frações de fase aquosa com maiores valores de q e picos assimétricos em quantidades intermediarias de fase aquosa com menores valores de q, estes dados de SAXS podem ser correlacionados com o tamanho das estruturas e também com os valores de condutividade elétrica. Esta última correlação sugere a que a nifedipina interage com o sistema devido a modificação estrutural. Os experimentos de permeação in vitro revelaram que o fluxo da nifedipina foi de 5 a 22 vezes maior que os controles, sugerindo que o sistema atua como promotor de permeação transdérmico.

Acknowledgements: CNPq, FAPITEC, CAPES, LNLS

Correlating Structure and Reactivity of Nanoparticles by In-situ XAS and S-XPS

Morais, J.[1], Bernardi, F.[2], and Alves, M.C.M.[1]

[1] Universidade Federal do Rio Grande do Sul - Porto Alegre RS Brazil
[2] Lawrence Berkeley National Laboratory - Berkeley CA United States of America

Numerous efforts have been focused towards the search of new and more efficient catalysts for their use in the petroleum refinement processes. However, many catalysts are very susceptible to sulfur poisoning and their use is limited, unless sulfur tolerance can be greatly improved. Recently [1], we used in situ XAS (X-ray Absorption Spectroscopy) to study non-supported PtxPd1-x (x = 1, 0.7 or 0.5) nanoparticles under hydrogen reduction and posterior sulfidation. The Pt L3 edge spectrum was monitored and we observed that the reduction process is a necessary step prior to the occurrence of any sulfur reaction and that Pd migrates toward the surface, forming a Pt-rich core Pd-rich shell structure. This work describes an investigation by x-ray photoelectron spectroscopy associated with variable photon energy excitation of Synchrotron radiation (S-XPS) on the atomic arrangement of Pt-Pd nanoparticles [2, 3]. In addition, we have extended our in situ XAS investigations to systems with higher contents of Pd, i.e., non-supported PtxPd1-x (x = 0.5, 0.3 or 0) nanoparticles. They were also submitted to hydrogen reduction and posterior H2S sulfidation at 300 oC and characterized by XAS at both Pt L3 and Pd K edges. The use of non-supported catalysts, instead of catalysts supported on zeolites or Al2O3, allows to evidence of any interaction between Pt and Pd. The atom-specific short-range order investigation by XAS provides a way of monitoring local structural changes induced by reduction and sulfidation processes. Using the structural parameters obtained from the fitting procedure of the EXAFS (Extended X-ray Absorption Fine Structure) oscillations, we searched for a correlation between the sulfur reactivity of the nanoparticles and the bimetallic interaction effect. The overall results allow sustaining the model for the bimetallic interaction effect that we propose in the present study. 1- Fabiano Bernardi, Maria C. M. Alves, Agnes Traverse, Dagoberto O. Silva, Carla W. Scheeren, Jairton Dupont and Jonder Morais, J. Phys. Chem. C 113(10), 3909 (2009). 2-Fabiano Bernardi, Agnes Traverse, Luca Olivi, Maria C. M. Alves and Jonder Morais, J. Phys. Chem. C (June 2011). 3- Fabiano Bernardi, Gerhard H. Fecher, Maria C. M. Alves and Jonder Morais, J. Phys. Chem. Letters 1, 912 (2010).

Acknowledgements: Work supported by CNPq, CAPES, LNLS, ELETTRA.

XANES and IR Spectroscopic Evidence of Cationic Gold on IronOxide Supported Gold During CO Oxidation Catalysis Conditions

Jimenez-Lam, Sergio A.[1] and Fierro-Gonzalez, J. C.[1]

Instituto Tecnologico de Celaya - Celaya GTO Mexico

The performance of supported gold catalysts has been widely investigated to elucidate the origin of their catalytic properties for a number of reactions such as CO oxidation, water-gas shift, oxidation of alcohols, etc. One of the most investigated reactions is the CO oxidation. The activation of CO and oxygen is a widely studied topic and much effort has been made to determine the nature of the sites where such as reactants are activated. Infrared (IR) spectroscopy has been used to determine the surface species, as the gold catalysts are exposed to CO or at CO oxidation conditions. It is commonly accepted that CO adsorbs and activates in gold sites. However, there are different hypothesis suggesting that CO bonds to cationic, metallic or anionic gold; and then, the structure of the active site remains in debate. In this work, we combined IR spectroscopy and dispersive X-ray absorption near edge structure (XANES) at the Au-LIII to investigate the oxidation state of gold and the CO surface species formed during the CO oxidation catalyzed by iron oxidesupported gold samples. The results suggest the adsorption of CO on partially oxidized gold sites originated by the co-adsorption of oxygen and CO.

Acknowledgements: Acknowledgements: We thank the staff at beamline D06A-DXAS at the Brazilian Synchrotron Light Laboratory. This research was supported by Consejo Nacional de Ciencia y Tecnología (Ciencia Básica, Convenio: 61856) and Fondos Mixtos Guanajuato (2007).

Biomimetic Method for Coating Micro and Macroporous Titanium Substrates

Rocha, M. N[1], Ribeiro, A.A.[2], Balestra, R. M.[2], Andrade, M. C.[3], L. C. Pereira[1], and Oliveira, M. V.[2]

[1] Universidade Federal do Rio de Janeiro - Rio de Janeiro RJ Brazil
[2] Instituto Nacional de Tecnologia - Rio de Janeiro RJ Brazil
[3] Universidade do Estado do Rio de Janeiro - Rio de Janeiro RJ Brazil

Titanium (Ti) surface with calcium phosphate (CaP) coatings has shown to improve osseointegration at the implant-bone interface, because of the biocompatibility of the mineral. The present work studied a biomimetic method for coating Ti substrates for surgical implant applications. A simplified solution (SS) was used with high calcium and phosphorus ion concentrations. Micro and macroporous titanium samples, produced by powder metallurgy, were used as substrates. The samples were pretreated for surface bioativation using a NaOH solution followed by heat-treating. Then they were immersed for 7 or 21 days in SS. The substrates characterization was performed by scanning electron microscopy, optical microscopy, quantitative metallographic analysis and confocal microscopy. The CaP coatings on Ti substrates were analyzed by scanning electron microscopy and high resolution low angle in X-ray diffraction. Hydroxyapatite, carbonate apatite and octacalcium phosphate were observed on the samples. The results attested that the SS solution is promising for precipitating CaP coating on Ti substrates, since bioactive CaP phases were observed.

Acknowledgements: The authors thank to CNPq, FAPERJ and LNLS/Campinas-SP/Brazil.

PROTECTIVE FILM FOR REACTORS OF HYDROLYSIS AND FERMENTATION OF BIOMASS

Santos, N. M.[1], Amorim, J.[2], Freire, C.M.A.[3], Nascente, P. A. P.[4], N.C.Cruz[1], and Rangel, E.C.[1]

[1] Universidade Estadual Paulista-Sorocaba - Sorocaba SP Brazil
[2] Laboratório Nacional de Ciência e Tecnologia do Bioetanol - Campinas SP Brazil
[3] Universidade Estadual de Campinas - Campinas SP Brazil
[4] Universidade Federal de São Carlos - São Carlos SP Brazil

The reactors used in the pilot bioethanol generation plant are subjected to drastic operating conditions (high temperatures and aggressive chemical environment). The AISI 304 steel is the material used in these reactors and surface modification by the deposition of protective coatings will enhance the chemical inertness of the steel surface, which might mitigate corrosion related problems. Films were prepared by the radio-frequency plasma enhanced chemical vapor deposition (RF-PECVD) method using a mixture of 70% hexamethyldisiloxane (HMDSO), 20% O_2, and 10% argon. Excitation power varied from 15 to 75 W, while the deposition time and total pressure were kept constant at 1800 s and 8.0 Pa. The thickness of the films was measured by the perfilometry technique. The molecular structure and chemical composition of the films were characterized by infrared reflectance absorbance spectroscopy (IRRAS) and X-Ray photoelectron spectroscopy (XPS), respectively. Wettability was determined from contact angle measurements using deionized water as probe liquid. Electrochemical impedance spectroscopy (EIS) was employed to investigate the corrosion resistance of the samples in 3.5% NaCl solution, at room temperature. The plasma coated AISI 304 steel surface presented an enhancement in the corrosion resistance of about four orders of magnitude in comparison with the uncoated surface. The results were interpreted in terms of the energy delivered to the growing layer by plasma excitation power.

Acknowledgements: This work was supported by Brazilian agencie FAPESP.

Evolution of structural and chemical properties of GeSi nanoparticles by combined synchrotron radiation techniques

Gasperini, A. A.[1], Malachias, A.[2], Gobbi, A. L.[1], and Azevedo, G. de M.[3]

[1] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[2] Universidade Federal de Minas Gerais - Belo Horizonte MG Brazil
[3] Universidade Federal do Rio Grande do Sul - Porto Alegre RS Brazil

Semiconductor nanoparticles are crucial systems for future optoelectronic applications due to their differentiated properties with respect to counterpart bulk materials. The formation and structural properties of GeSi nanoparticles on SiO_2 matrix are studied here by synchrotron-based techniques. Shape, average diameter and size dispersion were obtained from GISAXS. XRD measurements were used to obtain crystallite sizes and composition via resonant (anomalous) measurements. By using these techniques as input for extended EXAFS, the local composition surrounding Ge atoms is investigated. Although results for each of the methods above are commonly analyzed separately, the combination of such techniques leads to an improved understanding of nanoparticle structural and chemical properties. Crucial indirect parameters that cannot be quantified by other means are accessed in our work, such as local strain, possibility of forming core-shell structures, fraction of Ge atoms diluted in the matrix (not forming nanoparticles), amorphous and crystalline Ge fraction and the relative population of nanoparticles with single and multiple crystalline domains. The analysis was performed at different stages of formation of nanoparticles, allowing to track the evolution of structural parameters as the nanoparticles grow. EXAFS, GISAXS and XRD probe the material over several length scales (atomic-level, mesoscopic and long range structure, respectively) with chemical selectivity, yielding a complete characterization of the nanoparticles. Although the results presented herein illustrate the potentiality of such a combination of synchrotron techniques in the analysis of only one material system, these procedures are general enough to be directly applied to other nanostructured materials.

Acknowledgements: The authors would like to thank CNPq and LNLS for financial support. The measurements were carried in XAFS2 (EXAFS) and XRD2 (XRD and GISAXS) beamlines

Room temperature observation of orbital momentum enhancement of Co/Au(110) by XMCD

dos Reis, D. D.[1], Roa, D. B[1], de Siervo A.[2], simoes e silva,w.[1], and Magalhaes-Paniago, R.[1]

[1] Universidade Federal de Minas Gerais - Belo Horizonte MG Brazil
[2] Universidade Estadual de Campinas - Campinas SP Brazil

It is a technological challenge to implement magnetic nanostructures with stabilized magnetization and decreasing size. Cobalt nanoparticles deposited on different substrates are ideal candidates for such small magnetic bits due to their large magnetic anisotropy. It has already been observed at very low temperatures and high magnetic fields that Cobalt nanoparticles deposited on Pt(111) exhibit a large enhancement of the orbital momentum [1].

In this work we have grown Cobalt nanoparticles on Au(110) in an asymmetric geometry, rendering it possible to examine the variation of the Co magnetization as a function of coverage.

In order to confirm the magnetization of Cobalt we have performed in-situ X-ray Magnetic Circular Dichroism (XMCD) measurements at different regions of the substrate. The XMCD experiments were done at the new Plane Grating Monochromator (PGM) beamline at the Brazilian Synchrotron Light Source (Campinas, SP), in total electron yield mode. Our results clearly confirm the magnetization of Cobalt nanoparticles at room temperature. The analysis of the XMCD data near the Cobalt L2 and L3 edges was performed by fixing the spin moment of Cobalt and inferring the orbital momentum from the well-known sum rules of XMCD. Our results clearly show the variation of Cobalt orbital momentum as a function of coverage.

Keywords: Magnetic nanoparticles, XMCD, induced moments.

Acknowledgements: This work was supported by FAPEMIG, CNPq, INCT-Nanocarbono and ABTLuS.

Understanding the stability of cobalt supported catalysts during ethanol reforming as addressed by *in situ* XAFS analysis

Ávila-Neto, C.N.[1], Hori, C. E.[2], Noronha, F.B.[3], Zanchet, D.[4], and Bueno, J.M.C.[1]

[1] Universidade Federal de São Carlos - São Carlos SP Brazil
[2] Universidade Federal de Uberlandia - Uberlândia MG Brazil
[3] Instituto Nacional de Tecnologia - Rio de Janeiro RJ Brazil
[4] Universidade Estadual de Campinas - Campinas SP Brazil

Recently, attention has been attracted to reforming of ethanol with Co-based supported catalysts. Despite the high conversions and selectivities obtained, these catalysts still undergo significant deactivation, which is generally attributed to sintering of Co particles, accumulation of carbon deposits on the catalyst surface or oxidation of Co metal particles. The coexistence of Co^0 and CoO_x phases is observed and the equilibrium between deposition and oxidation of carbon can be achieved by tuning the Co^0/Co^{2+} ratio. However, the nature of active sites is still a challenge and requires *in situ* studies. In this work, we examine the phase changes of Co by *operando* XAFS studies under steam reforming (SRE) and oxy-reforming of ethanol (ORE) conditions highlighting its correlation with resistance to carbon accumulation and competitive reactions. Co-based catalysts promoted with Pt or Cu and supported on CeO_2-Al_2O_3 or CeO_2-$MgAl_2O_4$ were characterized by thermogravimetry, XANES-H_2, *operando* XANES and EXAFS in SRE (H_2O/ethanol = 3) and ORE (H_2O:ethanol:O_2 = 3:1:0.5). The rate of carbon accumulation in SRE is dependent on the catalyst composition and decreases with the coordination number of Co-Co scattering (N_{Co-Co}) and with the addition of oxygen as a reactant. Spatial-resolved XANES in ORE shows that the catalyst is predominantly oxidized at the entrance of the catalyst bed but it features a reducing profile towards the exit region. The Co crystallite size can be controlled by changes in the nature of support, Co loading or addition of promoters (Cu,Pt), which associated to the right composition of reactants results in catalysts with tunable Co^0/Co^{2+} ratio. The correlation between rate of carbon accumulation in SRE and N_{Co-Co} indicates that catalysts resistant to carbon deposits may be found when N_{Co-Co} is lower than about 4. The presence of both Co^0 and Co^{2+} sites on catalyst surface helps to equilibrate the steps of ethanol activation and carbon oxidation, resulting in stable catalysts.

Acknowledgements: We thank VALE-FAPESP, the laboratory of heterogeneous catalysts of DQ/UFSCar and LNLS for the use of XAFS1 and DXAS beamlines.

Reciprocal space maps of thin layers of CdTe / Si - The Effect of Growth Temperature and Thickness

Mello, J. O.[1], Ferreira, S. O.[1], and A. Malachias[2]

[1] Universidade Federal de Viçosa - Viçosa MG Brazil
[2] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

The production of thin films of cadmium telluride (CdTe) has been investigated for several years for possessing semiconducting properties suitable for many applications, for example, in various opto-electronic devices such as optical modulators and detectors and also for x-ray and gamma detectors. Although very important technologically, the growth of CdTe on silicon substrates is a big challenge due to a very big lattice mismatch of about 19 percent. In this work we have used reciprocal space maps around the reflections (311) and (200) to investigate the effect of growth temperature and layer thickness on the defects which are formed during growth. The samples were grown by a home made molecular beam epitaxy system on silicon (111) substrates. The substrates were treated by a two percent solution of hydrofluoric acid, immediately before the introduction in the growth system. Two series of samples with two different growth temperature (250 and 400 C) and different thicknesses were investigated by Atomic Force Microscopy and X-ray Diffraction. The AFM images were obtained using the semi contact technique and the x-ray experiments were performed at the Brazilian Synchrotron Facility (LNLS). Although we were not able to measure quantitatively the defect density, qualitative results show that density of defects decreases with growth temperature but increase with film thickness in the studied range. In order to identify the nature of the defects observed high resolution transmission electron microscopy investigation will be necessary.

Acknowledgements: we would like to thank the CAPES,CNPQ, FAPEMIG andLNLSfor the financial support.

Estruturas micelares como molde dos poros em espumas cerâmicas de zircônia

Alves-Rosa, M. A.[1], Pulcinelli, S.H.[1], and Santilli, C.V.[1]

Universidade Estadual Paulista - Araraquara - Araraquara SP Brazil

A produção de cerâmicas porosas usando moldes moles permite obter materiais com estruturas hierárquicas de poros, que são amplamente aplicados em processos catalíticos como suporte para catalisadores. Misturas de tensoativos iônicos e não-iônicos permitem a formação de numerosas estruturas porosas de acordo com o tipo e concentração de tensoativo. O uso do processo sol-gel associado a estes moldes moles faz com que a gelatinização do material previna o colapso da estrutura porosa durante a secagem e o tratamento térmico. Para a preparação da espuma, um sol aquoso de zircônia sulfatada (3,5 molL^{-1}) foi aerado sobre agitação vigorosa e constante (12000rpm) na presença de uma mistura de dois tensoativos: dodecilsulfato de sódio (SDS) e Pluronic F-127 (10-15%m/m). A gelatinização ocorre em poucos minutos pela adição de ácido sulfúrico e após secagem (50^{o}C, 24 h) e tratamento térmico (600^{o}C, 2h) a cerâmica porosa é obtida. Amostras contendo diferentes quantidades de tensoativos e proporções SDS/Pluronic foram analisadas por SAXS no estado de gel e após calcinação. No gel pôde-se observar a presença de picos finos e intensos, característicos de fenômenos de difração por arranjos periódicos. Algumas amostras apresentaram dois picos de difração cuja razão entre as posições é um número inteiro, geralmente associado a harmônicos de difração em estruturas lamelares. A formação da estrutura lamelar está diretamente relacionada ao aumento da concentração de tensoativos e da proporção SDS/Pluronic no sistema. Os picos correspondentes a estrutura lamelar desaparecem nas amostras secas a 100^{o}C e tratadas termicamente a 600^{o}C. Com o acompanhamento *in-situ* do aquecimento da amostra há o desaparecimento do pico em 1nm^{-1} entre 58 e 60^{o}C. O aumento da temperatura e a eliminação do solvente fazem com que a estrutura formada pelo tensoativo desapareça. Além disto, é importante ressaltar que a região linear no gráfico log-log apresenta inclinação em torno de 3,6, indicativo do espalhamento de superfícies de grandes objetos no interior dos quais se situam as estruturas com arranjo periódico lamelar. Como propriedades porosas estes materiais apresentaram duas famílias de poros, na região de macroporos (entre 20 e 70μm) e na região de mesoporos (entre 3,5 e 30nm), áreas de superfície entre 5 e 60m^2g^{-1} e porosidades de até 92%. Estas propriedades certificam estes materiais como promissores para aplicações em catálise heterogênea.

Acknowledgements: Este trabalho foi financiado por CNPq, CAPES e FAPESP

Study of metal oxide nanowires grown by resistive heating

Lima, P. G.[1] and Criado, D.[1]

Universidade Federal do ABC - Santo André SP Brazil

Since carbon nanotubes were discovered in the 90's, nanostructures have been studied due to their fascinating properties which differ from those of the bulk [1]. The study of 1D structures started later than 2D and 0D structures due to the difficulties encountered in growing such geometries [1]. The methods commonly used to obtain these structures are expensive and/or contain many steps. Cupric oxide nanowires (CuO) have been recently studied for applications such as gas sensors [2], field emission [3] and photovoltaic devices [4] due to its semiconducting properties. However, its magnetic properties have been not totally explored [5,6]. Even more, it can be mentioned that CuO has been presented as an alternative to others nanostrutures since it is non-toxic, chemically stable, has a high surface area, and is easy to fabricate [7].

In this work we studied copper oxide nanowires grown by the resistive heating method. This method is characterized by its low cost and short processing times (seconds or minutes). The method is based on the resistive heating of a metal controlling the current applied to the material [8], with no use of a furnace. The entire process is performed at room conditions and no especial atmosphere is necessary, which makes the process inexpensive. The CuO nanowires were grown by applying different current intensities to commercial wires of 0.40 mm in diameter for different exposition times. The same technique was applied to aluminum wires. However, no aluminum oxide nanowires were obtained, but porous aluminum oxide instead.

[1] Y. Xia et. al, Adv. Mater. 15 (2003) 353.

[2] N. D. Hoa et. al, Physica E 42 (2009) 146149

[3] L. Yu et. al, Journal of Crystal Growth 310 (2008) 3125 3130

[4] P. Raksa et. al, Thin Solid Films 517 (2009) 47414744

[5] S.R. Mishra et. al, Journal of Magnetism and Magnetic Materials 279 (2004) 111117

[6] D. Shang at. al, Applied Surface Science 255 (2009) 40934096

[7] N. Mukherjee at. al, Materials Letters 65 (2011) 32483250

[8] S. Rackauskas et. al, A novel method for metal oxide nanowire :Synthesis, Nanotechnology 20 (2009)

Acknowledgements: This work was financed by the Programa de Iniciação Científica da UFABC (PIBIC-AF/UFABC), CNPq. We also thank the LNLS (Research Proposal ID SEM FEG-11414) and LSI-POLI-USP for the SEM observations.

Effect of the structural properties of the Mn_yO_x /C on the kinetics of the oxygen reduction reaction in alkaline electrolyte

Garcia, Amanda Cristina[1] and Ticianelli, E. A.[1]

Universidade de São Paulo - São Carlos - São Carlos SP Brazil

Many studies have been made aiming at developing effective low-cost electrocatalysts for alkaline oxygen/air electrodes, for applications on alkaline fuel cells and/or metal/air batteries . Several kinds of manganese oxides (Mn_yO_x) it has been found that the catalytic activity towards the oxygen reduction reaction (ORR) depends strongly on the Mn oxidation state and on the oxide structure. In this work, the ORR was studied in NaOH electrolyte on manganese oxides supported on a carbon powder, prepared by thermal decomposition of manganese nitrate at different temperatures and atmospheres. X-ray absorption spectroscopy (XAS) in the X-ray absorption near edge structure (XANES) region and X-ray diffraction (XRD) were employed to get information of the oxidation state and local structure around manganese in these oxides. The electrocatalysts were composed by manganese oxides supported on a carbon powder, prepared as described previously . XANES experiments were conducted at the DXAS beam line in the LNLS. The working samples for these measurements consisted of pellets formed with $Mn(NO_3)_2.4H_2O$ dispersed onto carbon, agglutinated with boron nitrite. The temperature was varied in the range of 25 to 500 ^{o} C , and stepped at 220 and 500 ^{o} during 1 hour. XANES spectra were obtained at the Mn K edge (6540 eV) under air and nitrogen atmospheres. XRD patterns for the manganese oxide prepared at 220 ^{o} under air showed sharp peaks, indicating that the material presents high crystallinity. The synthesis resulted in a major phase composed by β-MnO_2, and by minor phases composed of MnOOH and Mn_2O_3. Under nitrogen the main product was Mn_2O_3. It was compared XANES spectra obtained during the syntheses of Mn_yO_x at 220 ^{o} under air and nitrogen with those for MnO_2 and Mn_2O_3 standards. It was noted that both catalysts is composed just by Mn_2O_3. Results obtained for the material prepared under air after exposition to the moisture of the ambient denotes that it is transformed into the mixture of β-MnO_2, MnOOH, and Mn_2O_3, as also evidenced by XRD . The steady-state ORR polarization results obtained at various revolution rates denoted considerable activity for the ORR, particularly for the material prepared under air.

Acknowledgements: The authors thank FAPESP, CNPq, CAPES for financial supports, and Brazilian Synchrotron Light Laboratory (LNLS) for the XAS measurements.

Síntese de nanopartículas de TiO_2 de tamanho controlado nos poros da SBA-15

Silva, JMDE[1], Strauss, M.[1], Maroneze, C. M.[1], Souza, E. R.[1], Sigoli, F.A.[1], and MAZALI, I. O.[1]

Universidade Estadual de Campinas - Campinas SP Brazil

Nanopartículas de TiO_2 foram sintetizadas na SBA-15[1] através de metodologia que envolve ciclos sucessivos de impregnação da SBA-15 com precursor metalorgânico de Ti(IV) seguida de tratamento térmico. Espectroscopias Raman e UV-Vis indicam que as partículas de TiO_2 encontram-se em escala nanométrica e que variam de tamanho em função do número de ciclos de impregnação-decomposição térmica empregados, o que resulta em mudança do valor da banda proibida da titânia de 4,0 eV para o material preparado com apenas um ciclo para 3,6 eV no material obtido após 10 ciclos. Ciclos de impregnação-decomposição térmica sucessivos causam aumento do teor de TiO_2, que se encontra nas fases rutilo e anatásio, conforme XRD e XRF. Análises de sorção de N_2 e SAXS mostram que ocorre redução do diâmetro do mesoporo da SBA-15 sem que haja contração da sua estrutura e sugerem que as nanopartículas de TiO_2 encontram-se nos mesoporos deste material. Análise por TEM reforça esta hipótese, pois mostra nanopartículas cristalinas de forma esférica localizadas preferencialmente dentro dos mesoporos da SBA-15. A metodologia apresentada no presente trabalho para a síntese de nanopartículas de TiO_2 imobilizadas na SBA-15 permite o controle do tamanho das partículas obtidas e, consequentemente, a variação da largura da banda proibida da titânia, além de possibilitar a modificação do volume total de poros e da área superficial do material final apenas pelo controle do número de ciclos de impregnação-decomposição empregados.

Acknowledgements: Os autores agradecem à FAPESP, à CAPES e ao CNPQ pelo auxílio financeiro e ao LNLS pelas análises de raios X e de SAXS e ao LNNano pelas imagens por TEM.

Unveiling the early stages of formation and growth of GeSi nanoparticles with *in situ*, time-resolved Dispersive X-ray Absorption Spectroscopy (DXAS)

Gasperini, A. A.[1], Malachias, A.[2], Garcia, F.[1], and Azevedo, G. M.[3]

[1] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[2] Universidade Federal de Minas Gerais - Belo Horizonte MG Brazil
[3] Universidade Federal do Rio Grande do Sul - Porto Alegre RS Brazil

Nanoparticles (NPs) have been attracting great attention since it has been realized that the reduction of dimensionality offers an alternative pathway to manipulate and control materials properties, besides the more traditional control over chemical composition. The tailoring of NPs properties requires a fine control over the formation and growth processes, which are, nevertheless, still incompletely understood in several systems. Due to their reduced dimensions, the early stages of formation and growth of NPs are difficult to access with conventional characterization techniques, requiring the use of time-resolved and short-range order sensitive techniques.

In this work, the formation and growth stages of GeSi NPs encapsulated in silica thin films has been followed *in situ* by time-resolved Dispersive X-ray Absorption Spectroscopy in Ge K-edge. Our samples consisted of silica thin films uniformly doped with Ge atoms, prepared by RF co-sputtering. As the annealing temperature is increased from room temperature, we observe the thermal decomposition of the supersaturated mixture of silica and Ge atoms, and the nucleation of small molten metallic GeSi clusters, as revealed by absorption edge energy shifts and modifications in the intensity of the white line. During a two-hour annealing plateau at 1050°C, the molten metallic clusters increase in size, as indicated from a continuous increase in the white line. Upon cooling, the XANES spectra change continuously in the 1050°C to 750°C temperature range, from the liquid metallic to the diamond semiconductor structure, as revealed by well known spectral features. The molten and crystallized fractions were determined as a function of temperature during cooling. Our results reveal that the NPs crystallize at much lower temperatures than the bulk GeSi melting/crystallization temperature. EXAFS results indicate the NPs become compressively strained on cooling due to the NPs volume expansion across the liquid-solid transition, in good agreement with *ex situ* XDR results. The particle size distribution after cooling was determined from TEM measurements, enabling direct comparison between our DXAS results and theoretical models for the size-dependent melting temperature of semiconducting NPs.

Acknowledgements: Work supported by LNLS, CNPq and FAPESP.

Effect of zirconia morphology on reduction properties of Cu/ZrO_2 carried out by XANES investigation in hydrogen and in ethanol environment

Sato, A.G.[1], Volanti, D.P.[2], Damyanova, S.[3], Longo, E.[2], and Bueno, J.M.C.[1]

[1] Universidade Federal de São Carlos - São Carlos SP Brazil
[2] Universidade Estadual Paulista - Araraquara - Araraquara SP Brazil
[3] Bulgarian Academy of Sciences - Sofia Bulgaria

Cu/ZrO_2 were found to be excellent catalysts for ethanol dehydrogenation to Ethyl acetate. ZrO_2 has polymorphs of cubic, tetragonal, monoclinic, and amorphous structures. Interaction between the metal and the support on a solid was shown to play a significant role in the determination of its catalytical properties. In this work Cu K-edge XANES spectras of fresh samples showed different coordination state of copper II species supported over monoclinic, tetragonal and amophous ZrO_2 based on its pre-edge peaks positions attributed to a 1s-3d eletronic transition. The reduction properties of Cu/ZrO_2 samples studied by temperature programmed reduction in H_2 also seems to have been affected by these distincts copper-suport interactions leading to different active sites according to ZrO_2 morphology.

Acknowledgements: The authors thank CNPq, FAPESP and Bulgarian Ministry of Education, Science and Youth (project DTK-02/36) for their financial support. The XAS facilities were supplied by LNLS (National Laboratory of Synchrotron Light, Brazil) beamline (D06A-DXAS-10156). We express our gratitude to D. C. Oliveira, F. R. Zambello, C. N. A. Neto, D. M. Meira and I. C. de Freitas for useful XPS, XANES and FT-IR contributions.

TiO_2 modified nanoparticles prepared by sol-gel process for use in liquid crystal as a multifuncional system

MANAIA, E. B.[1], Kaminski, R. C. K.[1], Santilli, C.V.[1], Pulcinelli, S.H.[1], and Chiavacci, L.A.[1]

Universidade Estadual Paulista - Araraquara - Araraquara SP Brazil

In Brazil and in other tropical countries, the skin cancer is the most frequent. The titanium dioxide is an inorganic compound used as sunscreen in cosmetic/ pharmaceutical formulations that is a way to prevent the skin cancer. Using the sol-gel process, it is possible to prepare TiO_2 nanoparticles with desirable size, transparence and adequate protection of the skin from UVA and UVB radiations. After being incorporated in the liquid crystal, this organized system can be used for controlled release of anti cancer drug. In this work we have used an unprecedented thermo-reversible sol-gel transition for titania nanoparticles[1] that showed transparency in the range of temperature typical for sunscreen use (between 30 and 60 degrees celsius). The propose of this work was to analyze the citotoxicity of these nanoparticles, their zeta potencial and the phase behavior of liquid crystal formulations containing titania nanoparticles by SAXS and polarized light microscopy. In the violet crystal assay the nanoparticles showed no citotoxicity on the two cell lines tested, humans keratinocytes and fibroblasts, presenting more than 70% of cell viability. The zeta potential measurements revealed a charged surface for TiO_2 nanoparticles, responsible to prevent aggregation and to maintain the final transparence of the liquid crystalline sunscreen formulations. The polarized light micrographies associated to SAXS curves showed the presence of hexagonal and lamellar liquid crystalline phases both without and in the presence of TiO_2. The charged surface maintain the stability of the formulations and the liquid crystalline structure containing TiO_2 nanoparticles makes this system a good candidate for use simoutaneously as sunscreen and as controlled release system of anti cancer drugs.

Acknowledgements: Work supported by FAPESP and CNPq.

Simple synthesis of mesoporous silica with a high capacity for the immobilization of lysozyme and antimicrobial effectiveness

de Oliveira, L. F.[1], Cardoso, M.B.[1], Gonçalves, K. A.[2], and Kobarg, J.[2]

[1] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[2] Laboratório Nacional de Biociências - Brazil

Fabrication of materials which are able to inhibit infections and bacterial colonization in chirurgical devices is necessary to reduce infections originated from medical procedures. Actually, bacterial infection is a persistent and serious public health issue. Often, these infections are originated from the bacterial colonization in chirurgical devices[1]. Thus, the first step in order to reduce these infections is inhibiting bacterial proliferation on chirurgical devices[2]. Recently, a wide range of antimicrobial methods have been tested involving either surface modification or application of coatings which would be able to resist cell adhesion[3]. Obviously, these procedures invariably increase the overall cost of device production and, most commonly, are not effective to avoid colonization along time. In this study, we describe a facile and low-cost route to encapsulate lysozyme (a protein that holds bactericidal properties) in mesoporous silica through one-pot synthesis process. The high capacity of lysozyme immobilization into the silica cage is determined by UV-vis spectroscopy that evidences an entrapment yield of approximately 95%. Along the reaction process, lysozyme acts as catalyst favoring silica hydrolysis and condensation allowing the formation of quasi-spherical nanoparticles. The structural organization of silica-lysozyme composites is investigated by scanning electron microscopy, nitrogen adsorptiondesorption, small-angle X-ray scattering, FT-IR spectroscopy, thermal gravimetric analysis and X-ray diffraction techniques. Finally, the antimicrobial effectiveness of silica-lysozyme composites was tested against *Escherichia coli* and *Staphylococcus aureus.* The encapsulation of lysozyme in mesoporous silica maintained not only its stability and enzymatic activity but also had its biomedical activity markedly improved. Due to the tailorability of composite and the simplicity of reaction procedures, a wide range of possible applications can be envisaged such as coating containers used to storage chirurgical devices, catheters, artificial prosthetics and others materials in order to reduce hospital infection.

[1] Gilbert, P. *et al. Antimicrobial Agents and Chemotherapy* **1990**, 34 (10), 1865;
[2] Eby, D. M. *et al. Acs Applied Materials & Interfaces* **2009**, 1 (7), 1553;
[3] Hetrick, E. M. *et al. Chemical Society Reviews* **2006**, 35 (9), 780.

Acknowledgements:

Nanostructured europium doped lanthanum fluoride and oxifluoride

Rodrigues, E. M.[1], Souza, E. R.[1], and Sigoli, F.A.[1]

Universidade Estadual de Campinas - Campinas SP Brazil

This work reports on the synthesis of europium-doped lanthanum fluoride nanoparticles using different ligands, as oleylamine, DMA and DMF in order to avoid the nanoparticles growth. The nanoparticles presented high cristalinity and about 6 nm diameter size. The nanoparticles were characterized by x ray diffraction, luminescence spectroscopy and transmission electronic microscopy.

Acknowledgements: The authors acknowledge to Capes and CNPq for financial support and to LNLS for the use of the LME.

Study of the morphology exhibited by polyurethane/montmorillonite nanocomposites during different shape memory thermo-cycles applying Porod, Guinier and Debye-Bueche models

Pereira, I. M.[1] and Orefice, R. L.[2]

[1] Centro Tecnológico do Exército - Rio de Janeiro RJ Brazil
[2] Universidade Federal de Minas Gerais - Belo Horizonte MG Brazil

Segmented polyurethanes (PU) are thermoplastic urethanes characterized by high elongation, low modulus and multiphase morphology. Their unique properties are affected by composition, processing condition and phase segregation. Shape memory (SM) polyurethane are thermo-responsive PUs that and can store and recover deformations by application of a prescribed thermo-mechanical cycle. Previous works showed that SM properties, shape recovery and shape fixation, are driven by hydrogen bonding and crystallization. The results also showed that the ability to recover shape is related to the rapid re-establishment of specific macromolecular architectures to have their nanostructure rebuilt after the SM cycle. During the recovery stage, soft segment crystallites progressively melt and phase separation increase until a new thermodynamic equilibrium is achieved. The new thermodynamic equilibrium defined the final PU nanostructure. The present work investigates the SM behavior of montmorillonite (MMT) nanocomposites. Recent approaches have studied PU/MMT nanocomposites in order to produce materials with improved properties. The objective of this study was to monitor morphology development of shape memory PU reinforced with Na+/MMT. The structure and SM properties were investigated using small angle X-ray scattering (SAXS) and wide angle X-ray scattering (WAXS). Furthermore, to study the influence of the temperature during recover, the specimens were subjected to different thermo-cycles. In each condition, the morphology was investigated by Porod's law for a non ideal two phase system. At low angles, the X-ray scattering data were analyzed using Guinier's law and Cebye-Bueche model. The results were associated with the morphological changes. The features controlling the recovery process were established.

Acknowledgements: The authors acknowledge the financial support from the following institutions: National Council for Scientific and Technological Development (CNPq). a foundation linked to the Ministry of Science and Technology (MCT) of the Brazilian Government; the State of Minas Gerais Research Foundation (FAPEMIG); and the National Synchrotron Light Laboratory (LNLS-Brazil) for the use of the SAXS beamline facilities.

PREPARATION AND CHARACTERIZATION OF HYBRID FILMS CONTAINING LIGNIN FROM SUGAR CANE BAGASSE

Cerrutti, B.M.[1], Gonçalves, V. C.[1], Hammer, P.[1], Pulcinelli, S.H.[1], and Santilli, C.V.[1]

Universidade Estadual Paulista - Araraquara - Araraquara SP Brazil

Damage caused by corrosion is responsible for large financial losses in industry. Because it is not possible to avoid long-term corrosion in metals, new methodologies with special alloys, corrosion inhibitors and protecting films have been produced to retard the corrosion processes for increasingly long times. The polysaccharide lignin is the second largest source of renewable biomass, normally obtained from wood, plants and sugar cane bagasse. This bagasse is a residue from the production of biofuels with serious environmental implications. Lignins have macromolecular structure rich in aromatic, aliphatic and phenolic groups, being thus reactive against nucleophilic substitution reactions and able to form complexes with ions and metals. In this work, lignin was used as the organic component in preparing hybrid lignin-silica films to be used as anti-corrosion coating. A silica-lignin precursor was obtained through the reaction of lignin with a modified isocianate propyl trietoxysilane silicon alkoxide (IsotrTEOS). FT-IR and 1HNMR measurements confirmed the link between lignin and the IsotrTEOS urethane. A hybrid organic-inorganic material was obtained using the sol-gel process with this precursor, from which spin-coated films were fabricated. Various proportions between 0% and 75% SIO $_2$O in mass were used and the film properties changed with this proportion, according to UV-VIS. and fluorescence spectroscopy measurements. The films will now be characterized with atomic force spectroscopy (AFM), photoelectron spectroscopy (XPS) and small angle X-ray scattering (SAXS), with the aim of correlating the films morphology and their optical properties.

Acknowledgements: Acknowledgements: The authors gratefully acknowledge FAPESP, CNPq and CAPES for the financial support.

Epitaxial graphene on SiC(0001): a photoelectron diffraction (XPD) study

de Siervo A.[1], Landers R[1], and Lima,L.H.[1]

Universidade Estadual de Campinas - Campinas SP Brazil

A flat, single layer of graphite known as graphene has become the focus of studies due to its exceptional properties and fascinating applications. Large scale graphene layers for a possible application can be grown epitaxially on SiC by Si sublimation [1]. Even before the interest in graphene, the surface of SiC was already extensively studied [2][3]. It exhibits a large variety of surface reconstructions and these reconstructions are very dependent of sample preparation and orientation (0001) or (000-1). In this study, we show a preliminary investigation of the structural properties of graphene layers on SiC (0001) by photoelectron diffraction (XPD). The surfaces were prepared by heating the 1x1 surface to temperatures of about 1150°C in high ultra vacuum and the various reconstructions were monitored by Low Energy Electron Diffraction (LEED) and X-Ray Photoelectron Spectroscopy (XPS). In particular for the Si terminated surface, that is SiC(0001), the interface between graphene and SiC is characterized by the so-called $(6\sqrt{3} \times 6\sqrt{3})R30°$ reconstruction (buffer layer). The interpretation of this reconstruction, which is the initial stage of graphitization, has lead to controversy in the literature [2]. We will further discuss the buffer layer structure in terms of the XPD results. The XPD experiments were performed at SGM beam line at LNLS using photons with 450 eV probing the Si2p and C1s core level. The C1s signal was separate in to contributions from volume and surface and compares the experimental results with photoelectron multiple scattering calculations performed with the MSCD package [4].

Referências

1. U. Starke, C. Riedl; **J. Phys. Condens. Matter**; 596, 176 (2005).
2. K. Heinz *et al.*; **J. Phys. Condens. Matter**; 16, S1705 (2004).
3. L. I. Johansson *et al.*; **PRB**; 53, 13793 (1996).
4. *Multiple Scattering Calculation of Diffraction* by M. Van Hove and Y. Cheng.

Acknowledgements:

Transição sol-gel termorreversível em sistemas a base de titania

Lins, R. F.[1], Kaminski, R. C. K.[1], Santilli, C.V.[1], and Pulcinelli, S.H.[1]

Universidade Estadual Paulista - Araraquara - Araraquara SP Brazil

Os géis termorreversíveis são sistemas de duas fases que adquirem propriedades elásticas em resposta ao aumento ou diminuição da temperatura voltando a ter propriedades típicas de líquidos ao retornar á temperatura inicial. Neste trabalho realizou-se o estudo da transição sol-gel termorreversível em sistemas a base de óxido de titânio com a intenção de entender os fenômenos de agregação e de gelatinização durante a transição. As suspensões coloidais de TiO_2 foram obtidas a partir da adição do ácido p-tolueno sulfônico (PTSH) em tetraisopropoxido de titânio e isopropanol. A fase sol foi obtida a partir de diferentes envelhecimentos (0, 12 e 21 horas) a 60 ^{o}C, enquanto a fase gel foi obtida quando as amostras foram submetidas a temperatura de 10 ^{o}C. As amostras foram avaliadas por espalhamento de raios X a baixo ângulo (SAXS) durante o aquecimento e em condições isotérmicas. Observa-se que para todas as amostras o raio de giro das partículas aumenta com a diminuição da temperatura, levando a menores valores de superfície específica. O valor do invariante praticamente não muda com a temperatura, demonstrando que a fração em volume dos objetos espalhadores permanece constante. Por outro lado, dois comportamentos de crescimento de partículas foram observados durante a formação do gel. O primeiro, fractal, foi obtido a partir dos valores de dimensões fractais, Df = 2 observados para valores de q grandes, característico de um processo cinético de agregação cluster-cluster com crescimento limitado por difusão (DLCCA). O segundo comportamento foi obsevado em condições isotérmicas a partir de uma relação hiperbólica entre o raio das partículas primárias determinado por Guinier e o tempo, característica de um mecanismo de agregação entre partículas primárias.

Acknowledgements: LNLS pelo suporte técnico, à FAPESP e ao CNPQ pelo auxílio financeiro.

Síntese e caracterização de xerogéis de carbono dopados com nitrogênio

Botelho, M. B.[1], Martelli, P. B.[1], and Gorgulho, H. F.[1]

Universidade Federal de São João del Rei - São João del Rei MG Brazil

Os xerogéis de carbono são materiais nano-estruturados que possuem uma ampla aplicação como suportes de catalisadores e na produção de supercapacitores. Tais materiais são formados por nano-esferas de carbono interconectadas em uma estrutura tridimensional. A porosidade dentro desta rede pode ser predominantemente de mesoporos ou macroporos dependendo da forma e preparação do material. Estes materiais são em geral obtidos pela policondensação de benzenos hidroxilados com aldeído através do processo sol-gel.Variando alguns parâmetros de síntese pode-se obter estruturas com diferentes distribuição de poros e tamanho das nano-esferas. Outra modificação do processo de síntese destes materiais é a introdução de precursores nitrogenados que podem modificar a natureza acido-base final da superfície destes materiais. Neste sentido, a introdução de nitrogênio na estrutura dos carbonos xerogéis é um procedimento que tem sido recentemente explorado com o objetivo de incrementar o carater básico de sua superfície. Neste trabalho, preparou-se carbonos xerogéis utilizando resorcinol, formaldeido, água e carbonato de sódio como catalisador. Para introduzir nitrogênio na sua estrutura foi utilizado melamina como precursor. Outro parâmetro explorado neste estudo foi o grau de diluição dos reagentes no sentido de se obter diferentes nano-esferas. Os materiais produzidos foram caracterizados em relação à morfologia através da técnica de microscopia eletrônica de varredura. As propriedades da superfície foram investigadas através de técnicas de ponto de carga zero e titulação de Boehm. Os resultados obtidos até o momento confirmam a obtenção dos xerogéis de carbono, com nano-esferas bem definidas e homogêneas. Verificou-se também que a introdução do precursor nitrogenado aumenta a basicidade e o numero de grupos funcionais. A melhor caracterização da distribuição dos tamanhos de poros (dentro da estrutura) e da natureza dos grupos superficiais ainda devem ser investigadas pelas técnicas de XPS e microscopia eletrônica de transmissão.

Acknowledgements: Este trabalho tem o apoio da Capes, Fapemig e CNPq. Agradecemos também ao Departamento de Ciências Naturais e ao Programa de Mestrado em Física e Química de Materiais da UFSJ.

Structural characterization of ternary compounds based in rare earth oxides using x-ray spectroscopy, Rutherford backscattering and scanning electron microscopy

D. R. Huanca[1] and Santos, S. G.[1]

Universidade de São Paulo - São Paulo - São Paulo SP Brazil

Due to the continue miniaturization of semiconductor devices, it is necessary to find new dielectrics to replace the traditional SiO_2, because thin film of it lose their bulk features; to solve this drawback, the high-k material arise as promising candidates. We have deposited two types of thin dielectric films (TDF) on Si via atomic layer deposition, mixing Gd or Lu with Al and O. After, they were submitted to rapid thermal annealing (RTA) process during 60 seconds at 1000^oC in N_2 or N_2 + 5% O_2. Their structural and chemical features along with the effect of the RTA upon the nanostructure were characterized by X-ray spectroscopy, Rutherford backscattering spectroscopy (RBS) and Scanning electron microscopy (SEM). It was found that during the RTA the DTF undergoes clear phase separation divided in three layers, being the superficial layer composed by Al_2O_3 (18.7 nm for Gd and 4.3 nm for Lu), whereas the others are composed by compound with rare earth concentration growing in depth. In addition, the RTA also yields the diffusion of Al and O into the Si substrate giving rise to the formation of an underneath layer composed by $Al_{5,65}Si_{0,35}O_{9,175}$. Because this layer, the thickness measurement by X-ray reflectometry (XRR) becomes larger than those measured by RBS and SEM. It was also observed that Gd-TDF forms thicker films (43 nm) than that based in Lu (28 nm), but the latter has rougher surface. The fit of the XRR and RBS spectra was made using the multilayer model due to the variation of chemical elements that promotes the variation of the electron density along the thickness.The GISAXS pattern formation only in Lu-DTF points out that the Al_2O_3 is not a suitable medium to form nanoparticles. The analysis of the GISAXS pattern indicates that within the Lu-DTF it was formed nanoparticles with sphere, prolate and oblate spheroid shape with mean radius varying from 1.5 to 2.5 nm. This analysis also shows that adding 5% O_2 into the RTA environment enhances both the nanoparticles size and the polydispersivity of the system. The X-ray diffraction using $= 0.5^o$ indicates that the Lu-TDF is predominantly composed by $Lu_3Al_2Al_3O_{12}$, while in those based in Gd the predominance is of the Al_2O_3 compound.

Acknowledgements: Authors thanks FAPESP by the financial support of the processc 2010/09509-5

SYNTHESIS AND CHARACTERIZATION OF MONODISPERSE SILICA NANOSPHERES USING SAXS

Reis, F. V.[1], Cerrutti, B.M.[1], BERTHOLDO, R.[2], Pulcinelli, S.H.[1], and Santilli, C.V.[1]

[1] Universidade Estadual Paulista - Araraquara - Araraquara SP Brazil
[2] Universidade Federal de Alfenas - Alfenas MG Brazil

In this work, silica (SiO_2O) nanospheres presenting diameters between 10 and 50 nm and narrow size distribution were obtained from the hydrolysis of the silica precursor (TEOS) in the presence of aminoacids with a basic character. This system has been extensively studied as it can be prepared with relatively simple syntheses and possesses a variety of applications, in catalysis, high performance liquid chromatography, luminescent materials and in the pharmaceutical and high tech industries. Silica nanospheres have been investigated using small angle X-ray scattering (SAXS), which provides information on the geometry (size and shape) of the particles and on their relative positioning. From the SAXS data we could determine the temporal evolution of the size distribution during the synthesis, in addition to verifying that the particles grew uniformly. Furthermore, the particles were monodisperse and their number was not altered after the initial nucleation stage. In addition, the time duration of the synthesis and the concentration of the catalyst affected the geometry of the particles.

Acknowledgements: Acknowledgements: The authors are grateful to FAPESP CNPq and CAPES for the financial support. LNLS is gratefully acknowledged for the technical support.

Efeito do plasma de oxigênio, nitrogênio e argônio na propriedade de molhabilidade e morfologia do não tecido de polipropileno

Sinézio, J.C.C.[1], Lopes, S.A.[1], Gobbi, A. L.[2], and Piazzetta,O.M.H[2]

[1] Universidade Estadual de Campinas - Campinas SP Brazil
[2] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

O presente trabalho investiga o comportamento de molhabilidade de material não tecido de polipropileno (NTPP), ao ser submetido por tratamento por plasma de oxigênio (O2), nitrogênio (N2) e argônio (Ar). Este não tecido tem aplicação básica em produtos de higiene pessoal, como fraldas e absorventes descartáveis. O polipropileno (PP) confere característica não-polar e hidrofóbica; no sentido de melhorar a hidrofilidade utiliza-se da técnica de tratamento por plasma, a qual quando aplicada de forma adequada pode promover o aumento da molhabilidade, sendo que tal fato esta relacionada com a formação de grupos polares na superfície do material. O tratamento aplicado na superfície do NTPP foi realizado seguindo os mesmos parâmetros (potência, pressão e frequência) para todas as atmosferas citadas. Para quantificar o efeito do tratamento amostras em quintuplicatas são utilizadas em medidas de ângulo (uma gota dágua depositada na superfície do material (gota séssil), espectroscopia de infra vermelho (FTIR/ATR) e microscopia eletrônica exploratória (SEM), ou seja, tais medidas são realizadas antes e após o tratamento. Os resultados, de modo geral e independente do tipo de atmosfera do plasma, mostram que: (i) à medida que o tempo de tratamento por plasma aumenta diminui o ângulo de contato, indicando assim um aumento da molhabilidade; (ii) os espectrogramas (FTIR/ATR) das amostras tratadas revelam a incorporação de grupos polares na superfície e (iii) por SEM observa-se aumento na rugosidade superficial das amostras. Tais fatos indicam que o tratamento efetuado por plasma melhora as propriedades de molhabilidade do material NTPP.

Acknowledgements: CNPq

Formation of an extended $CoSi_2$ thin nanohexagons array coherently buried in silicon single crystal

Requejo, F. G.[1], Kellermann, G.[2], A. F. Craievich[3], Giovanetti, L. J.[4], dos Santos Claro, P. C.[1], Montoro, L. A.[5], and Ramirez, A.J.[5]

[1] Universidad Nacional de La Plata - La PLata B.A. Argentina
[2] Universidade Federal do Paraná - Curitiba PR Brazil
[3] Universidade de São Paulo - São Paulo - São Paulo SP Brazil
[4] Universidad Nacional de La Plata - La Plata Bs.As Argentina
[5] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

A Co-doped silica film was deposited on the surface of a Si(100) wafer and isothermally annealed at 750C. This thermal treatment induced the formation of spherical Co nanoparticles embedded in the silica film and a few atomic layer thick $CoSi_2$ nanoplatelets within the Si(100) wafer. The structure, morphology and spatial orientation of the $CoSi_2$ nanoplatelets incrusted in the Si crystal were characterized by Transmission Electron Microscopy (TEM) and synchrotron Grazing-incidence small-angle X-ray scattering (GISAXS) techniques. The experimental results indicate that the $CoSi_2$ nanoplatelets exhibit a nearly regular hexagonal shape and a uniform thickness. The $CoSi_2$ nanostructures lattice is coherent with the Si lattice and each of them is parallel to one of the four planes belonging to the 111 crystallographic form of the host lattice, indicating a crystal growth with a Si111 habit plane. Furthermore, in order to study the growth kinetics of the formation of these nanostructures, in situ experiments were performed, annealing the samples from room temperature to 750C and following the evolution of the GISAXS signal in the process. TEM studies and GISAXS experiments were performed at the Brazilian Nanotechnology National Laboratory (LME-LNNano) and XRD2 X-ray diffraction beam line of the Brazilian Synchrotron Light Laboratory (LNLS), respectively, in Campinas, Brazil.

Acknowledgements: This work was partially supported by Brazilian Synchrotron Light Laboratory (LNLS), Brazilian Nanotechnology National Laboratory (LME-LNNano), CNPq and FAPESP, Brazil; ANPCYT (PICT 2008-00038) and CONICET (PIP 112-200801-03079), Argentina and CIAM collaborative project (CONICET/CNPq).

Understanding the stability of nickel supported catalysts for reforming of ethanol as addressed by *operando* temperature and spatial resolved XANES analysis

Dantas, S.C.[1], Resende, K. A.[2], Ávila-Neto, C.N.[3], Bueno, J.M.C.[3], and Hori, C. E.[4]

[1] Universidade Federal Rural do Rio de Janeiro - Seropédica RJ Brazil
[2] Universidade Federal de Uberlândia - Ituiutaba MG Brazil
[3] Universidade Federal de São Carlos - São Carlos SP Brazil
[4] Universidade Federal de Uberlandia - Uberlândia MG Brazil

Hydrogen can be produced by steam reforming (SRE) and oxidative steam reforming of ethanol (ORE) catalyzed by metal surfaces. Ni-based catalysts have been studied for both reactions. In this study we tried to elucidate the nature and stability of the Ni species formed in Ni-based catalysts supported on CeO_2, $CeZrO_2$ and alumina in *operando* conditions during SRE and ORE. In general, samples with smaller particle sizes presented higher activity. Also, the redox properties of ceria were not enough to prevent catalyst deactivation by carbon accumulation. Temperature-resolved XANES analyses indicated that the samples supported on alumina showed smaller degree of reduction than those supported on $CeZrO_2$. These samples were more easily oxidized when in the presence of ethanol reforming reagents. Spatial-resolved XANES data indicate that Ni is in oxidized state at the entrance of the catalytic bed. Therefore, Ni^{2+} and Ni^0 species coexist, and Ni^{2+}/Ni^0 ratio decreases slowly throughout the bed. Thus, it is reasonable to suppose the existence of a number of Ni sites on surface that are oxidized. This effect decreases the density of active Ni sites on the surface and creates potential Ni^0/NiO sites for oxidation of adsorbed C*, which helps to maintain catalyst stability during the reaction. The nature of support determines the degree of reduction of Ni under reaction conditions. Also, the Ni^{2+}/Ni^0 ratio is strongly sensitive to the degree of Ni reduction and to the amount of oxidizing reactants (O_2, H_2O). The control of Ni^{2+}/Ni^0 ratio can be accomplished by manipulating Ni clusters size. Furthermore, the composition of the feed can equilibrate the steps of ethanol activation and carbon oxidation, resulting in stable catalysts.

Acknowledgements: The authors would like to thank Vale for the financial support and the Brazilian Synchrotron Light Laboratory (LNLS), which is acknowledged for the use of its facilities and technical support in XANES (DXAS beamline) experiments.

Estudo de XANES *in situ* de nanopartículas de platina suportadas em ceria-alumina aplicadas à reação de deslocamento gás- água

Ribeiro, R.U.[1], Meira, D. M.[1], Zanchet, D.[2], and Bueno, J.M.C.[1]

[1] Universidade Federal de São Carlos - São Carlos SP Brazil
[2] Universidade Estadual de Campinas - Campinas SP Brazil

A reação de deslocamento gás-água (WGS, do inglês *water gas shift*) é uma reação chave na produção de hidrogênio para um grande número de processos tais como a reforma a vapor de hidrocarbonetos como o metano [1]. Estudos na literatura mostram que o mecanismo dessa reação ocorre em rotas bifuncionais e que tanto o metal como o suporte participam da reação. A utilização de nanopartículas de Pt para a síntese dos catalisadores proporcionou a fixação do parâmetro dispersão da fase metálica com o objetivo de investigar o efeito do suporte na atividade catalítica para reação WGS. Para que o mecanismo dessa reação pudesse ser compreendido nanocatalisadores de Pt foram preparados empregando-se três suportes distintos contendo cério. As nanopartículas de Pt foram sintetizadas de acordo com metodologia descrita na literatura e em nossos trabalhos anteriores [2,3]. Os catalisadores foram nomeados: Pt-3Ce-Al, Pt-12Ce-Al e Pt-20Ce-Al preparados pelo método sol-gel de em que o cério foi adicionado na síntese da alumina (3, 12 e 20% de cério em massa, respectivamente). As amostras foram caracterizadas por difração de raios X (XRD) e espectroscopia de absorção de raios X próximo à borda (XANES). Os dados de XANES *in situ*, em condições de reação, mostraram que o estado de oxidação do Ce das amostras com menor teor de Ce é mais susceptível à variação com atmosfera reacional. Essa menor variação no estado de oxidação da amostra Pt-20Ce-Al pode estar associada à segregação do Ce com estrutura fluorita nessa amostra, o que foi confirmado por XRD. A maior variação no estado de oxidação do cério nas amostras contendo menor teor pode estar relacionada ao menor tamanho de partícula de cério. A ativação da H_2O etapa limitante da reação WGS ocorre provavelmente nas vacâncias de Ce(III), destacando assim o feito promotor da Pt no mecanismo de reação. O aumento no teor de cé ria no catalisador favoreceu o aumento de conversão do CO, provavelmente devido à maior concentração de sítios de Ce(III) para a ativação da água na superfície do catalisador. Neste trabalho destacamos que as espécies de cério presentes na superfície do catalisador em condições de reação são influenciadas pela dispersão de Ce dos catalisadores e além disso, a atividade catalítica para a reação de Shift pode estar associada ao efeito de redução de cério com estrutura fluorita promovida pela Pt. [1] I.B. Whittington et al Catal. Today 26 (1995) 4144. [2]H. Song et al. J. Am. Chem. Soc. 128 (2006) 3027. [3]D. M. Meira et al. Anais CICAT-Chile (2010) 200.

Acknowledgements:

XANES in situ e operando de sensores de gás a base de CuO

Volanti, D.P.[1], Felix, A.A.[1], Suman, P. H.[1], Longo, E.[1], Varela, J.A.[1], and Orlandi, M.O.[1]

Universidade Estadual Paulista - Araraquara - Araraquara SP Brazil

Sensores químicos resistivos baseados em dispositivos de óxidos metálicos tem atraído significante atenção devido a sua simplicidade, baixo custo, tamanho reduzido e habilidade de integralização em dispositivos eletrônicos [1]. Este trabalho demostra que o estado de oxidação de sensores a base de CuO bem como estrutura química pode estar relacionados com a resposta de sensibilidade e estabilidade [2]. Assim, o uso da técnica de XANES in situ elucidou a mudança estrutural local de cada sensor em condições de trabalho (operando). Foi estudado a influencia dos gases (CO, H2 e O2) sobre os sensores. Dessa forma, determinou-se o quanto a exposição de um determinado gás pode modificar a estrutura do sensor em uso, ou seja, durante a caracterização elétrica. O entendimento da interação do sensor óxido com os gases em análise poderão contribuir para a aplicação de sensores mais sensíveis e seletivos. Em suma, foi medida a condutividade dos sensores (caracterização elétrica) de CuO para obter informações acerca das propriedades do óxido nanoestruturado quando estes sensor foram submetidos a ciclos de tratamento térmico em atmosfera controlada dos gases analitos. [1]Franke, M E., Koplin, T J., Simon, U., Small 2006, 2, 36-50. [2] Volanti, D P., Felix, A A., Suman, P H., Longo, E., Varela, J A. and Orlandi, M.O. (Artigo em preparação).

Acknowledgements: CNPq, CAPES, Processo FAPESP (2011/02408-1) e Proposta DXAS-11845

Surface Structure Determination of Rh on α-Fe_2O_3/Pd(111) Studied by Angular Photoelectron Diffraction

Pancotti A.[1], G.J.P.Abreu[1], de Siervo A.[1], and Landers R[1]

Universidade Estadual de Campinas - Campinas SP Brazil

In this study we used X-ray photoelectron diffraction to determine the structure of Rh nanoparticles grown on ordered α-Fe_2O_3 supported by a Pd(111) single-crystal. Rh nanaparticles have received much attention for their extraordinary catalytic activity[**1**] for reactions such as low temperature CO oxidation or for the hydrogen production [**2**]. We have determined that Rh nanoparticles exhibits 3D growth on α-Fe_2O_3 thin film and 5.26% of expansion in the lattice parameter relative to Rh bulk. We also show that the interlayer spacings for the first four layers are expanded relative to the interlayer spacing of Rh bulk. Rh nanoparticles were grown epitaxialy on α-Fe_2O_3/Pd(111) by MBE deposition in ultrahigh vacuum ($1.0.10^{-9}$ mBar) and annealed at 700 K which promotes the 3D island coalescence of Rh on the α-Fe_2O_3 surface[3]. The electronic structure and the surface composition were determined by XPS. For low coverage an ordered ($\sqrt{3}$x$\sqrt{3}$)R30^o structure is observed. To determine precisely the atomic structure of the Rh nanoparticles, we used a combination of Low Energy Electron Diffraction (LEED) and Photoelectron Diffraction (PED)[**4**], exploring the forward and multiple scattering regimes, using synchrotron radiation and a conventional x-ray source of Al Kα radiation. The experimental spectra were collected using hemispherical electron analyzer at the Brazilian Synchrotron Laboratory.

[**1**] S. Blügel, M. Weinert, P.H. Dederichs, Phys. Rev. Lett. **60** (1988) 1077

[**2**] D.K. Liguras, D.I. Kondarides, X.E. Verykios, Appl. Catalysis B: Environmental **43** (2003) 345-354

[**3**] H. J. Freund, Catalysis Today **100** (2005) 3-9

[**4**] C. Westphal, Surface Science Reports **50**, 1 (2003)

Acknowledgements: This project was supported by **CNPq**, **FAPESP** and **LNLS**. The authors would like to thanks Gustavo Lorencini, Daiane Chaves, Horácio Moraes, and Camile Ambrósio for help during the experiment setup at the SGM beamline.

Estudo da morfologia de nanocompósitos poliuretana/nanocristais de celulose utilizando espalhamento de raios-X a baixos ângulos.

Pereira, I. M.[1] and Patrício, Patrícia S.[2]

[1] Centro Tecnológico do Exército - Rio de Janeiro RJ Brazil
[2] Centro Federal de Educação Tecnológica de Minas Gerais - Belo Horizonte MG Brazil

Os estudos envolvendo poliuretanas obtidas via dispersão aquosa (WPU) tornaram-se crescente a partir da década de 90. O interesse nesse tipo de material encontra justificativa principalmente na rota sintética do polímero, uma vez que não faz uso de solventes orgânicos e isocianatos aromáticos. Com o intuito de produzir materiais ambientalmente mais corretos, os nanocristais de celulose (NCC) foram utilizados como carga de reforço para a matriz de WPU. A WPU foram preparados segundo a rota de síntese descrita em nossos trabalhos prévios. Além disso, três diferentes nanocompósitos (contendo a mesma concentração de nanocargas) foram produzidos, a partir da introdução dos nanocristais de celulose em diferentes etapas da rota sintética do polímero. O primeiro denominado WPU/NCC-PP, foi obtido a partir da adição dos nanocristais de celulose na etapa de pré-polimerização do WPU. Já aquele designado como WPU/NCC-P, a adição ocorreu na etapa de polimerização e por fim, para o material WPU/NCC os a adição das nanopartículas ocorreu na dispersão finalizada do WPU. Os resultados da análise estrutural e do ensaio mecânico indicaram que os NCC atuam como um poliol quando adicionados na etapa de pré-polimerização (WPU/NCC-PP) ou como extensor de cadeia quando introduzidos na etapa seguinte de polimerização. Estudos de espalhamento de raios-x a baixos ângulos comprovaram alterações morfológicas observadas nos ensaios de tração. Desvios positivos nas curvas de Iq^4 em função de Iq^4, na região de Porod foram observados para todas as amostras. Na região de Guinier, a análise das curvas de lnI em função de q^2, permitiu determinar os valores correspondentes ao raio de giro.

Acknowledgements: Os autores agradecem o apoio das instituições FAPEMIG, CNPq e LNLS.

Comportamento do processo de intumescimento de matrizes híbridas orgânico-inorgânicas para liberação controlada de fármacos utilizando espalhamento de Raio-X a baixo ângulo

MENDES, J.F.[1], Gonçalves, V. C.[1], Lopes, L.[1], Santilli, C.V.[1], Pulcinelli, S.H.[1], and Chiavacci, L.A.[1]

Universidade Estadual Paulista - Araraquara - Araraquara SP Brazil

O uso de matrizes híbridas orgânico-inorgânicas como formadores de filmes para liberação controlada de fármacos apresenta vantagens sobre os sistemas convencionais. Esses materiais são sintetizados através de uma rota química denominada sol-gel e o solvente geralmente utilizado é o tetrahidrofurano (THF), entretanto, esse solvente é muito tóxico para aplicação tópica. Assim sendo, o objetivo desse trabalho foi substituir o THF pelo etanol e analisar a influência desse solvente nas condições de síntese e no processo de intumescimento dessas matrizes. Quatro polímeros foram utilizados: dois à base de polióxidoetileno (PEO) e dois à base de polióxidopropileno. O perfil de intumescimento das matrizes foi avaliado por medidas in situ de SAXS e os resultados revelaram que a substituição do solvente não alterou de forma drástica o intumescimento das matrizes híbridas. Assim, a substituição do THF pelo etanol não alterou as características estruturais das matrizes híbridas nem mesmo o grau de intumescimento, influenciando apenas nas características mecânicas das matrizes.

Acknowledgements: FAPESP, CNPq, PADC-FCF/UNESP

Synthesis of polythiophene-silica hybrid materials

Gonçalves, V. C.[1], Pulcinelli, S.H.[1], and Santilli, C.V.[1]

Universidade Estadual Paulista - Araraquara - Araraquara SP Brazil

The purpose of this work is to obtain polythiophene-silica hybrid materials with these two components linked together through a covalent bond to avoid the phase separation. As a first step to obtain these materials, we prepared copolymers of 3-hexythiophene (3HT) and 3-thienylethyl-N-triethoxylsilylpropyl urethane (3SiT) from 0 until 100 mol% of the 3SiT. Oxidative polymerization in chloroform using ferric chloride was performed to synthesize these materials. It was observed that copolymers with 3SiT content higher than 25 mol% are insoluble in common organic solvents. In addition, the presence of 3SiT unity in the soluble fraction of the copolymers with 0-10 mol% of SiT in chloroform could not be confirmed by FITR and ^{1}H NMR techniques. Then, the powders of copolymers were characterized by FTIR, thermal analysis (DSC and thermogravimetry), XRD, SAXS and ^{29}Si NMR. These characterizations confirmed the presence of SiT unity in these powders, but the alcoxy silane groups from 3SiT units were hydrolyzed and some silanol groups were condensed during the poltyhiophene polymerization. The presence of silica networks is responsible for the insolubility of polythiophene chains containing 3SiT, which limited the application of these materials as thin films.

Acknowledgements: Work supported by CAPES/COFECUB, CNPQ and FAPESP.

Avaliação de soluções aquosas de monômeros e polímeros emulsificados por CTABr utilizando SAXS

Araujo, J. D.[1], Cruz, F. T.[1], Cruz, I.H.[1], Marciniuk, L L[1], and D. Cardoso[1]

Universidade Federal de São Carlos - São Carlos SP Brazil

Atualmente tem-se discutido muito a respeito de fontes alternativas de energia, mas que sejam renováveis e pouco poluentes [1]. O biodiesel tem sido um candidato em potencial a integrar definitivamente a matriz energética, uma vez que já vem sendo utilizado em misturas com o diesel de petróleo [2]. A pesquisa industrial e acadêmica têm-se dedicado na busca de catalisadores heterogêneos mais eficientes de modo a aumentar os rendimentos em biodiesel nas reações de transesterificação. Assim, nosso grupo tem estudado sílica mesoporosa com cátions CTA^+ ocluídos (CTA-MCM-41) para formação de biodiesel [3]. Há uma discussão entre os pesquisadores sobre que mecanismo dominante se estabelece para formação da MCM-41 [4], as duas principais são: a) mecanismo por Direcionador de Cristal Líquido (LTC) ou b) mecanismo cooperativo. Com o objetivo de também esclarecer esse ponto e utilizando uma composição molar de síntese baseada no trabalho de Shumacher [5], foram conduzidos experimentos em que se analisaram amostras aquosas de CTABr em concentrações abaixo da concentração micelar crítica (cmc), e que, portanto não apresenta na solução qualquer formação micelar que caracterize um sistema hexagonal de cristal líquido. Sendo assim, confirmou-se a partir das curvas de SAXS, que não houve a detecção de picos de difração característicos dessa fase, cujos planos de difração seriam (10), (11), (20) e (21). No entanto, os sólidos obtidos a partir dessas soluções aquosas e também as preparadas com monômero e polímero dentro das micelas levaram à formação da fase mesoporosa com organização hexagonal. Deste modo, para nossas condições experimentais o mecanismo predominante é o cooperativo, em que a organização que leva à estrutura hexagonal se dá a partir da interação dos ânions silicato com os cátions CTA^+. Além disso, a partir das análises de SAXS, foi possível verificar nas soluções aquosas micelares expandidas com monômero e também com polímero, que houve uma mudança de perfil da curva quando se aumentou a concentração de monômero nas soluções. Isso indica que houve uma expansão micelar provocada pela inserção do monômero e do polímero. Referências: [1] Zabeti *et al.*. Fuel Proces. Techn.. (2009), 90, 770-777. [2] Dermibas, A. Energ. Conv. and Manag.. (2009), 50, 14-34. [3] Fabiano *et al.*. J. Catal. (2010), 276, 190-196. [4] Edlar, K. J. Aus. J. Chem. (2005), 58, 627-643; [5] Schumacher, *et al.*. Microp. Mesop. Mater., (1999), 27, 201-206.

Acknowledgements: Ao CNPq e a CAPES pelo suporte financeiro. Aos Físicos da linha SAXS2, Mateus Cardoso e Jean Marie, pela condução dos experimentos.

Effect of the polymer chain length in photochromic hybrid material obtained by sol gel process. FTIR, Uv-Vis and SAXS characterization

Molina, C[1], Sarmento, V.H.V.[2], Ribeiro, S.J.L.[3], and Obara, P. A[4]

[1] Universidade Federal de São Paulo - Diadema SP Brazil
[2] Universidade Federal de Sergipe - São Cristóvão SE Brazil
[3] Universidade Estadual Paulista - Araraquara - Araraquara SP Brazil
[4] Universidade Federal de São Paulo - Sao Paulo SP Brazil

Photochromism refers to the effect observed when materials change its color in a reversible way under ultraviolet, visible or infrared irradiation [1]. This behavior is promising for many applications such as sensors, information storage and smart windows. Organic inorganic hybrid materials obtained by sol gel process are interesting host suitable to incorporate active molecules such as rare earth and polyoxomethalates (POMs)[2]. These hybrids so called di-ureasil are represented by U(Y) (with Y = 230 or 1900) were U represents the urea groups and Y denotes the average molecular weight of the polymer chain. In this work, we studied the effect of the polymer chain length containing different concentration of phosphotungstic acid (PWA). Interaction between PWA and polymer chain for both xerogels with short and long polymer chain were characterized by FTIR, UV-vis and SAXS. FTIR show that PWA molecules are located at the region of the ether-type oxygens of the polymer chain. Preliminary results from SAXS measurements show a single peak in wich the average distance between siloxane clusters, ds, were estimated 2 nm by using ds = 2 pi/ qmax. For the long hybrid polymer chain, FTIR suggest that the coordenation of PWA are located at the region of the carbonyl groups of the urea groups in the polymer chain. SAXS measurements show a single peak in wich the average distance between siloxane clusters, ds, were estimated 4 nm[3]. Photochromic behavior was observed for both hybrids by exposure to UV irradiation (UV lamp) and its color change from transparent in visible region to blue in which W^{6+} species are reduced to W^{5+} due to d-d transition bands and intervalence charge transfer after UV exposure. Furthermore, the effect is reversible taking less than 1 hour for short chain and 1 week for long ones in the presence of the air. As conclusion, polymer chain has a direct relationship with photochromic behavior. [1] He Tao; Yao, J.; Progress in Materials Science. 51, 810 (2006) [2] Huang, Y.; Qing, Y. P.; Dong, X. W.; Cheng, Z. X . Mater. Chem. Phys. 97, 431 (2006) [3] P. A. Obara; S. J. L. Ribeiro; V. H. V. Sarmento; C. Molina (em execução)

Acknowledgements: Authors acknowledge FAPESP agency, LMH and LaMF

Parte X

Projetos dos Bolsistas de Verão

Estudo da utilização da microscopia eletrônica de varredura para macromoléculas biológicas preparadas com sais de metais pesados

Costa, V. Z.[1] and Bettini J.[2]

[1] Universidade Federal de Santa Catarina - Florianópolis SC Brazil
[2] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

O estudo de macromoléculas biológicas por microscopia eletrônica de transmissão está estabelecido há décadas. Para amostras com baixa massa molecular a utilização de sais de metal pesado aumenta o contraste apresentado nas imagens. A microscopia eletrônica de transmissão por varredura é uma técnica que possibilita melhorar ainda mais o contraste das imagens de macromoléculas biológicas preparadas com sais de metal pesado, tanto pela maior interação com a amostra devido a baixa aceleração utilizada, quanto pelo próprio modo de transmissão por varredura. Neste projeto, o bolsista aprenderá a utilizar um microscópio eletrônico de varredura em modo transmissão e analisará a relação sinal/ruído entre as imagem de microscopia eletrônica de transmissão e microscopia eletrônica de transmissão por varredura para diferentes sais metálicos.

Acknowledgements:

Estudo do uso de séries de imagens de microscopia eletrônica de transmissão para análise de partícula única

Sassi, L. M.[1] and Portugal, R. V.[2]

[1] Universidade Federal do Rio de Janeiro - Rio de Janeiro RJ Brazil
[2] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

Crio-microscopia eletrônica e análise de partícula única são técnicas que visam a obtenção de modelos estruturais de complexos macromoleculares. A amostra é congelada em gelo amorfo e em seguida milhares de imagens de partículas individuais de proteínas, em diferentes orientações, são coletadas em um microscópio eletrônico de transmissão. Posteriormente, essas imagens são processadas para obtenção do modelo estrutural da macromolécula. Entretanto, ao se utilizar a microscopia eletrônica de transmissão para aquisição de dados de amostras biológicas, o dano por radiação torna-se um fator de limitação da resolução, devendo ser evitado. Para isso, a aquisição de dados é feita em regime de baixa dose (entre 10 e 20 e^-/A^2), ocasionando perda da relação sinal/ruído nas imagens obtidas. Sendo assim, há necessidade de se buscar a minimização do dano à amostra, obtendo-se contraste suficiente para visualização e processamento das imagens. Visto que o dano por radiação está relacionado à dose aplicada na amostra, uma das possibilidades para evitá-lo é a aquisição de séries de imagens, com doses abaixo do limite de dano. Em seguida, essas imagens podem ser somadas, melhorando a relação sinal/ruído sem ocasionar dano por radiação à proteína. Nesse projeto, será investigado, através do uso de nanopartículas de ouro, a possibilidade de obtenção de imagens de alta resolução, para análise de partícula única, através da aquisições de séries de imagens.

Acknowledgements:

Growth and characterization of InAs self-assembled islands

Neto, P. M.[1] and Deneke, C.[2]

[1] Universidade Federal de Minas Gerais - Belo Horizonte MG Brazil
[2] Laboratório Nacional de Nanotecnologia - Campinas SP Brazil

Self-assembled semiconductor nanostructures are one of the largest research areas in the last three decades. One of the ways to fabricate these structures is the self-assembled growth by molecular beam epitaxy (MBE). Developed in the in the 70s of the last century, it is one of the most precise and well established thin film growth methods available. MBE is used to produce high quality semiconductor nanostructures with a wide range of applications form laser to elements for quantum computing.

In this project, we want to establish the growth of self-assembled InAs islands, sometimes also called self-assembled quantum dots, in our new MBE chamber. Therefore, a systematic growth study of InAs islands on top of GaAs (001) substrates will be carried out. Fabricated structures should be characterized mainly by atomic force microscopy (AFM) as well as various other microscopy techniques. Parameters of interest includes island shape and density as function of growth parameter like substrate temperature, Arsenic counter pressure and InAs deposition rate. Finally, if a good InAs island growth is achieved, structures can be characterized by x-ray diffraction using the facilities of the LNLS. A successful work will not only contribute to the establishment of the MBE growth to the institute, but should also provide a first set of samples of interest for further research projects.

Acknowledgements:

Estudo de catalisadores de metais de transição suportados em ZnO para a reforma do etanol

Felipe Ramsés, H. R.[1] and Oliveira, D. C.[1]

Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

As reações de reforma do etanol através de processos catalíticos são amplamente estudadas para a obtenção de hidrogênio. Neste trabalho foram preparadas diferentes composições de catalisadores bimetálicos (Ni-Fe e Ni-Cu, suportados em ZnO, modificados ou não por Ag) para realização de testes catalíticos de reforma a vapor do etanol. Os testes catalíticos foram realizados em uma unidade catalítica manual, que consiste de um reator de quartzo, um forno, um controlador de temperatura, gases e controladores de fluxo de gases. Os catalisadores foram ativados sob fluxo de hidrogênio diluído em hélio e posteriormente foram submetidos à atmosfera de vapor de água e de etanol arrastados por hélio para a síntese de hidrogênio sob diferentes temperaturas. A avaliação da atividade catalítica foi realizada comparativamente pelo estudo dos gases residuais por um espectrômetro de massas acoplado na saída do reator.
A caracterização dos catalisadores foi realizada por espectroscopia de fotoelétrons (XPS), com o objetivo de determinar as composições metálicas da superfície dos materiais (composição química e estado de oxidação) antes e depois dos testes catalíticos e correlacionar com os resultados de obtenção de hidrogênio a partir da reforma do etanol. Além disso, foram realizados experimentos de e espectroscopia de absorção de raios X (XANES) *in situ*, onde as propriedades de estado de oxidação, vizinhança química e geometria ao redor dos átomos de interesse podem fornecer informações importantes a respeito do mecanismo de ativação e reação dos catalisadores.

Acknowledgements: Ao LNLS pelo uso das linhas de luz e XPS

The phosphate-binding protein PstS and its involvement in citrus canker disease caused by Xanthomonas citri and viability of the bacteria

Arantes, M. R.[1] and Balan, A.[2]

[1] Universidade Federal do Ceará - Fortaleza CE Brazil
[2] Laboratório Nacional de Biociências - Campinas SP Brazil

Xanthomonas citri is a phytopathogenic bacterium that causes citrus canker, a disease that affects millions of plants in Brazil and the world leading to significant economic losses. Understanding how the bacteria attacks the plants and the pathways that are important for pathogenesis will be of great advantage to the development of inhibitors and drugs for containment of this microorganism. In this context, our group has worked on structural and functional characterization of a family of proteins of the type ABC transporters, involved in the transport of various molecules, from small ions to sugars and polypeptides. These transporters are composed of two integral membrane domains that form the pore passage, two ATPases to provide energy to transport and a periplasmic binding protein that is responsible for the capture and transport of ligand to the membrane. In order to characterize the importance of the phosphate transporter, we constructed a mutant of X. citri, carrying the deletion of the gene encoding the periplasmic protein PstS. In this project, we intend to evaluate the growth of the mutant compared with the wild strain in both in vitro and in vivo, in plants of sweet orange or Citrus sinensis. This will be performed by the following experiments: (i) growth curves of strains of interest in different culture media with or without phosphate (ii) infection of plants of C. sinensis with the strains and phenotypic analysis of the development of citrus canker for 3 weeks, (iii) infection of plants with mutant and wild type and comparison of growth in vivo; (iv) structural characterization of the protein PstS by molecular modeling and determination of possible sites of interaction with ligands or inhibitors, (v) determining the role of PstS and its carrier protein for growth and viability of bacteria and development of cancer by X. citri.

Acknowledgements: ABTLuS e CNPEM

DEVELOPMENT OF A RECOMBINANT LENTIVIRAL SYSTEM WHICH ALLOWS HIGH FLEXIBILITY TO CHANGE PROMOTERS AND EXPRESSION CASSETTES

Manrique, A.J[1] and Marcio, C Bajgelman[1]

Laboratório Nacional de Biociências - Campinas SP Brazil

Lentiviral vectors are widely used as a gene transfer tool because they can efficiently integrate in the cell genome, have low immunogenicity, can be extensively modified to produce recombinant particles, can be engineered to be defective and are relatively straightforward to produce. These features allow the establishment of permanent cell lines, and also the generation of transgenic animals expressing transgenes or even RNAi to several applications as gene function studies, production of recombinant protein and gene therapy.

The engineering of a recombinant lentiviral vector relies on designing a plasmid backbone which encodes the expression cassette, promoter or gene of interest replacing pathogenic viral genes, and/or genes dedicated to replication. Therefore, to produce the virus, this plasmid should be transfected to a packaging cell line which provides the replication genes in trans. The modifications at the plasmid backbone are carried out using molecular biology techniques, restriction and modification enzymes. The efficiency of these procedures are prone to a lot of variation due different parameters, and can be time consuming. Aiming to enhance flexibility and to speed up the vector construction we are generating a lentiviral platform which encodes recombination elements instead the multiple cloning site. Vectors that incorporate these elements could be recombined with commercial plasmids to generate the viral backbone. These commercial plasmids can be easily modified, cloned and sequenced and are components of the gateway system (Invitrogen-USA). The Gateway system allows in vitro recombination and negative selection of parental vectors.

In this way, the recombinant lentiviral plasmid encoding gateway recombination sites and the negative selection marker can be recombined, in vitro, with a donor plasmid which encodes the gene of interest, promoter or expression cassette. The recombinant plasmid integrates the viral backbone and can be used for virus production. Development of this recombination system contributes to enhance viral vector engineering.

Acknowledgements: This work was supported by the program Bolsas de verão of CNPEM and CNPq

Avaliação de possíveis rotas tecnológicas para estocagem de energia/carbono na usina a partir do uso da palha de cana-de-açúcar. Aspectos técnicos e econômicos

Montoya, J.C[1], Olivares, E.G.[2], and C. Vaz Rossell[2]

[1] Universidad Tecnológica Nacional - Facultad Regional Córdoba - CORDOBA Argentina
[2] Centro de Ciência e Tecnologia do Bioetanol - Campinas SP Brazil

No Brasil, açúcar, etanol (principalmente álcool carburante) e uma determinada parcela de energia elétrica são produzidos a partir de uma única matéria-prima, a cana-de-açúcar. Dentre os subprodutos biomássicos da indústria da cana a palha de cana está ganhando cada vez mais espaço devido ao seu elevado potencial teórico de uso para a produção de energia e outros produtos. Dentre as aplicações energéticas para a palha de cana aquela relacionada com a produção de energia elétrica, através de empreendimentos em cogeraçáo de energia, estáo atraindo a atençáo das usinas e empresas do setor energético em geral. Entretanto, estudos realizados na Austrália (**THORBURN,2011**) mostram que prováveis impactos negativos da retirada da palha do campo, relacionados com aspectos agronômicos e custos significativos nos processos ligados à cadeia de aproveitamento deste material podem inviabilizar projetos deste tipo. Em este trabalho apresentam-se os resultados preliminares de um estudo técnico-econômico realizado com base em diferentes rotas tecnológicas para realizar a estocagem de energia/carbono na usina sucroenergética sob diversas formas energéticas. As rotas avaliadas foram: cana integral, palha a granel, fardos, briquetes in natura, briquetes torrados (pré-carvão), pellets e óleos pirolíticos. Os modelos correspondentes a cada fluxograma de processo (flowsheet) foram desenvolvidos usando-se o software Superpro Designer 8.0. Os resultados mostram a relevante importância de otimizar cada operação unitária considerada.

Acknowledgements: Os autores agradecem a colaboração do Engenheiro em Alimentos João Paulo Fernades Vieira, doutorando pela Faculdade de Engenharia Química FEQ da Universidade Estadual de Campinas UNICAMP, e ao Programa de Bolsas de Verão do CNPEM pela Bolsa otorgada.

Síntese e funcionalização de sílica mesoporosa com propriedades bactericidas

Borges, R. M.[1], de Oliveira, L. F.[2], and Cardoso, M.B.[2]

[1] Universidade Federal de Ouro Preto - Ouro Preto MG Brazil
[2] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

Atualmente, a infecção bacteriana é um problema de saúde pública persistente e grave. Muitas vezes, essas infecções são originadas por colônias bacterianas em dispositivos cirúrgicos. Diante disso, a primeira medida a ser tomada para reduzir estas infecções é inibir a proliferação bacteriana em dispositivos cirúrgicos. Recentemente, uma ampla gama de métodos antimicrobianos foram testados recorrendo tanto a modificação da superfície quanto a aplicação de revestimentos que seriam capazes de resistir à adesão celular. Esses procedimentos invariavelmente aumentam o custo global da produção de dispositivos e, geralmente, não são eficazes para evitar a colonização ao longo do tempo. Dentro deste contexto, suportes sólidos têm sido usados para imobilizar diferentes moléculas através de adsorção, encapsulamento e ligação covalente. O aprisionamento de uma variedade de biomoléculas tem sido feito com sucesso em sílica mesoporosa para a obtenção de materiais com propriedades estruturais e funcionais adaptados. A funcionalização da superfície de sílica mesoporosa com um grupo orgânico adequado pode melhorar a interação de proteínas com o suporte sólido e aumentar a operacionalidade da proteína imobilizada. Portanto, o objetivo deste projeto é realizar a funcionalização de sílica mesoporosa com grupos orgânicos, para posterior ligação covalente com a lisozima. Para estudar as propriedades estruturais e estabilidade do composto, o material será caracterizado por microscopia eletrônica de varredura e de trasmissão, BET(adsorção-dessorção de nitrogênio), SAXS (espalhamento de raio-X em baixo ângulo), espectroscopia FT-IR e potencial Zeta. A eficácia antimicrobiana dos compostos será testada contra *Escherichia coli (E. coli)* e *Staphylococcus aureus (S. Aureus)* para demonstrar a retenção das propriedades bactericidas da lisozima.

Acknowledgements: R.M.B. agradece ao CNPEM pela opotunidade de participar de um projeto como bolsista do 21° PROGRAMA BOLSAS DE VERÃO.

Phenotypic and molecular characterization of transgenic citrus plants for resistance to *Xanthomonas citri*.

Sousa Filho, J.C.G[1], Oliveira, M. L. P.[2], and Benedetti C.E.[2]

[1] Universidade Federal de São Carlos - São Carlos SP Brazil
[2] Laboratório Nacional de Biociências - Campinas SP Brazil

Citrus canker, caused by *Xanthomonas citri*, is a bacterial disease that affects most of the commercial citrus varieties leading to economic losses. With the aim of producing citrus plants resistant to *X. citri* our laboratory is developing transgenic lines for citrus rootstock and scion varieties. Based on a large scale gene expression analysis undertaken by the group previously, two strategies for the production of citrus plants resistant to *X. citri* are been used. The first involves the overexpression of a WRKY transcription factor known to regulate basal defense responses in plants. The second strategy involves the expression of a bacterial type III transcription activator effector, or TAL effector, which acts as a modulator of gene expression in the host. The expression of the transgenes will be evaluated by quantitative PCR and Western blot analysis. Transformed plants will be challenged with *X. citri* for the development of canker symptoms, which are characterized by the formation of raised pustules on the leaf surface. The expression levels of a number of defense-related genes as direct targets of the *Xanthomonas* TAL effector will also be examined in the transgenes.

Keywords: *Xanthomonas citri*, TAL effectors, WRKY.

Supported by: FAPESP, CNPq and LNBio.

Acknowledgements:

Estudos estruturais e celulares de complexos formados entre receptores ativadores da proliferação de peroxissomos e outros fatores de transcrição

Osterne, V.J.S[1], Campos, J. L. O.[2], and Figueira, A. C. M.[2]

[1] Universidade Federal do Ceará - Fortaleza CE Brazil
[2] Laboratório Nacional de Biociências - Campinas SP Brazil

Os receptores nucleares são proteínas que atuam como fatores de transcrição sendo responsáveis pela ativação de genes específicos após a ligação de moléculas sinalizadoras como ácidos graxos e hormônios. Eles são caracterizados como reguladores da expressão de genes relacionados ao metabolismo, crescimento celular e diferenciação celular. A regulação transcricional realizada por essas proteínas requer, na maioria das vezes, duas importantes interações: o reconhecimento de elementos responsivos no DNA e a heterodimerização com outros receptores nucleares como, por exemplo, o receptor do ácido retinóico (RXR). Além disso sabe-se atualmente que os receptores nucleares estão envolvidos com diversas patologias importantes como obesidade, cardiopatias, diabetes, hipertensão, sendo que seus efeitos resultam na síndrome metabólica. Por isso, cerca de 10 por cento dos fármacos no mercado atuam direta ou indiretamente nos receptores nucleares. Este projeto visa o entendimento e a busca de complexos relacionados ao receptor ativador da proliferação de peroxissomos (PPAR). Conforme já descrito na literatura, o PPAR pode interagir com proteínas correguladoras (GRIP) e fatores de transcrição (p53). Neste contexto, nosso primeiro objetivo será o de caracterizar biofisicamente a formação de complexos entre PPAR-Grip e PPAR-p53. Para tanto, deverão ser desenvolvidas atividades de expressão e purificação heteróloga desse receptor, formação de complexos, além de ensaios de eletroforese nativa e espalhamento dinâmico de luz. Mais ainda, nosso segundo objetivo será o de buscar a formação de complexos inéditos, em estudos celulares. Nesse caso, deverão ser realizadas subclonagens do receptor, o qual será superexpresso em células de mamíferos. Por fim, os complexos formados dentro das células deverão ser imunoprecipitados e caracterizados por espetrometria de massas. Pretendemos com isso avançar um pouco mais no conhecimento da biologia desse receptor e também, com isso, pretendemos dar um passo a mais na produção de novos fármacos.

Acknowledgements: Esse trabalho foi financiado pelo programa Bolsas de Verão do CNPEM. Agradeço a pesquisadora Ana Carolina Migliorini Figueira e suas orientandas pelo apoio.

Contribuição da palha da cana-de-açúcar para sustentabilidade do etanol

Lombardi, G.M.R.[1] and Carvalho, J. L. N.[2]

[1] Universidade Federal de Lavras - Lavras MG Brazil
[2] Laboratório Nacional de Ciência e Tecnologia do Bioetanol - Campinas SP Brazil

A eliminação da queima da palha da cana-de-açúcar modificou substancialmente o setor sucroenergético na última década. Atualmente, após a colheita do canavial, a palha é deixada na superfície do solo visando à proteção contra erosão, fornecimento de matéria orgânica e nutrientes, manutenção da umidade do solo, dentre outros benefícios. Entretanto, o setor sucroenergético tem exibido uma demanda de retirar esta palha do campo e levar para indústria para a geração de energia e etanol de 2ª geração. Nesse sentido, o objetivo deste projeto é quantificar os benefícios da manutenção da palha da cana-de-açúcar na superfície do solo e fazer uma análise econômica comparativa entre os três cenários de utilização desta palha. Para tanto, será realizada uma revisão de literatura enfocando conteúdo de água no solo, ciclagem de nutrientes, sequestro de carbono e, pragas e doenças do canavial em áreas com presença e ausência de palha na superfície do solo. Ao final deste trabalho, pretende-se valorar os benefícios diretos e indiretos da manutenção da palha no solo e comparar com utilização industrial deste material para obtenção de eletricidade e etanol de 2ª geração. Este resultado poderá contribuir para a discussão sobre quanto deve ser retirada do canavial para fins ser utilizado para fins industriais.

PALAVRAS-CHAVE: água no solo; sequestro de carbono; pragas e doenças; ciclagem de nutrientes; produtividade

Acknowledgements: Agradecemos ao Departamento de Agronomia da Universidade Federal de Lavras e ao Laboratorío Nacional de Ciência e Tecnologia do Bioetanol por auxiliar na realização desse trabalho.

Study of the magnetic vortex properties

Prestes, N. F.[1], Garcia, F.[2], and Bonelle, T.[3]

[1] Universidade Federal do Paraná - Curitiba PR Brazil
[2] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[3] Universidade Estadual de Campinas - Campinas SP Brazil

The vortex is a ground state magnetic structure that occurs in low-dimensional systems. It has a great interest for spintronics and nanomagnetism due to its dimensional scale and its singular magnetization scheme but the most special properties are related to its peculiar core dynamics. In this project we studied the core dynamics under influence of an interaction between the vortex, in a ferromagnetic layer (FM) and an antiferromagnetic layer (AFM). This interaction is called **Exchange bias** and occurs by the exchange coupling at the AFM/FM interface.

Arrays of 3 μm diameters disks of FeNi/FeMn bilayers have been prepared using optical lithography and sputtering. The magnetic characterization it was carried out using Magnetic Optical Kerr Effect, Magnetic Force Microscopy and X-ray Magnetic Circular Dichroism. The dichroism measure was performed at SGM beamline. Using **XMCD** we were capable to study the magnetization of the biased interface, because it can obtain information about magnetization with chemical selectivity. In parallel, it was conducted micromagnetic simulations with a framework called **OOMMF**. The simulations were made in order to study the core dynamic under influence of **Exchange Bias**.

Acknowledgements: LNLS, LME, LMF.

Estudo eletroquímico de dispositivos memristores baseados em óxidos de metais de transição

Natori, W. M. H.[1] and Montoro, L. A.[2]

[1] Universidade Federal de São Carlos - São Carlos SP Brazil
[2] Laboratório Nacional de Nanotecnologia - Campinas SP Brazil

Memristores são componentes eletrônicos que se tornaram bastante populares a partir do trabalho de R.S. Williams e colaboradores da HP Labs em Palo Alto CA [1]. Eles são considerados o quarto componente eletrônico passivo (os outros são o resistor, o capacitor e o indutor), e o seu nome é um acrônimo para a expressão resistor com memória. Sua existência já havia sido prevista teoricamente na década de 1970 [2], com inúmeras possibilidades de aplicação. Diferentemente dos resistores comuns, eles apresentam uma função não-linear entre tensão e corrente, apresentando uma resistência variável como função da carga elétrica e fluxo magnético. Além disso, eles possuem uma memória resistiva; onde suas propriedades não-lineares intrínsecas, e dependentes do tempo, podem ser modificadas e preservadas eletricamente, o que é atrativo para desenvolvimento de memórias não-voláteis. Apesar dos esforços realizados para o entendimento dos mecanismos de funcionamento e na busca por novos materiais, há ainda um enorme interesse para compreender em nível atômico, a origem das mudanças na resistência dos dispositivos e em maneiras para torná-los mais eficientes. Ainda não existe um consenso na literatura a respeito dos mecanismos responsáveis pela memresistência, sendo mais comum a utilização de modelos da física do estado sólido. Existem evidências, porém, da ocorrência de reações redox em alguns dispositivos, o que faria com que os modelos atualmente utilizados estivessem negligenciando importantes mecanismos químicos associados a este fenômeno. O projeto abordará o memristor do ponto de vista eletroquímico, caracterizando-o como uma célula eletroquímica de estado sólido. Para isto, serão realizadas medidas potenciostáticas e galvanostáticas sobre dispositivos baseados em óxidos de metais de transição, bem como medidas de espectroscopia de impedância eletroquímica. Estes dados fornecerão evidências experimentais que irão contribuir para o esclarecimento dos mecanismos de memresistência, além de possibilitar a verificação da ocorrência de reações redox nos eletrodos. Esperamos obter dados que comprovem o modelo eletroquímico dos memristores e que possam ser utilizados em modelos úteis em futuras pesquisas com estes dispositivos.

[1] R.S. Williams, et al. Nature, 453, 80 (2008)

[2] L.O. Chua, IEEE Trans. Ciucuit Theory, 18, 507 (1971)

Acknowledgements: Agradeço ao CNPEM.

Potential nanostructures for cancer therapy by hyperthermia: synthesis and study of structural and magnetic properties

E. C. Mendonça[1], Wender, H.[2], dos Reis,R.D.[3], Cardoso, M.B.[2], and Garcia, F.[2]

[1] Universidade Federal de Sergipe - São Cristóvão SE Brazil
[2] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[3] Universidade Estadual de Campinas - Campinas SP Brazil

Regarding the developing of potential nanomaterials for the cancer therapy by magnetic hyperthermia, hematite (α-Fe_2O_3) nanorings (NAs) and nanotubes (NTs) were synthesized via a hydrothermal process using $FeCl_3$ and phosphate and sulfate ions as dissolving agents. After that, nickel, cobalt and magnesium ferrites were obtained by a solid state reaction using the NAs and NTs as template. The morphological properties were investigated by transmission electron microscopy (TEM) and field emission scanning electron microscopy (FEG-SEM) showing the formation of NAs of $\sim$ 130 nm of external diameter, 50 nm of internal diameter and 90 nm of thickness. The NTs showed similar diameters, however, with an expected enlarged thickness of $\sim$ 400 nm. Both kept their characteristic after the solid state reaction for the formation of NAs and NTs ferrites. The results indicate that the NAs and NTs are single crystals with a ring axis in the [001] direction probably due to adsorption of phosphate ions on those crystalline facets. The structural and magnetic properties were studied by X-ray diffraction (XRD), X-ray absorption spectroscopy (XAS), X-ray magnetic circular dichroism (XMCD) and conventional magnetization. The materials showed potential properties for heat generation in a alternating magnetic field regarding cancer therapy by hyperthermia, whose experiments are under development.

Acknowledgements: The authors would like to thank LNNano by the scanning and transmission electron microscopes (proposals numbers 12765, 12399 and 13057), XAFS2 and SGM stuff for support during synchrotron based experiments and the CNPEM for acceptance of E.C.M. in the “21° Programa Bolsas de Verão”.

ASPERGILLUS NIDULANS COMO MODELO PARA EXPRESSÃO HETERÓLOGA DE CELULASES E HEMICELULASES

Oliveira, J. P.[1], Oliveira, D. M.[2], Almeida, R.F.[3], Segato, F[4], Damasio, A. R. L.[4], and Squina, F. M.[5]

[1] Universidade Federal de São Carlos - São Carlos SP Brazil
[2] Universidade Estadual de Maringá - Maringá PR Brazil
[3] Universidade Paulista - Campinas SP Brazil
[4] Laboratório Nacional de Ciência e Tecnologia do Bioetanol - Campinas SP Brazil
[5] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

No âmbito da energia renovável, o pré tratamento enzimático da biomassa está se tornando uma alternativa mais atraente do que a utilização de pré-tratamentos químicos ou processos mecânicos. A bioconversão de resíduos agro industriais através da catálise enzimática, apresenta grande potencial para produção de bioenergia em substituição a combustíveis fósseis. A atração de fungos filamentosos como maquinaria de expressão é baseada em sua habilidade natural em secretar grandes quantidades de proteínas (principalmente enzimas hidrolíticas) para o meio de cultivo. O principal foco desta proposta é consolidar *Aspergillus nidulans* (linhagem A773) como um modelo rápido e estável para expressão e secreção heteróloga de celulases e hemicelulases. Para este estudo utilizaremos o fungo filamentoso *Aspergillus niveus* como fonte para clonagem de um gene que codifica para uma xiloendoglucanase (EC 3.2.1.151) da família GH74. Desenvolveremos estudos bioquímicos (pH, temperatura, Km e Vmax), funcionais (análise de produtos de hidrólises) e, se possível, estudos estruturais preliminares (CD).

Acknowledgements: JPO e DMO são bolsistas do 21^o Programa Bolsas de Verão do Centro Nacional de Pesquisa em Energia e Materiais (CNPEM). ARLD é bolsista da FAPESP (2011021697). FS é bolsista PNPD CNPq.

Caracterização de um sistema de imagens de alta resolução para utilização em tomografia de raios X

Pontes, T. F.[1], MIGUEL, D. I.[2], Pérez, C. A.[2], Isaac, A.[2], and Ferreira, V. T.[2]

[1] Universidade Católica de Pelotas - Pelotas RS Brazil
[2] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

O Laboratório Nacional de Luz Síncrotron está direcionando esforços na construção de uma estação experimental dedicada à técnica de imagem e tomografia de raios X IMX. Além da técnica convencional de tomografia por absorção, será também utilizado um interferômetro de raios X na IMX (Interferômetro de Talbot), o qual possibilitará a aquisição de imagens de contraste de fase. O presente projeto de pesquisa teve como objetivo contribuir para este processo de implementação da técnica de tomografia de raios X no LNLS. Experimentos preliminares foram realizados na linha de Fluorescência de Raios X XRF, tendo como principal enfoque a caracterização de novos equipamentos adquiridos e sua integração à linha de luz. Mais especificamente, um sistema de detecção de imagens de alta resolução, que consiste de uma tela luminescente, um conjunto de lentes e um fotodetector (i.e. um dispositivo de carga acoplada ou CCD), foi caracterizado no que se refere à sua resolução espacial e linearidade de resposta, dentre outros fatores. Este sistema de imagens foi integrado à linha de luz de modo a automatizar o processo de obtenção das projeções, para tal foram utilizados recursos da linguagem C++ visando à comunicação entre o *software* de controle da CCD e de controle da linha 3-Windcm.

Acknowledgements:

Caracterização bioquímica e produção de enzimas recombinantes para suplementação de coquetéis enzimáticos aplicados na conversão eficiente de biomassas vegetais

Kashiwagi, F. M.[1], Diogo, J. A.[2], Almeida, G. B.[2], Hoffmam,Z.B.[3], Delabona, P. S.[3], Pradella, J.G.C.[3], Freitas, S. S.[2], Squina, F. M.[4], and Ruller,R.[5]

[1] Universidade Federal do Paraná - Curitiba PR Brazil
[2] Universidade Estadual de Campinas - Campinas SP Brazil
[3] Laboratório Nacional de Ciência e Tecnologia do Bioetanol - Campinas SP Brazil
[4] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil
[5] Laboratório Nacional de Ciência e Tecnologia do Bioetanol - CAMPINAS SP Brazil

Tem-se buscado alternativas viáveis para aumentar expressivamente a produção de etanol sem aumento da área plantada. Consensualmente, a mais promissora é produzir etanol a partir da biomassa gerada como resíduo na produção do álcool de primeira geração. Para tanto, é necessário hidrolisar essa biomassa e liberar açúcares fermentescíveis. Porém, dada à recalcitrância dos resíduos, é complexa a tarefa de propor um processo de hidrólise eficiente, de baixo custo e que não gere compostos tóxicos que diminuem o rendimento da etapa de fermentação posterior. Nesse sentido, hidrolisar completamente a biomassa depende da ação sinérgica de várias atividades catalíticas distintas, principalmente celulases e hemicelulases, com as quais se espera obter níveis sinérgicos de rendimento para sacarificação destes polímeros complexos. O presente projeto terá como foco principal estudar os dois grupos principais de enzimas (hemicelulases e celulases) e uma ligninase (lacase) de *Bacillus subtilis*. Uma vez concluída todas as etapas de manipulação de DNA e clonado os genes de interesse, estes genes serão submetidos a testes de expressão em duas linhagens diferentes de *Escherichia coli* (BL21 e Rosetta-gami2), onde serão avaliados tempo de expressão, quantidade e solubilidade da enzima recombinante. A linhagem e a enzima avaliada, apresentando a melhor solubilidade e mais altos níveis de produção, será alvo de estudos de purificação e análise bioquímica (pH ótimo, temperatura e efeitos de íons). Uma vez otimizada a expressão destes genes alvo (celulases, hemicelulases e ligninase), estas enzimas recombinantes deverão ser utilizadas na suplementação de coquetéis fúngicos, para avaliar a melhor combinação enzimática e iniciar os primeiros passos no desenvolvimento de um coquetel sintético protótipo para hidrólise eficiente da biomassa da cana de açúcar.

Acknowledgements: Este trabalho foi realizado com o apoio de CNPEM, pelo programa Bolsas de Verão.

Modelamento e simulação de uma fonte de corrente usando topologia Full-Bridge

BAADER, J. E.[1], Rodrigues, C.[2], and Tavares, D. O.[2]

[1] Fundação Universidade Regional de Blumenau - Blumenau SC Brazil
[2] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

Uma fonte de corrente de alta precisão, denominada modelo PSB, baseada em um conversor DC/DC com topologia full-bridge e filtro amortecido de segunda ordem (Praeg) foi desenvolvida pelo Grupo de Eletrônica de Potência (ELP) do Laboratório Nacional de Luz Síncrotron (LNLS). Trata-se de fontes de corrente responsáveis por alimentar as Bobinas Corretoras de Órbitas do anel. Dez unidades foram construídas, dos quais oito estão em operação, apresentando um comportamento satisfatório até o presente momento. No entanto, não houve tempo para um estudo completo e sistemático dessa fonte a fim de que se obtivesse uma solução otimizada. Como mais 60 unidades estão sendo construídas, este projeto tem o propósito de elaborar um modelo matemático que descreve com precisão aceitável a operacionalidade da fonte, permitindo assim verificar se os valores adotados para os componentes são os mais adequados, propondo modificações em caso contrário. Simulações usando o software Matlab deverão ser usadas para validar o modelo, com base em comparações com resultados práticos obtidos. Em seguida, novas simulações serão usadas para testar modificações no circuito original, visando melhorar seu desempenho.

Acknowledgements: LNLS

EXPRESSÃO HETERÓLOGA DE HIDROLASES FÚNGICAS COM POTENCIAL BIOTECNÓLOGICO NA SACARIFICAÇÃO DE BIOMASSA DE CANA-DE-AÇÚCAR

Oliveira, D. M.[1], Oliveira, J. P.[2], Almeida, R.F.[3], Dias, B. A.[4], Damasio, A. R. L.[5], Squina, F. M.[6], and Segato, F[5]

[1] Universidade Estadual de Maringá - Maringá PR Brazil
[2] Universidade Federal de São Carlos - São Carlos SP Brazil
[3] Universidade Paulista - Campinas SP Brazil
[4] Centro de Ciência e Tecnologia do Bioetanol - Campinas SP Brazil
[5] Laboratório Nacional de Ciência e Tecnologia do Bioetanol - Campinas SP Brazil
[6] Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

O uso da biomassa como fonte de energia renovável, apresenta uma importante contribuição para o desenvolvimento de uma sociedade industrial sustentável e que virá a contribuir para a diminuição do efeito estufa. Materiais lignocelulósicos, como resíduos agroflorestais são fontes de energias estocadas e de baixo custo presentes na biosfera. Portanto, a conversão da biomassa em açúcares tem movimentado indústrias responsáveis pela produção de biocombustíveis. No entanto, a sacarificação da biomassa tem se mostrado como um processo lento e complicado, devido a recalcitrância e complexidade dos polímeros da parede celular das plantas. Os materiais lignocelulósicos devem ser submetidos a etapas de pré-tratamento, após os quais devem ser tratados com coquetéis enzimáticos para sua degradação em açúcares simples, que podem ser utilizados na fermentação para a produção de etanol. Visando a completa utilização dos polissacarídeos presentes na parede celular como fonte renovável de energia, um extensivo repertório de enzimas hidrolíticas com diferentes especificidades são necessárias para a produção de biocombustíveis. Sendo assim, o objetivo deste trabalho é a geração de uma biblioteca enzimática que poderá ser estudada para aplicações biotecnológicas, incluindo o uso destas enzimas em estudos para a produção efetiva de etanol de segunda geração. Desta maneira propõe-se o estudo e a prospecção de um conjunto de enzimas de diferentes fungos filamentosos. Adicionalmente este estudo deve contribuir extensivamente para o desenvolvimento e melhorias no campo de bioenergia com técnicas de detecção de hidrólise e implementando a expressão heteróloga em fungos filamentosos.

Acknowledgements: Este trabalho foi realizado com o apoio do CNPEM, com a concessão da bolsa de verão, ao CTBE pela infra-estrutura fornecida, a F.S. pela orientação no projeto, a F.M.S., J.P.O., R.F.A., B.A.D., A.R.D. que contribuíram com este projeto e toda equipe do Laboratório de Biologia Molecular.

Estudo de transições estruturais em dispersões de lipossomas utilizando a técnica de SAXS

Puentes, X.[1], Cavalcanti, L. P.[1], and Gasperini, A. A.[1]

Laboratório Nacional de Luz Síncrotron - Campinas SP Brazil

Dispersões de lipossomas são utilizadas como carreadores de fármaco para facilitar o transporte, diminuir a toxicidade e controlar a liberação do fármaco no sítio de ação. Algumas vezes é necessária a combinação de diferentes lipídios ou mesmo de agentes surfactantes para controlar sua estabilidade. Um dos muitos processos de preparação de lipossomas inclui o emprego de ultrassom para diminuir o número de bicamadas de lipídeos, o que facilita a liberação do fármaco. SAXS é uma das técnicas utilizadas para o controle da estrutura de lipossomas para suas diversas aplicações. No projeto estudaremos as modificações estruturais das bicamadas lipídicas induzidas pela introdução de um agente surfactante durante um experimento *in situ* previamente realizado. Isto será feito através da modelagem, simulação do espalhamento de raios X a baixos ângulos e comparação com os dados coletados. Numa segunda parte do projeto propomos um experimento de monitoramento *in situ* da estrutura de empacotamento molecular de uma dispersão de lipossomas multilamelares durante exposição à agitação mecânica. Para tanto, faremos uma introdução aos métodos de preparação de lipossomas e a montagem do experimento na linha SAXS2 do LNLS. Por fim, iniciaremos a simulação e ajuste dos dados experimentais obtidos utilizando modelos propostos na literatura.

Acknowledgements: Agradecemos ao CNPq e ao CNPEM pelo auxílio financeiro

Análise de Nanofios Heteroestruturados via Microscopia Eletrônica de Transmissão

Silva Y. C.[1], Oliveira, S. O.[2], T. Chiaramonte[3], Cotta, M.A.[2], and Zagonel, L. F.[4]

[1] Universidade Federal do Ceará - FORTALEZA CE Brazil
[2] Universidade Estadual de Campinas - Campinas SP Brazil
[3] Universidade Federal de São João del Rei - São João del Rei MG Brazil
[4] Laboratório Nacional de Nanotecnologia - Campinas SP Brazil

A física dos semicondutores apresenta diversas aplicações tecnológicas e, por possibilitar a construção de estruturas complexas, auto-organizadas e livres de defeitos, a preparação de nanofios representa uma importante linha de pesquisa. O objetivo deste trabalho é estudar o crescimento de nanofios III-V e determinar a morfologia de nanofios heteroestruturados de semicondutores III-V. Os nanofios propostos à análise neste projeto foram crescidos pelo método VLS (Vapor - Líquido - Sólido) e apresentam duas regiões de compostos binários, InP e InAs, e uma camada de composto ternário, $In_xAs_{1-x}P$, crescida entre as anteriores. A versatilidade desta técnica, capaz de formar heteroestruturas, tem grande importância e permite, entre outros, a formação de poços quânticos devido à combinação de materiais com diferentes propriedades eletrônicas. Estas estruturas podem ser projetadas visando novos dispositivos de alto desempenho que explorem processos físicos em semicondutores de baixa dimensionalidade. A morfologia dos fios será analisada via microscopia eletrônica de transmissão (MET) e a composição química será mapeada através de espectroscopia de raios-x dispersiva em energia (EDS). A análise EDS determinará a variação da composição química ao longo do comprimento do nanofio, permitindo o estudo das interfaces entres as heteroestruturas. Também será estudado o mecanismo de crescimento e o papel do catalisador.

Acknowledgements:

Development of an activity assay for detection of anti-tumor compounds.

Venegas, F.A.[1], Gonçalves, K. A.[2], and Dias, SMG[2]

[1] Universidad de Chile - Santiago Chile
[2] Laboratório Nacional de Biociências - Campinas SP Brazil

Although tumor cells are simultaneously expose to a variety of nutrients, the intensive uptake of both glucose and glutamine (the most abundant aminoacid in the plasma) is a metabolic hallmark for tumor transformation. The aerobic metabolism of glucose (also known as the Warburg effect), and high levels of glutaminolysis in cancers cells supply for the high energetic and biosynthetic demands. A strong effect of the intensification of these pathways is the increase on the secretion of lactate by the tumor cells. The search of compounds capable of inhibiting enzymes of the glycolytic and glutaminolytic pathways is a recent new opportunity on the development of new cancer therapies, with the promise of high efficiency and range of action, since they are based on common elements of these type of cells: the metabolism reprogramming focused on promoting biosynthetic activity. The therapy with anti-glycolytic and anti-glutaminolytic compounds has the potential to stop cell proliferation and induce apoptosis, reduce the drug resistance of tumor cells related to hypoxia, enhance the cytotoxic effects of other drugs already in use and finally increase selectivity and reduce the phenotype of multidrug resistance ATP-dependent. The goal of this project is to develop a biological assay aiming at the search for inhibitors of the glycolytic and glutaminolytic pathways. The bioassay is composed of the enzyme lactate dehydrogenase (LDH), which promotes the covertion of lactate to pyruvate, using NAD as a proton acceptor to produce NADH. The NADH is used to reduce the compound rezasurin releasing resorufin (a fluorescent compound) in the presence of the enzyme diaphorase. The developed assay is currently being usedto detect differences in lactate levels secreted by four different tumor cells (two of breast cancer and two of prostate cancer), evaluated in two conditions, with and without treatment using one anti-glutaminolytic compound (2-deoxyglucose) and two inhibitors of the glutaminase (the first enzyme in the glutaminolytic pathway).

Acknowledgements:

Selection of strains of *Bacillus sp.* potential for the production of hydrolases.

Montoya, L. R.[1], Azzoni, S. F.[1], and Tavares, A.G.[1]

Laboratório Nacional de Ciência e Tecnologia do Bioetanol - Campinas SP Brazil

The use of lignocellulosic biomass for liquid fuel production has led to intensive studies in search of new enzyme-producing microorganisms and the development of production processes based on these microorganisms. In this context, the work proposed here aims to select *Bacillus* species from a bank of 107 isolates of juice after pasteurization. A preselection was conducted by culturing on solid medium, having been selected 25 potential strains. Another selection was made based on those 5 strains (BH02, BH05, BH19, BH51 and BH62) that showed a higher amount of total reducing sugars and increased xylanase activity in a medium with commercial xylene. This draft screening tests performed in submerged culture using different carbon sources and other operating conditions.

By observing the cellulose depolymerization through cellulase production into its surrounding medium, preliminary results show that the strains BH19, BH 05 and BH 62 has great potential for the production of cellulases. Added to this a preliminary study on the growth of *Bacillus sp* strains in submerged culture with mineral medium with 1% carboxymethyl cellulose, show that strains BH62, BH51 and BH 19 have tentatively the ability to produce large quantities of cellulases which allow its development. In this growth stage was tested the effect of high agitation of the medium and apparently this condition in the medium induces the secretion of several proteases that could interfere with the quantification of cellulolytic activity as FPAs tests that did not show the expected results in relation to the observed growth. The inhibitory effect in protease activity of low oxygen concentration and other inhibitors are being developed.

Also, the selection will be made from and in terms of process, the parameters used are: The specific growth rate, performance factors $Y_{X/S}$ and $Y_{P/S}$, the total specific activity (IU/mg) and productivity (mg/L h). Through this work is expected to contribute, through a process approach for the identification and characterization of novel enzymes producing microorganisms applied to the production of second generation ethanol.

Acknowledgements: Thanks to the CTBE for all of your support and especially to the 21^o Programa Bolsas de Verão do CNPEM.

Índice Remissivo