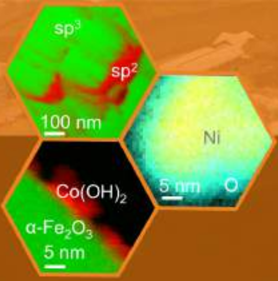


6th TEM Summer School

LNNano Brazilian Nanotechnology National Laboratory

Campinas, Brazil | 11 – 29 Jan/2016

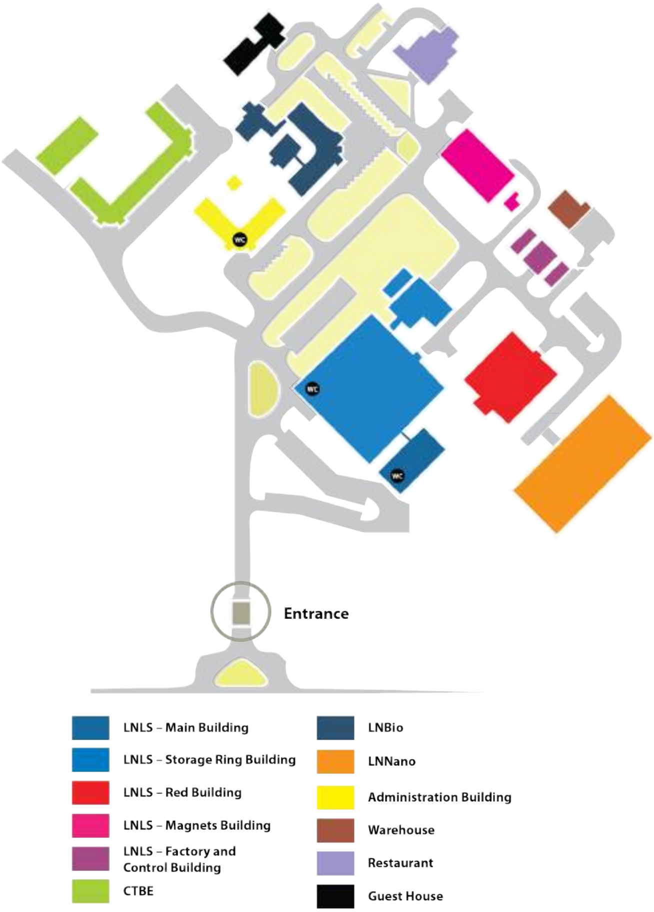
pages.cnpem.br/temsummerschool/

LNNano

CNPEM

Ministério da
Ciência, Tecnologia
e Inovação

GOVERNO FEDERAL
BRASIL
PÁTRIA EDUCADORA



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

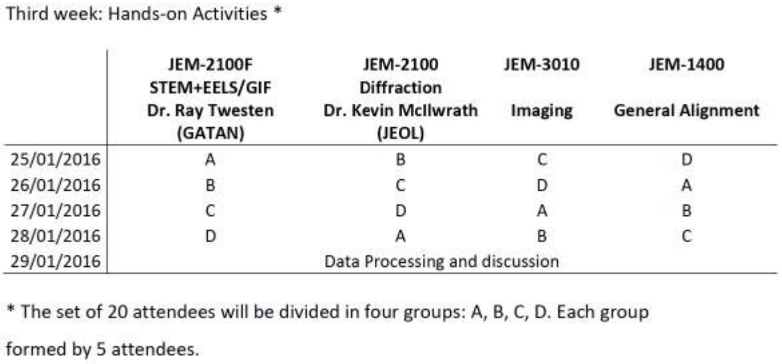
PROGRAM

First week: Basic TEM

	Monday 01/11/2016	Tuesday 01/12/2016	Wednesday 01/13/2016	Thursday 01/14/2016	Friday 01/15/2016
8:15 – 9:00	Shuttle				
9:00 – 10:30	1. Opening **Prof. Pacheco (CNPEM)** **Prof. Arruda (FAPESP)** **Prof. Balzuweit (SBMM)** **Dr. Portugal (LNNano)** Introduction to TEM **Dr. Ospina**	5. Guns, Electron optics and Pumps **Prof. Rossi**	9. Sample Preparation **Dr. Teixeira**	13. Electron Diffraction II **Prof. Afonso**	17. Imaging **Prof. Afonso**
10:30 – 11:00	Coffee Break				
11:00 – 12:30	2. Interaction Electron – Matter **Prof. Fichtner**	6. The Instrument **Dr. Mogili**	10. Electron Diffraction I **Prof. Rossi**	14. HRTEM **Dr. Bettini**	18. STEM **Prof. Zagonel**
12:30 – 14:00	Lunch				
14:00 – 15:30	3. Visit to CNPEM (LNLS, CTBE, LNBio)	7. TEM alignment I (demo) **Dr. Mogili**	11. Electron diffraction I (demo) **Dr. Ospina**	15. Detectors **Dr. Portugal**	19. Introduction to electron spectroscopy **Prof. Zagonel**
15:30 – 16:00	Coffee Break				
16:00 – 17:30	4. Visit to LNNano	8. TEM alignment II (demo) **Dr. Teixeira**	12. Electron diffraction II (demo) **Dr. Mogili**	16. HRTEM (demo) **Dr. Ospina**	20. STEM (demo) **Dr. Teixeira**
17:30 – 18:00	Shuttle				

Second week: Advanced TEM

	Monday 01/18/2016	Tuesday 01/19/2016	Wednesday 01/20/2016	Thursday 01/21/2016	Friday 01/22/2016
8:15 – 9:00	Shuttle				
9:00 – 10:30	21. Convergent Beam Electron Diffraction **Dr. Mogili**	25. Electron Holography I **Dr. Snoeck**	29. Electron Holography II **Dr. Snoeck**	33. Quantitative Electron Microscopy I **Prof. Kirkland**	37. Quantitative Electron Microscopy II **Prof. Kirkland**
10:30 – 11:00	Coffee Break				
11:00 – 12:30	22. Electron Tomography I **Dr. Yang**	26. Electron Tomography II **Dr. Yang**	30. Advanced Spectroscopy III **Dr. Gloter**	34. Advanced Spectroscopy IV **Dr. Gloter**	38. Cryo-TEM **Dr. Portugal**
12:30 – 14:00	Lunch				
14:00 – 15:30	23. Advanced Spectroscopy I **Prof. Arenal**	27. Advanced Spectroscopy II **Prof. Arenal**	31. STEM EELS I (demo) **Dr. Bettini**	35. Solutions for TEM **TEM Companies**	39. Aberration-Corrected TEM **TEM Companies**
15:30 – 16:00	Coffee Break				
16:00 – 17:30	24. STEM EDS (demo) **Dr. Teixeira**	28. Poster session	32. Poster session	36. STEM EELS II (demo) **Dr. Bettini**	40. Cocktail
17:30 – 18:00	Shuttle				



Third week: Hands-on Activities *

	JEM-2100F **STEM+EELS/GIF** **Dr. Ray Twesten** **(GATAN)**	**JEM-2100** **Diffraction** **Dr. Kevin McIlwrath** **(JEOL)**	**JEM-3010** **Imaging**	**JEM-1400** **General Alignment**
25/01/2016	A	B	C	D
26/01/2016	B	C	D	A
27/01/2016	C	D	A	B
28/01/2016	D	A	B	C
29/01/2016	Data Processing and discussion			

* The set of 20 attendees will be divided in four groups: A, B, C, D. Each group formed by 5 attendees.

TEM Summer School

The Electron Microscopy Laboratory (LME), of the Brazilian Nanotechnology National Laboratory (LNNano), which is a part of Brazilian Center for Research in Energy and Materials (CNPEM), Campinas, Brazil, organizes every two years a short course on theory and practical concepts of Transmission Electron Microscopy. This is the sixth edition of the event, between January 11 and 29, 2016.

This school aims to contribute to the advanced training of graduate students and researchers in the fields of engineering, materials science, physics, chemistry and related fields from academic and industrial communities, in Brazil and abroad, on theoretical and practical concepts of TEM techniques applied for materials characterization. We encourage the formation of new users and complement the training of users who has experience in the application of TEM techniques. The school instructors are leading researchers associated to important international and Brazilian research and educational institutions.

The school had its first edition in 2007 with 15 participants. Along its history the number of participants grows. In the last edition, the school was attended by 85 graduated students and PhDs from different areas. For this edition, we count with 90 participants, from Brazil and abroad. The school is organized for a duration of three weeks and in the first week, basic TEM theory are covered. Further, in the second week, several advanced topics including Electron Holography, Electron Tomography, Spectroscopy, and Quantitative analyses are the main focus. Finally, hands-on activities are scheduled for the third week. Additionally, several changes were implemented for the organization of this new edition. For the first time, a registration fee was charged and a poster section was opened. The school will count with the participation of manufacturers of electron microscopes and detectors and vendors.

We thank the financial support from FAPESP (Grant 2015/11990-7), CNPq (Grant 441899/2015-3), the sponsorship from JEOL, FEI, Hitachi and Analítica companies, and the participation of Gatan and JEOL during the third week of school.

CNPEM: A cutting-edge research center

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

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

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

The Brazilian Nanotechnology National Laboratory (LNNano)

The Brazilian Nanotechnology National Laboratory (LNNano) is part of the Brazilian Center of Research in Energy and Materials (CNPEM), an organization certified by the Ministry of Science, Technology and Innovation (MCTI) located in Campinas-SP. The LNNano offers to the academic community and professionals, from Brazil and abroad, timely access to up-to-date equipment operated by experienced personnel within an innovative environment. It is dedicated to the creation, dissemination and application of nanotechnologies aiming at innovation. As a multiuser National Laboratory, it collaborates on multidisciplinary projects with researchers and R&D professionals in universities, research centers and companies and also with the other laboratories of CNPEM.

Organizers | Scientific Committee

Carlos Alberto Ospina Ramirez (LME/LNNano) - Event Coordinator
Alexandre Cassago (CME/LNNano)
Érico Teixeira Neto (LME/LNNano)
Jefferson Bettini (LME/LNNano)
Marcelo Alexandre de Farias (CME/LNNano)
Rodrigo Villares Portugal (CME/LNNano)
Naga Vishnu Vardhan Mogili (LME/LNNano)

Local Committee

Gustavo Martins Moreno (CNPEM)
Ildéria Maira dos Santos (CNPEM)
Pâmela Fernandes Machado (CNPEM)

Funding agency

CNPq
Conselho Nacional de Desenvolvimento
Científico e Tecnológico

FAPESP

Institutional Partners

LNNano

CNPEM

Ministério da
Ciência, Tecnologia
e Inovação

GOVERNO FEDERAL
BRASIL
PÁTRIA EDUCADORA

Sponsors

FEI™

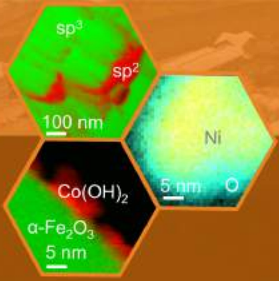
JEOL
Solutions for Innovation

Hitachi High-Tech

analítica

Participation

GATAN



6th TEM Summer School

LNNano Brazilian Nanotechnology National Laboratory

Campinas, Brazil | 11 – 29 Jan/2016

Speakers

pages.cnpem.br/temsummerschool/

Speakers

International invited speakers
Dr. Alexandre Gloter, Laboratoire de Physique des Solides, Université Paris Sud, France.Lectures: Advanced Spectroscopy III and IV
Prof. Angus Kirkland, Department of Materials, University of Oxford, United Kingdom.Lectures: Quantitative Electron Microscopy I and II
Dr. Etienne Snoeck, Group NanoMaterials, Centre d'Élaboration de Matériaux et d'Etudes Structurales, Centre National de la Recherche Scientifique, France.
Lectures: Electron Holography I and II
Dr. Yongsoo Yang, Coherent Imaging Group, Department of Physics and Astronomy, University of California, USA.
Lectures: Electron Tomography I and II
Prof. Raul Arenal, Advanced Microscopy Laboratory, University of Zaragoza, Spain.
Lectures: Advanced Spectroscopy I and II

Brazilian invited speakers
Prof. André Linhares Rossi, Brazilian Center for Research in Physics, Rio de Janeiro, RJ.
Lectures: Guns, Electron Optics and Pumps.
Prof. Conrado Ramos Moreira Afonso, Department of Materials Engineering, Federal University of São Carlos, São Carlos, SP.
Lectures: Electron Diffraction II; Imaging
Prof. Luiz Fernando Zagonel, Institute of Physics, University of Campinas, Campinas, SP.
Lectures: STEM; Introduction to Electron Spectroscopy.
Prof. Paulo Fernando Papaléo Fichtner, Institute of Physics, Federal University of Rio Grande do Sul, Rio Grande do Sul, RS.
Lectures: Interaction Electron – Matter

Local speakers
Dr. Alexandre Cassago, Cryo-Electron Microscopy Group (CME), Brazilian Nanotechnology National Laboratory (LNNano).
Dr. Carlos Alberto Ospina Ramirez, Electron Microscopy Laboratory (LME), Brazilian Nanotechnology National Laboratory (LNNano).
Dr. Jefferson Bettini, Electron Microscopy Laboratory (LME), Brazilian Nanotechnology National Laboratory (LNNano).
Dr. Marcelo Alexandre de Farias, Cryo-Electron Microscopy Group (CME), Brazilian Nanotechnology National Laboratory (LNNano)
Dr. Rodrigo Portugal, Cryo-Electron Microscopy Group (CME), Brazilian Nanotechnology National Laboratory (LNNano).
Dr. Vishnu Mogili, Electron Microscopy Laboratory (LME), Brazilian Nanotechnology National Laboratory (LNNano).

Technicians:
Fabiano Emmanuel Montoro, Electron Microscopy Laboratory (LME), Brazilian Nanotechnology National Laboratory (LNNano).
Sidnei Ramis de Araújo, Electron Microscopy Laboratory (LME), Brazilian Nanotechnology National Laboratory (LNNano)

Electron energy loss spectroscopy in (Scanning) transmission electron microscope

Alexandre Gloter
Laboratoire de physiques des Solides, CNRS UMR 8502
91405, Orsay, France

During these courses, we will mostly described the Electron Energy Loss Spectroscopy (EELS) in the core loss domain, corresponding to an energy range of few tens of eV to several keV. We will firstly described how they can be used to obtain local chemical composition. With modern STEM microscopes equipped with Cs corrector, atomic resolution spectroscopy can be obtained opening the possibility to quantify chemical composition at the scale of a single atomic column. Examples of interface investigation by atomic STEM-EELS will be given.

We will also pay a particular attention on the description of the "fine structures", that are legible in the EELS spectra, notably since the development of monochromatized gun. Indeed, such spectroscopic details can reveal some elements on the electronic structures of the studied materials. Two mains classes of fine structures will be reported. (i) The one associated to B,C, N (light element) at the K-edge. They enable investigation of graphite associated materials, but also of organic materials. (ii) The one associated to transition metal and rare earth EELS excitations. In particular, we will see how to quantify the local the valence of these elements by STEM-EELS. If we have some time, we will also see how these edges can be used to investigate some magnetic properties of the materials.

Guns, Electron optics and Pumps

The vacuum system, electron source and lenses lectures aims to present the basic theoretical fundamentals of operation of the electron microscope. The electron source is one of the most important parts of the microscope and its characteristics determine the performance of the equipment in different operating modes. Different types of electron sources may be used, and each requires a specific vacuum system. The electromagnetic lenses of the electron microscope can be compared to the converging glass lens of a optical microscope.

Electron Diffraction

This lecture includes fundamental principles of crystallography, Bravais lattice, reciprocal space, Laue zones, Bragg condition and Ewald sphere, structure factor, and indexing diffraction patterns. One of the great advantages of the transmission electron microscope is the possibility to associate crystallographic data and image at the nanoscale.

Electron diffraction II

- Two-beam condition
- Kikuchi lines
- Column Approximation
- Selected Area Electron Diffraction (SAED)
- Nanobeam Electron Diffraction (NBD)
- Practical Applications of Electron Diffraction (conventional and advanced/nanostructured materials)

Lecture: TEM specimen preparation

The characterization of materials using TEM requires the use of samples that are thin enough so that they are transparent to electrons (thicknesses between a few nanometers and a few hundreds of nanometers). A TEM specimen must be representative of the material under investigation. Ideally, the specimen obtained should be uniformly thin, stable under the electron beam and in the laboratory environment, conducting and non-magnetic. Few specimens approach this ideal figure and usually the microscopists have to compromise. It is very important that the preparation technique do not affect or change the material under investigation. There are many ways to produce a TEM specimen, depending on the type of material involved, the information needed, time constraints, availability of equipment and skill. In this lecture, I will summarize some possible techniques, suggest procedures to be followed and show that there are many ways to produce a TEM specimen.

Lecture: X-ray spectrometry

When the electron beam strikes a material, ionization events generates the emission of characteristic X-rays, providing chemical information from the irradiated area. Chemical analysis with very high spatial resolution, approaching atomic-level, may be accomplished in the latest aberration-corrected scanning transmission electron microscopes (STEMs). In this lecture, I will describe the detector functioning, its interface with the TEM microscope and discuss the benefits and limitations of the use of the X-ray energy-dispersive spectrometers (XEDS) for chemical analysis and mapping.

Electron holography in Material Science:
Quantitative mapping of local electric, magnetic and strain fields

Etienne SNOECK
CEMES-CNRS
Toulouse - France

TEM is well known to be a powerful tool for the study of the structure, microstructure and chemistry of (nano)materials at the sub-nanometer scale. In conventional imaging modes TEM contrasts reveal the intensity distribution of the electron beam after interaction with the materials while information on the phase shift the electron wave experienced is lost. These phase shifts however contain information on the electrostatic potentials and magnetic induction the electron beam interacts with. Electron holography is an interferential method, which allows retrieving these phase shifts and therefore to quantify and map these local fields. Electrostatic fields can then be quantitatively mapped with a resolution of the order of the resolution of the microscope while magnetic field measurements require more delicate experiments and in particular necessitates to be performed in a magnetic field free environment with a dedicated microscope. Electron holography can also be carried out to extract the phase shift of the diffracted beams exiting from a strained crystal. The so-called "Dark field electron holography" method recently developed then allows mapping the strain field in deformed crystal and devices. In the presentation I will first introduce the basic principles of electron holography and describe the experimental precautions and procedures for quantitative measures of local electrostatic, magnetic and strain fields. The potentiality of this method will then be illustrated through various examples on nanomaterials and devices. Additionally I will show how these technics can be used to study materials in operando *in-situ* in a TEM.

<u>Outline</u>

- General principle of Electron Holography
- Experimental method and phase extraction
- Electrostatic field measurements by EH
    - Measurement of internal potential and thickness
    - Electrostatic measurements
    - In-situ biaising
- Magnetic field measurements by EH and Lorentz TEM
    - Electrostatic and magnetic phases separation
    - Magnetic induction measurements
    - In-situ experiments
    - Lorentz microscopy
- Stain mapping using Dark Field Holography "HoloDark"
    - Method
    - Examples

Quantitative Electron Microscopy. I. Image Simulation.

Professor Angus Kirkland,
Department of Materials, University of Oxford, Parks Road, OX1 3PH, UK.

High Resolution Electron Microscopy (HRTEM) has turned into one of the most important tools in the study of atomic structure and chemistry in a wide range of materials. However conventional phase contrast HRTEM images can rarely be interpreted directly due to a variety of effects including multiple electron scattering, the microscope lens aberrations and incoherence in the illumination. For quantitative interpretation it is therefore necessary to simulate images and to compare these to experimental data. This talk will describe simulation methods used to calculate HRTEM images. In particular I will describe the "multislice" approximation in which the sample is divided into several thin "slices".

The key steps in this approach require models for:
The electron scattering within the slices calculated as a transmission function,
Fresnel propagation between slices,
The effects of the microscope objective lens,
The influence of the electron detector.

EELS: principles, instrumentation, techniques and recent illustrative examples

Raul Arenal[a,b]

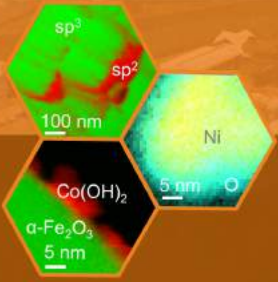
[a] *Laboratorio Microscopias Avanzadas, INA, U. Zaragoza, 50018 Zaragoza - Spain*
[b] *Fundacion ARAID, 50018 Zaragoza - Spain*

Electron energy-loss spectroscopy (EELS) is the most powerful of the TEM-based analytical techniques for structural and chemical composition studies at the (sub)nanometer/atomic scale, and is therefore well suited to the inspection of individual nanostructures. The last two decades, TEM have undergone a large number of improvements allowing ~ 10 meV energy resolutions for a close to one angstrom electron beam. These performances offer new possibilities for probing the optical, dielectric and electronic properties of nanomaterials with unprecedented spatial information, as well as for studying the atomic configuration of nanostructures. In these two lectures, I will introduce this technique, the required instrumentation and I will present a selection of the recent works involving all the above mentioned matters. These works will concern the study of the atomic structure & configuration of nanostructures as well as the opto-electronic properties studies carried out via EELS measurements of different kind of (nano)materials. These works will illustrate the excellent capabilities offered by the use this technique.

Electron Tomography

With the rapid development in aberration correction and electron source techniques, modern microscopes now provide high-quality 2D images in sub-atomic resolution. However, to fully utilize functional materials for current Nano-architecture devices, it is important to truly understand 3D atomic properties of materials, such as 3D strain tensor, atomic dislocations, defects, and grain boundaries.

Tomography is a technique which recovers a higher dimensional object from lower dimensional projections, based on a concept initially introduced by Radon in 1917. X-ray computed tomography (CT) is widely being used in medical diagnosis nowadays since its first demonstration in 1971. Electron tomography is also becoming more and more powerful and popular in recent years with better (S)TEM instrumentation, higher computational power, and novel reconstruction algorithms. In this lecture, I will introduce the basic principle of electron tomography and its applications, and present recent achievements of obtaining 3D structure in individual atomic coordinate level.



6th TEM Summer School

LNNano Brazilian Nanotechnology National Laboratory

Campinas, Brazil | 11 – 29 Jan/2016

Abstracts

pages.cnpem.br/temsummerschool/

LNNano

CNPEM

Ministério da
Ciência, Tecnologia
e Inovação

GOVERNO FEDERAL
BRASIL
PÁTRIA EDUCADORA

Compositional Analysis on the Retained Austenite After Diffusive and Partitioning Mechanisms

J. D. Escobar [I,II], J. D. Poplawsky [IV], W. Guo [IV], P. R. Mei [II], S.S. Babu [V], A. Ramirez [VI]
I Brazilian Nanotechnology National Laboratory - LNNano - CNPEM, Campinas-SP, 13083-970, Brazil.
ii School of Mechanical Engineering, University of Campinas – FEM - Unicamp, Campinas-SP, 13083-860, Brazil.
iii Metallurgical and Materials Engineering Department, University of São Paulo - USP - Sao Paulo, 05508-030, Brazil.
iv The Center for Nanophase Materials Sciences, Oak Ridge National Laboratory
v Mechanical, Aerospace and Biomedical Engineering, University of Tennessee, Knoxville-TN, 37996-2210, USA.
vi Department of Materials Science and Engineering, Ohio State University, Columbus-OH, 43221, USA.
julian.escobar@lnnano.cnpem.br

TRIP-assisted advanced high strength steels (TRIP-AHSS) and TRIP-assisted Supermartensitic Stainless Steels (SMSS) have microstructures based on dispersion of reverted austenite (γr), from 10 to 30%. The stabilization process depends on how much γ-stabilizing elements enrich the austenite during the heat treatment, changing the Ms and Mf transformation temperatures. Despite these two materials show γr and TRIP effect, the austenite retention process is attributed either to diffusion of substitutional elements (SMSS) or to carbon partitioning (TRIP AHSS). Atom Probe Tomography of needle-shaped specimens was performed using a CAMECA Instruments LEAP® 4000X HR local electrode atom probe, which is equipped with an energy-compensating reflectron lens for improved mass resolution. The specimens were field evaporated in laser mode with a 200 kHz pulse repetition rate, 30 K specimen temperature, 100 pJ (SMSS) and 50 pJ (TRIP-AHSS) laser power, and a 0.5-1.0% detection rate. In SMSS, γr is stabilized mainly through diffusion of Ni, being 4 times higher than in martensite (α'). However, Cr, Ni and Mo showed almost no difference in the bulk; but instead evidenced accumulation in the grain boundaries due to the diffusive process. Both γr and α' were virtually carbon-free due to the presence of Ti, forming TiMoC carbides. Regarding TRIP AHSS, results showed that C plays the major role in γr stabilization. The C bulk content in γr was almost 26 times higher than in bainite (αb). The mechanism of αb transformation can be associated to local equilibrium with minor partitioning of Mn and Si. Some carbon clusters inside the αb were observed, and no cementite was detected. The γr showed homogeneous distribution of C, due to the presence of Si. The use of TEM is proposed to correlate the 3D APT compositional results, characterize the morphology, and to obtain electron diffraction of the phases of interest.

The APT research was supported by ORNL's Center for Nanophase Materials Sciences (CNMS), which is a DOE office of Science User Facility; Science Without Borders scholarship (202766/2014-4) from the National Counsel of Technological and Scientific Development (CNPq), Brazil; and The Brazilian Center for Research in Energy and Materials (CNPEM).

Synthesis and characterization of $Sr_{1-x}Cu_xTiO_3$ and $SrTi_{1-x}Cu_xO_3$ compounds applied to catalysis of the water-gas shift reaction

Vitor C. Coletta[1], Francielle C. F. Marcos[2], Francisco G. E. Nogueira[2], Maria I. B. Bernardi[1], Alain Michalowicz[3], Renato V. Gonçalves[1], Elisabete M. Assaf[2], Valmor R. Mastelaro[1]

[1]São Carlos Institute of Physics, University of São Paulo, São Carlos, São Paulo, Brazil
[2]São Carlos Institute of Chemistry, University of São Paulo, São Carlos, São Paulo, Brazil
[3]Universite Paris-Est Creteil Val de Marne – ICMPE-CNRS, Thiais, France
vitor.coletta@usp.br

The water-gas shift reaction is carried out in the production of H_2 free from CO, necessary in applications such as the use in proton exchange membrane (PEM) fuel cells. [1] Oxides with perovskite structure containing copper are promising for catalysis of this type of reaction for presenting a good chemical stability. [2] This research consists in performing the synthesis and characterization of nanoparticles of composition $Sr_{1-x}Cu_xTiO_3$ and $SrTi_{1-x}Cu_xO_3$ looking for the application as catalysts for the water-gas shift reaction. The synthesis was done through the polymeric precursors method with calcination in N_2 atmosphere followed by a heat treatment in O_2 for carbon removal, resulting in nanoparticles with large surface area in comparison to the conventional method. [3] X-ray diffraction results showed that the copper atoms are segregated from the perovskite phase for $x \geq 0.06$ in form of CuO phase. The composition $SrTi_{0.80}Cu_{0.20}O_3$ presented the better activity with 74% of CO conversion at 350°C. Thus, our TEM analyses, at the Chemistry Institute of Unesp, Araraquara, begun with this sample compared to the undoped $SrTiO_3$. Figure 1 shows a high-resolution TEM image of a crystallite of the $SrTiO_3$ sample. The distance of 0.27 nm between the observed crystallographic planes corresponds to that between (110) planes of $SrTiO_3$ cubic phase (PDF 35-0734). As expected from the X-ray diffraction results, the $SrTi_{0.80}Cu_{0.20}O_3$ sample has $SrTiO_3$ as the main phase and also regions rich in CuO phase on the surface as showed in Figure 2a. The high-resolution image of the region in Figure 2b shows planes spaced with a distance close to that reported for (11-1) of CuO phase (PDF 48-1548). The presence of the phase is also confirmed by the EDS spectrum in the region (Figure 2c). The next steps of our TEM characterization will involve analyzing the difference between substituting strontium and titanium sites for copper in the morphology and copper segregation.

The authors are grateful for the financial support provided by São Paulo Research Foundation – FAPESP (grant 2013/09573-3) and National Council for Scientific and Technological Development – CNPq (grants 304498/2013-0 and 140631/2013-5). The authors are also grateful to Marcelo O. Orlandi for the use of the transmission electron microscope.

[1] Gradisher, L. et al. Applied Energy, 139, 335-349 (2015).
[2] Maluf, S. S. et al. Applied Catalysis A: General, 413-414, 85-93 (2012).
[3] da Silva, L. F. et al. Materials Chemistry and Physics, 125, 168-173 (2011).

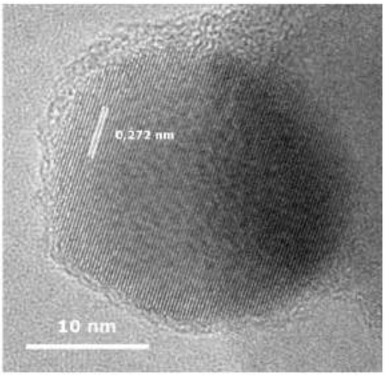


Figure 1 – High-resolution TEM image of $SrTiO_3$ sample.

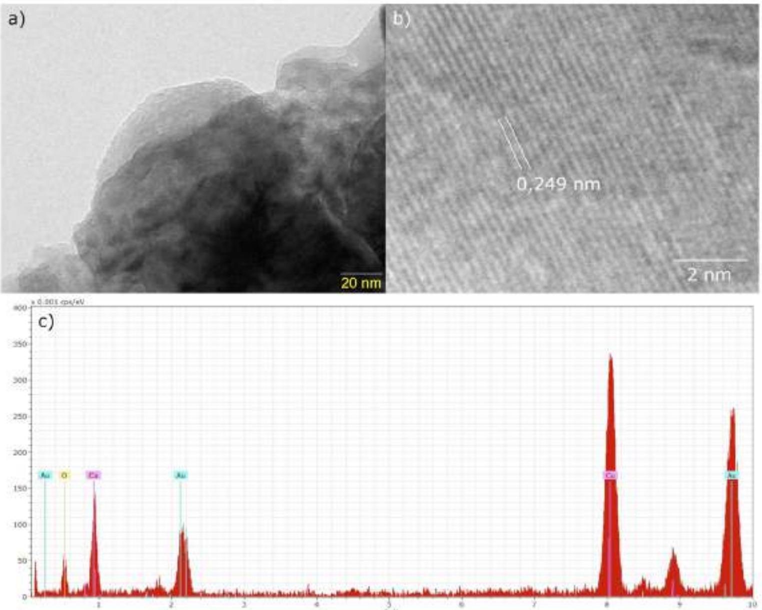


Figure 2 – (a) TEM image of $SrTi_{0.80}Cu_{0.20}O_3$ sample. (b) high-resolution image and (c) EDS spectrum of the region on the surface.

Identification of Bimetallic Electrocatalysts for Ethanol and Acetaldehyde Oxidation: Probing C2-Pathway and Activity for Hydrogen Oxidation for Indirect Hydrogen Fuel Cells.

Applied Catalysis B: Environmental 160–161 (2014) 423–435.

A.C. Queiroz[a], W.O. Silva[b], I.A. Rodrigues[b], F.H.B. Lima[a] [a]Instituto de Química de São Carlos, USP, São Carlos, SP, Brazil.
[b]Departamento de Química, UFMA, São Luiz, MA, Brazil.

The TEM images and the particle diameter distribution histograms obtained for the different investigated materials are presented in Fig. 1. The images reveal uniform distribution of the metal nanoparticles on the carbon powder support, but with heterogeneous distribution in size. According to the obtained histograms, the three different materials with 1:3 atomic ratios presented average particle size in the range of 2–10 nm, and some large particle agglomerates in the range of 12–20 nm. The effect of the thermal treatment was also investigated, and the TEM results of W/Pt/C (2:3) before and after thermal treatment under H_2 atmosphere at 300 ◦C are shown in Fig. 1(d) and (e), respectively. As can be observed, there is only a marginal change in the particle size distribution histogram (from ca. 4.5 to 5.0 nm), indicating that the thermal treatment involved in the synthesis procedure does not have a severe effect on increasing the electrocatalyst particle size.

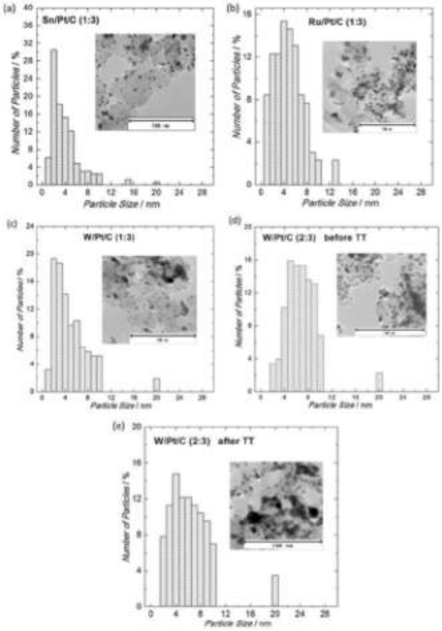


Fig. 1. TEM images and particle size distribution histograms for the different carbon- supported nanoparticles: (a) Sn/Pt/C (1:3); (b) Ru/Pt/C (1:3); (c) W/Pt/C (1:3); (d) W/Pt/C (2:3) before thermal treatment and (e) W/Pt/C (2:3) after thermal treatment.

Applications of Ag nanocubes as high performance SERS substrates

Santinom, A.[1], dos Santos, D. P.[1], Mazali, I.O.[1]
[1] Institute of Chemistry, Unicamp, Campinas, São Paulo, Brazil dri.santinom@gmail.com

This project proposes the optimization of silver nanocubes synthesis and SERS substrate. Associated with a theoretical study of the expected response to the SERS signal, these results will be compared with the experimental data in the application of silver cubic nanoparticles in glass substrate previously treated for quantifying a probe molecule, 4-aminobenzothiol (4-ABT) or rhodamine 6G. To ensure that the synthesis form the nanoparticles of interest, i.e. silver nanocubes, a technique that will permit the imaging of structures formed must be used. It is not possible to obtain these types of images in common optical microscope due to the very small scale (nanometer), requiring the use of Transmission Electron Microscopy (TEM). The characterization of the material by TEM as reported in the literature, will allow to elucidate, initially, which size, morphology and if oriented crystalline planes will be formed [1,2]. The importance of TEM in the project is to identify the nanostructures that will be formed on the substrate. It is necessary to know if dimers, trimers or clusters of nanocubes are on the surface of the dielectric substrate, because these determine the SERS signal intensities. Such information will allow us to correlate the structure of the nanoparticles aggregates with the SERS signals obtained at the same regions analyzed by TEM. Such results will be supported by theoretical calculations based on classical electrodynamics simulations, like the Discrete Dipole Approximation (DDA) [3] method. Such coordinated experimental/theoretical studies are aimed at a fundamental understanding of the factors that influence the enhancement of the local electric field, and consequently the SERS intensities. From the above, the TEM analysis of the substrates are a fundamental step for this work.

I would like to thank CAPES for the financial support, Professors Diego Pereira dos Santos and Italo Odone Mazali for the orientation and the Institute of Chemistry for the opportunity of researching.

[1] Siekkinen, A. R., et. al., Chem Phys Lett, 432, 491–496 (2006). [2] Xia, Y., et. al., Angew Chem - Int Ed, 48, 60–103 (2009).

[3] Zhao, J., et. al., Ac Chem Res, 41, 1710-1720 (2008).

Identification of secondary precipitates present at grain boundaries of Co based superalloy

A.M.S. Costa[1], E. S.N. Lopes[2], A. P. Tschiptschin[1,3]
[1]Brazilian Nanotechnology National Laboratory, Campinas, Sao Paulo, Brazil
[2]Faculty of Mechanical Engineering of Unicamp, Campinas, Sao Paulo, Brazil
[3]Department of Metallurgical and Materials Engineering at Polytechnic School of USP
alex.costa@lnnano.cnpem.br

Abstract: In this study was focused on the characterization of fine precipitates formed on grain boundaries in Co based superalloys. When the precipitates are presented in metallic materials they could improve materials properties such a mechanical, electrical, magnetic and chemical stability as well. Depending on the dimension in size and shape the precipitates can acting such a reforcement of grain boundaries and helps to prevent grain sliding during high temperature performance. In this way is imperative to know which the chemistry composition, what kind of phase it is (intermetallics, carbides, borides and so on), orientation relationship with the matrix phase, where they could be identified on the microstructure. The transmission electron microscopy technique provides a lot of important information about the more located microstructural characterization what is the main goal of this study. The samples have been studied in this work were prepared by focused ion beam (FIB) technique at the Center for Electron Microscopy and Analysis (CEMAS). The features of the samples were analysed by high resolution transmission electron microscope JEOL model JEM 3010 at LME. It was captured bright field images from grain boundaries region. Figure 1 shows the sample that was prepared by FIB technique. Figure 2 shows a couple of details about the microstructure of the material. It is observed the matrix is microconstituted of γ-Co austenitic phase having (A1) FCC structure and coherent $L1_2$ structure precipitates of γ'-$Co_3(Al,W)$ inside it. Fine precipitates of minor secondary phase are found at the grain boundaries are showed Figure 2. Because of the additions of C, B, Ni and Al certain kind of precipitates could be formed during the cooling of the material that was processed by arc melting technique. Chemical analysis using XEDS together electron diffraction technique should help to do a proper identification of which kind of phase are decorating grain boundaries.

This study has been supported by The São Paulo Research Foundation (Fapesp – Process Number 2014/13772-4). I would like to thank Dr. Eder Lopes for preparing FIB samples and Dr. Carlos Ospina for acquisition of TEM images.

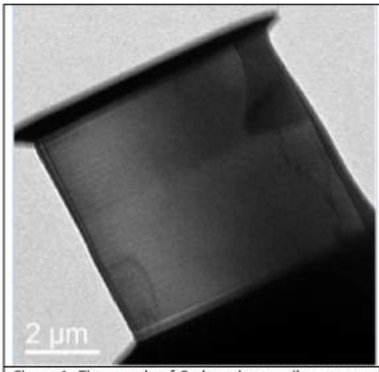


Figure 1- The sample of Co based superalloy prepared by FIB technique.

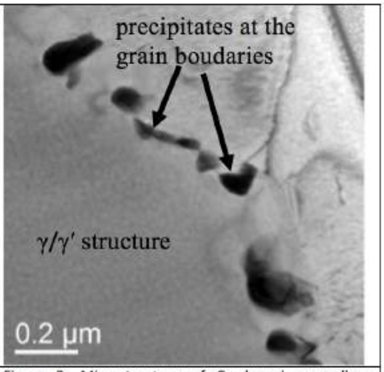


Figure 2- Microstructure of Co based superalloys showing matrix structure and secondary minor phases precipitated at the grain boundaries.

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

Ana Flávia Suzana[1,2], Celso Valentim Santilli[1], Stéphanie Blanchandin[3], Valérie Briois[3], Sandra Helena Pulcinelli[1], Florian Meneau[2]

[1] Universidade Estadual Paulista (UNESP), Instituto de Química, Departamendo de Fisico- Química, 14800-060, Araraquara, SP, Brazil

[2] Centro Nacional de Pesquisa em Enegia e Materiais (CNPEM), Laboratório Nacional de Luz Síncrotron (LNLS), 13083 970, Campinas, SP, Brazil

[3] Synchrotron SOLEIL, 91192 Saint Aubin, France

ana.suzana@lnls.br

Synthesis of metallic nanoparticles is an area of ever-growing interest for the scientific community. Gold nanoparticles (AuNPs) solutions are very fascinating systems due to their biocompatibility and the possibility to functionalise the surface of the nanoparticles with various biological molecules. This ensures original applications related to gold nanoparticles in various fields such as biology [1] and for example, curing diseases [2] but also catalysis. Room-temperature ionic liquids are attracting much interest in many fields of chemistry and industry, due to their potential as a "green" recyclable alternative to the traditional organic solvents. They are nonvolatile, nonflamability and have high ionic conductivity. Nevertheless, the applicability of such properties rely on the ability to produce stable monodisperse nanoparticles of specific shape and chemical compositions. The actual mechanisms of nanoparticle formation and growth often remain unclear due to limited accessibility to *in situ* time-resolved information about the evolutions of precursor speciation and particle size. There is thus a very strong need for a much better characterisation especially of the nucleation stage. In this work we have synthesized AuNPs stabilised by ionic liquids and the study of the nucleation and growth processes in real time, using a combination techniques: X-ray absorption (XAFS) and UV-Vis spectroscopies (UVvis), Small Angle X-ray Scattering (SAXS) and High Resolution Transmission Electron Microsocopy (HRTEM). UVvis enabled to follow the evolution of the characteristic gold plasmon band as a function of the synthesis conditions, while size and morphology have been characterised by SAXS. To study the size and distribution of the nanoparticles, we will do HRTEM at LNNano. Speciation of gold in solution is under study using XAFS. SAXS and UV-Vis spectroscopie were done at LNLS and XAFS will be performed at Synchrotron SOLEIL.

We would like to thank FAPESP for the funding (process number 2014/27127-3), CNPEM, where this project is being done, Synchrotron SOLEIL and the Institute of Chemistry of Unesp.

[1] Ye, X. et al., ACS Nano, 6, 2804-2817 (2012).
[2] Giljohann, D. A. et al., Angewandte Chemie-International Edition, 49, 3280-3294 (2010).

Omega phase analysis in β-metastable titanium alloy using transmission electron microscopy and electrical resistivity

Bruna Callegari[1], Verona Biancardi Oliveira[2], Haroldo Cavalcanti Pinto[1]

[1] School of Engineering of São Carlos, University of São Paulo, São Carlos, São Paulo, Brazil

[2] Polytechnic Institute, Rio de Janeiro State University, Nova Friburgo, Rio de Janeiro, Brazil

bruna2.callegari@usp.br

In this work, the occurrence of omega (ω) phase in a β-metastable Ti-5Al-5V-5Mo- 3Cr-1Zr (Ti-55531) alloy initially quenched in water from β field will be studied by transmission electron microscopy (TEM) after heating and cooling. The ω is a submicroscopic metastable phase that precipitates from the decomposition of β phase during either fast cooling (athermal ω, ω_{ath}) or long term treatment (isothermal ω, ω_{iso}) of β-stabilized titanium alloys [1]. This phase has been extensively studied due to its complex morphology, effects on properties such as ductility and superconductivity, and mechanism of formation from β phase [2]. TEM studies carried out by various researchers in different Ti alloys have shown that ω particles might present either ellipsoidal or cuboidal morphology, with dimensions ranging from 60 Å to 3000 Å, depending on misfit strains in the matrix [2]. The focus of the present study is to characterize the morphology, size and distribution of the omega phase in order to further understand its formation and decomposition mechanisms in the β-metastable Ti-55531 alloy. Hence, bright field and dark field TEM images will be performed in this alloy after subjecting it o different heating and cooling rates. Electrical resistivity measurements will complement the TEM analysis, due to its sensitivity to minor constitutional changes [3]. The work is motivated by the fact that it is extremely important to evaluate the effects of heat treatments on the kinetics of phase transformations, and there are still limited results on mechanisms of ω formation in the Ti-55531 alloy.

CNPq process n° 407399/2013-5.
CNPq grant n° 161959/2015-6.

[1] Hickman, B.S. Journal of Materials Science, v. 4, p. 554-563 (1969).
[2] Sikka, S.K. *et al*. Progress in Materials Science, v. 27, p. 245-310 (1982). [3]
Gloriant, T. *et al*. Scripta Materialia, v. 58, p. 271-274 (2008).

Vanadium interaction with biological systems

B. C. Costa[1], P. N. Lisboa-Filho[2]
[1] Programa de Pós-Graduação em Ciência e Tecnologia de Materiais – Universidade Estadual "Júlio de Mesquita Filho" - UNESP, Bauru, São Paulo, Brazil
[2] Departamento de Física, Universidade Estadual "Júlio de Mesquita Filho" - UNESP, Bauru, São Paulo, Brazil
brunah@fc.unesp.br

Among the most commonly used metallic materials as prosthetic implants are titanium-based alloys, specifically Ti-6Al-4V system, whose use corresponds to 45% of the total production of titanium as biomaterial [1]. In general, metallic materials may suffer corrosion when implanted, leading to release of metal compounds or *debris* (fragments) into the body. Furthermore, the human body is predominantly composed by water, polymers (proteins) and ceramics (bones) and metals are elements found as necessary only in very small quantities [2]. Thus, when a metallic material is implanted in the human body, the toxicity of their constituents elements should be evaluated before its application. Regarding to the evaluation of toxicological potential of elements of the Ti-6Al-4V system, aluminum may present acute toxicity at high doses, and is reported as an element related to neurological disorders and mitigating factor of various diseases. Vanadium plays a role that is still poorly understood in the human body and may present ambiguous cellular responses. Furthermore, vanadium compounds may have interactions with proteins within a living organism, changing its functionality [3]. In this context, the present proposal is based on the possibility of long-term exposure to an implant based on Ti-6Al-4V alloy, the adverse effects of *debris* release from its corrosion in a living system and also the studies related to toxicity of these alloying elements, and the importance of the interaction of this element, especially in its nanostructured form, regarding proteins. In this way, the *in situ* liquid TEM technique may allow the orientation and conformation analysis of proteins under the surface of this project samples (Ti-6Al-4V and vanadium *debris* obtained from tribocorrosion tests and V_2O_5 powder), and this is the key-role to understanding the interaction and toxicity mechanisms of vanadium in live systems. So a better understanding of this powerful technique is extremely recommended.

The authors would like to thank CAPES and CNPq - Brazilian Funding Agencies for the financial support.

[1] DAVIES, J.R. Handbook of Materials for Medical Devices, Ohio, ASM International, Materials Park, 2003.
[2] CHEN, Q. et al., Materials Science and Engineering R, 87, 1 – 57 (2015).
[3] MUKHERJEE, B. et al., Toxicology Letters, 150, 135 – 143 (2004).

Formation and characterization of hybrid $CaCO_3$ tube-like structures containing type I collagen: a potential biomaterial to bone replacement.

Camila Bussola Tovani and Ana Paula Ramos.
Universidade de São Paulo, Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto, São Paulo, Brazil.
camilabussola@usp.br

Tube-like structures have been widely employed in several fields due to its special properties such as high surface area and mechanical strength. Nevertheless the application of these materials in vivo is limited mainly by toxicity, biocompatibility, and bioactivity which are governed by several features such as composition, size, colloidal stability and crystal structure. In this sense the synergism between tubular geometries and the biological responses of biominerals can be an interesting strategy to build a new class of biomaterials.[1] Here we reported the synthesis of a promising osteoconductive material made of $CaCO_3$ and collagen using a biomimetic model. Uniform tubular structures were synthesized using polycarbonate membranes as templates to tune the size of diameter of the nanoparticles in range of 100 and 400 nm. Transmission electronic microscopy (TEM) images (performed at Faculty of Medicine of Ribeirão Preto -USP, Brazil) of synthesized hybrid $CaCO_3$ tube-like structures are shown in figures 1(A-B) corresponding to NT 100 ($CaCO_3$ tube-like structures with diameter of 100 nm) and 2(A-B) corresponding to NT 400, ($CaCO_3$ tube-like structures with diameter of 400 nm). It can be observed that the particles exhibit well-defined tube-like shape. The average diameter of the particles were 100 and 400 nm, thus confirming the effectiveness of particle size control through the use of membranes with different pores sizes as templates. The figures 1 and 2 also display the hybrid tube-like structures obtained after immersion of 100 nm (Figure 1 C-D, NT 100+COL) and 400 nm (Figure 2 C-D, NT 400 + COL) $CaCO_3$ particles for 12 h in type I-collagen solution. TEM images reveal the presence of a layer coating the surface of the NT 400 + COL particles. This alteration confirms the collagen incorporation onto the NT 400 nanoparticles surfaces. For NT 100+COL particles, this effect is less remarkable, although the presence of collagen can be pointed by zeta potential measumrements, infrared spectroscopy and cell viability assays, thereby confirming the incorporation onto both types of nanoparticles.

FAPESP- Process number:2014/24249-0

[1] Wei, W., Ma, G. H., Hu, G., Yu, D., Mcleish, T., Su, Z. G., & Shen, Z. Y. (2008. Journal of the American Chemical Society,130(47).

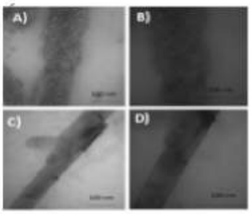


Fig. 1. SEM images of $CaCO_3$ nanoparticles (A-B)NT 100, (C-D) NT 100+ Col.

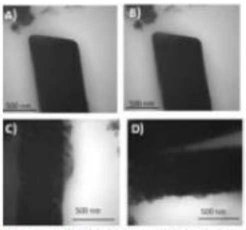


Fig. 2. SEM images of $CaCO_3$ nanoparticles (A-B)NT 400, (C-D) NT 400+ Col.

Effect of impurity segregation on intermediate temperature, ductility-dip cracking (DDC) in high-Cr, Ni-base alloys

Carolin Fink, John C. Lippold
The Ohio State University, Columbus, Ohio, USA
fink.242@osu.edu

The chemical composition of the filler metal has proven to be one of the most important factors controlling DDC in Ni-base weld metals. Alloying elements, such as Nb, determine the precipitation behavior at the end of weld metal solidification, mitigating DDC by grain boundary (GB) pinning and boundary "tortuosity" [1]. On the other hand, impurities and interstitials are also considered to play an important role in DDC susceptibility. Both hydrogen and oxygen embrittlement in Ni-base alloys has been reported [2, 3]. Both elements are known to have a detrimental effect on resistance to DDC. A possible contribution due to a GB decohesion effect or local oxidation at the grain boundary is considered possible [4]. However, on the atomic scale, there is very limited knowledge regarding interactions between interstitial elements at the GBs and at the interface between intergranular precipitates and the matrix. These interactions may not be the primary cause of DDC but may promote further intergranular embrittlement in the DDC susceptible temperature range, potentially helping to explain the variability in susceptibility within the same filler metal specification.

The proposed work will elucidate such interactions using electron microscopy (SEM, TEM) coupled with EDS and EELS measurements to understand their role on the cracking mechanism. Gleeble-based thermo-mechanical simulation will be performed with additions of either hydrogen or oxygen (via shielding gas or enriched atmosphere) for weld metal sample preparation. Samples for electron microscopy will be prepared from GB and crack-tip regions and analyzed for oxygen segregation, oxide formation or oxidation of GB particles. To determine the role of hydrogen migration to the GBs additional in-situ TEM analysis could be performed to study its influence on strain localization. This could be done by in-situ TEM tension [5] to observe and analyze the dynamic process of dislocation motion and crack nucleation.

[1] Ramirez, A.J. et al., Materials Science and Engineering A, 380(1-2), pp. 245-258 (2004).
[2] Woodford, D.A., Energy Materials, 1(1), pp. 59-79 (2006).
[3] Collins, M.G. et al., Welding Journal, 82(10), pp. 288s-295s (2003).
[4] Zheng, L. et al., Critical Reviews in Solid State and Materials Sciences, 37, pp. 181-214 (2012).
[5] Wang, Y., Materials Transactions, 54(5), pp. 729-731(2013).

Design and characterization of SnO_2-reduced graphene oxide nanocomposites

Cecilia de Almeida Zito[1], Diogo Paschoalini Volanti[1]

[1] Instituto de Biociências, Letras e Ciências Exatas – IBILCE, Universidade Estadual Paulista – UNESP, São José do Rio Preto, São Paulo, Brazil cecilia_zito@hotmail.com

Recent studies have demonstrated that reduced graphene oxide (RGO) can improve the gas sensing properties of SnO_2, such as selectivity, sensibility, and time response.[1-3] Therefore, we synthesized SnO_2-RGO composites in one-step by microwave-assisted hydrothermal (MAH) method for future application in volatile organic compounds (VOCs) sensing. First, graphene oxide (GO) was prepared by a modified Hummers' method.[4] The composites were synthesized using $K_2SnO_3.3H_2O$ and urea as precursors with different amounts of GO. For comparison purposes, pure SnO_2 was also synthesized. The samples were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), field emission gun scanning electron microscopy (FEG-SEM), transmission electron microscopy (TEM). XRD and FTIR analyzes were conducted in IBILCE/UNESP, and FEG-SEM and TEM were performed in Chemistry Institute/UNESP – Araraquara. The XRD pattern of all samples could be indexed to the tetragonal phase of SnO_2 and the characteristic peak of GO (at $2\theta = 11º$) disappeared, which indicates the reduction of GO by MAH treatment. Furthermore, a calculation by Scherrer's equation gives a crystallite size of about 5.8 nm for all samples, pure SnO_2 and composites. The FTIR results confirmed the reduction of GO, since the presence of oxygenated functional groups, which GO contains, could not be observed anymore in the composites, except one peak at ~3.290 cm^{-1} that is also observed in pure SnO_2. The FEG-SEM images revealed spherical SnO_2 nanoparticles that were not changed by RGO presence. In addition, the SnO_2 nanospheres had a greater dispersion in composites. The high resolution TEM (HRTEM) image and the selected area electron diffraction (SAED) pattern of SnO_2-RGO nanocomposite are exhibited in Figure 1. The HRTEM image shows an interplanar spacing of 0.33 nm, which corresponds to the (110) planes of SnO_2. The SAED pattern could be indexed to rutile phase of SnO_2.

The authors acknowledge FAPESP (grant #2015/05916-9, and #2014/17343-0) and CAPES. We also thank the LMA-IQ and LSQA-IBILCE for FEG-SEM and FTIR facilities, respectively.

[1] ZHANG, H. et al., Sensors Actuators B: Chemical, 190, 472 - 478 (2014). [2] KIM, I. et al., ACS Applied Materials & Interfaces, 6, 2588 – 2597 (2014). [3] GHOSH, R. et al., RSC Advances, 5, 50165 – 5013 (2015).

[4] HUMMERS, W. S. et al., J. American Chemical Society, 80, 1339-1339 (1958).

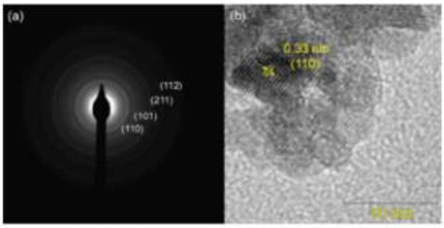


Figure 1. *(a) SAED pattern of SnO2-RGO composite and (b) HRTEM image of SnO2-RGO composite.*

Low Energy Ion Implanting of Silver or Copper Ion for antimicrobial activity

Cesar Henrique Wanke*, Tatiana Pacheco Soares, Andreia Valim de Souza, Carlos Alejandro Figueroa, Otávio Bianchi, Cesar Aguzzoli
University of Caxias do Sul, Caxias do Sul, Rio Grande do Sul, Brazil
*chwanke@ucs.br

In modern medicine, biomaterials have been widely used as implants. However, orthoses and prostheses infected with post-implanted microorganisms require surgeries and medical interventions that are costly and treatment can take months. To combat infections associated with implants, the best strategy is to prevent them from occurring. One strategy is the silver ion implantation in these biomaterials [1-4]. As the antimicrobial efficacy of the nanoparticle depends on the shape and size of them [5], this can be confirmed by studying the inhibition of bacterial growth by differentially shaped and size nanoparticles. In this work, silver or copper ions were implanted at low energies in medical titanium with the goal to render bactericidal substrate surface and therefore, inhibit biofilm formation. The implantation was done using the Ion Plating equipment. After ion implantation, the samples were analyzed by Rutherford Backscattering Spectrometry (RBS), Glow-Discharge Optical Emission Spectroscopy (GD-EOS) and X-Ray Diffraction. The RBS analysis was performed at the Federal University of Rio Grande do Sul. The results show that the silver was implanted at depths of until 10 nm, corroborating with simulation data. In addition, preliminary tests of antimicrobial activity show that the approach adopted in this work has been effective. However, for a better understanding of how the nanoparticles are distributed in the outer surface, i.e. if are sprayed or in the cluster form, are necessary to use techniques that enable to evaluate this distribution. The most widely used technique for this is the transmission electron microscopy. It is intended to verify how nanoparticles are distributed on the surface (Figure 1a) as well as its distribution in depth (Figure 1b). For this, it needs to analyze the surface and cross section. These analyses will be used to correlate with the process parameter of the equipment and thermal treatment of samples after ion implantation.

We are indebted to the Brazilian agency CAPES, University of Caxias do Sul and Ion Implantation Laboratory (Institute of Physics, Federal University of Rio Grande do Sul, Porto Alegre, RS, Brazil).

[1] L. Zhao et al., Biomaterials, 32, 5706 - 5716 (2011).
[2] A. Melaiye and W. J. Youngs, Expert Opinion on Therapeutic Patents, 15, 125 - 130 (2005).
[3] D. R. Monteiro et al., International Journal of Antimicrobial Agents, 34, 103 – 110 (2009).
[4] K. Hori and S. Matsumoto, Biochemical Engineering Journal, 48, 424 – 434 (2010).
[5] M. Rai et al., Biotechnology Advances, 27, 76 – 83 (2009).

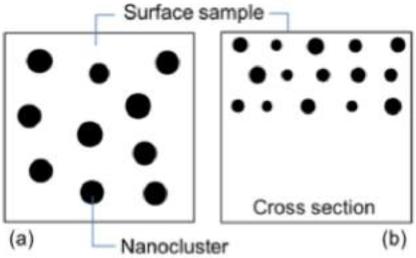


Figure 1. Representation of the formation of nanoclusters of the silver of copper nanoparticles on surface (a) and its distribution in depth (b).

Straightforward Synthesis of Bimetallic Co/Pt Nanoparticles in Ionic Liquid: Atomic Rearrangement Driven by Reduction-Sulfidation Processes and Fischer-Tropsch Catalysis

Dagoberto O. Silva,[a,b*] Leandro Luza,[b] Aitor Gual,[b] Daniel L. Baptista,[c] Fabiano Bernardi,[c] Maximiliano J. M. Zapata,[c] Jonder Morais [c] and Jairton Dupont [b*]

[a] Chemistry Department - UFSC, Florianópolis, SC, Brazil. [b]Institute of Chemistry - UFRGS, Porto Alegre, RS, Brazil. [c] Institute of Physics - UFRGS, Porto Alegre, RS, Brazil.
silvadago@gmail.com

Unsupported bimetallic Co/Pt nanoparticles (NPs) of 4.4±1.9 nm can be easily obtained by a simple reaction of [bis(cylopentadienyl)cobalt(II)] and [tris(dibenzylideneacetone) bisplatinum(0)] complexes in 1-n-butyl-3-methylimidazolium hexafluorophosphate IL at 150 ^{o}C under hydrogen (10 bar) for 24 h. These bimetallic NPs display core–shell like structures in which mainly Pt composes the external shell and its concentration decreases in the inner-shells ($CoPt_3$@Pt-like structure). XPS and EXAFS analyses show the restructuration of the metal composition at the NP surface when they are subjected to hydrogen and posterior H_2S sulfidation, thus inducing the migration of Co atoms to the external shells of the bimetallic NPs (Fig. 1). Furthermore, the isolated bimetallic NPs are active catalysts for the Fischer–Tropsch synthesis, with selectivity for naphtha products.

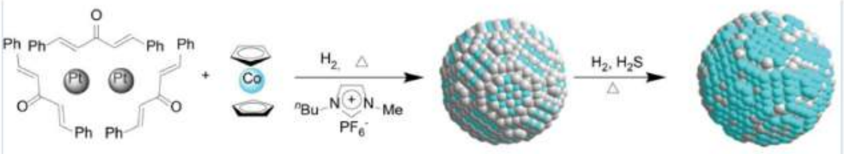


Fig. 1: *Unsupported bimetallic Co/Pt nanoparticles (NP) of 4.4±1.9 nm prepared in ionic liquid undergoes the restructuration of the metal composition at the NP surface when they are submitted to hydrogen and posterior H_2S sulfidation.*

The authors are thankful to LNLS (Campinas, SP) and INMETRO (RJ) for the use of the beam line and STEM microscope, respectively. Funding agencies: CNPq, CAPES, FAPERGS and INCT-Catal, and MCTI (Brazil).

[1] Silva D. O., et al., Nanoscale, 6, 9085-9082 (2014)

Synthesis of elongated Au and $AuCu_3$ nanoparticles via oleylamine mediated synthesis.

Moraes, D. A.(1)*; Varanda, L. C.*(1)

1 *Colloidal Materials Group, Chemistry of Institute of São Carlos, University of São Paulo, São Carlos, São Paulo, Brazil.*
damoraes15@gmail.com

Noble metals nanoparticles (NPs) as Au, Ag and Cu present size and shape- dependent optical properties called Localized Surface Plasmon Resonance (LSPR). The LSPR arise from radiation-matter interaction and lead to an absorption band on visible and near infrared region (plasmon band). Due to this property, these materials can be used as agents to diagnostics and therapy. For these applications, the plasmon band needs to be in the therapeutic window of spectrum (between 650 – 900 nm). Nanorods (NRs) and nanoshells present the plasmon band in this region.[1, 2] Here, it's reported partial studies upon syntheses of elongated NPs of Au and $AuCu_3$ aiming to achieve NRs. Au NPs were synthesized as follow: $HAuCl_4.3H_2O$, 1–octadecene, oleylamine (OLA) and, hexylamine (HXA) or triethylamine (TEA), was heated to 80ºC for 60 minutes under stirring and then it was kept at 60°C for 12 or 24 hours. The reaction was cooled down to room temperature and the NPs were purified with ethanol and centrifugation several times and dispersed in hexane. $AuCu_3$ NPs were synthesized as follow: a mixture of $HAuCl_4.3H_2O$, OLA was heated to 160°C for 20 minutes to promote Au nucleation. The suspension was cooled to 60°C and, a solution of copper (II) acetylcetonate in OLA was added. The mixture was heated to180°C for 20 minutes, after that the temperature was raised to 280°C and kept 20 minutes. The suspension was cooled down to room temperature and the purification was similar to Au NPs procedure. Mixture of nanowires (NW), ultrathin NW and nanospheres (NS) were obtained for Au NRs synthesis. It was used three surfactant mixtures: only OLA, OLA and HXA, and OLA and TEA, and It were observed that TEA led to slightly elongate NPs indicating an initial formation of NRs. So far, mixture of $AuCu_3$ NRs and NS was obtained and modifications in parameters of synthesis, temperature and time, was studied, however this NPs mixture are being obtained yet.

This work was supported by Brazilian agencies FAPESP (Grant No. 2013/01284-2) and

[1] Huang, X., et al., J. Am. Chem. Soc., 128, 2115-2120 (2006).

[2] Zhao, J., et al., et al., Nanomedicine, 9 (13), 2041–2057 (2014).

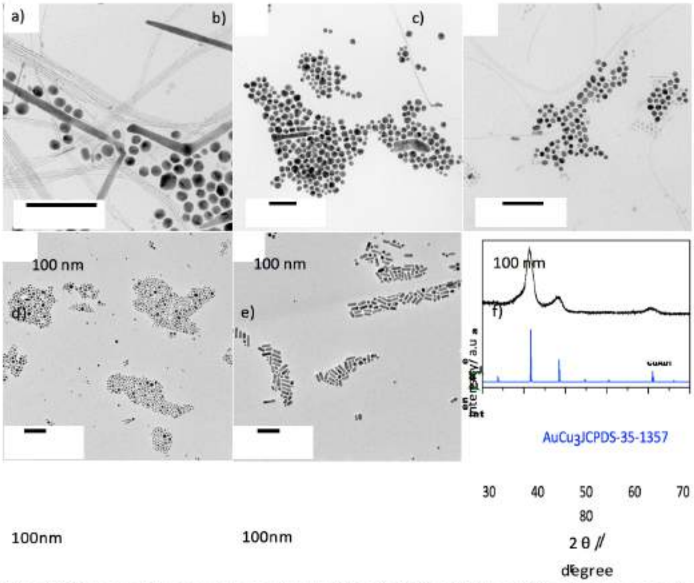


Figure 1: a), b) e c) TEM images of Au NPs using as surfactant, OLA only, OLA and HXA, and OLA and TEA, respectively; d) and e) TEM images of AuCu3 NPs after selective separation being c) nanospheres (supernatant) and d) nanorods (precipitate); f) X-Ray Diffractogram patterns of AuCu3 NPs before selective separation and JCPDS standard.

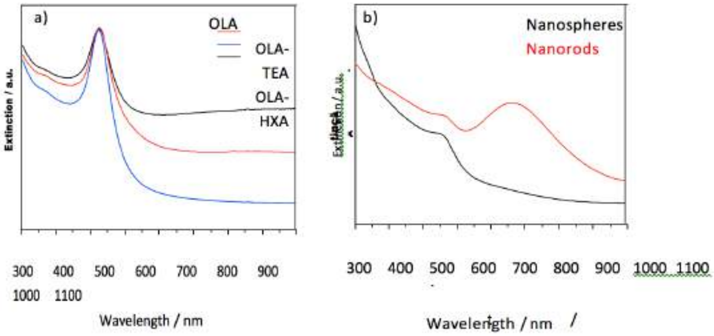
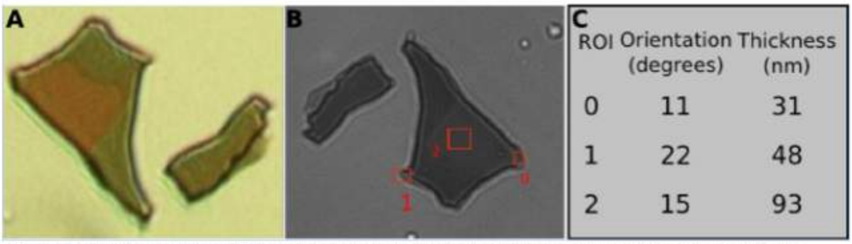


Figure 2: a) Extinction spectrum of Au NPs; b) extinction spectrum of AuCu3NPs after selective precipitation separation.

Characterization of Twisted Black Phosphorus Structures

Daniel Grasseschi[1], Helder Peixoto[2], José C. Viana Gomes[2], Christiano J. S. de Matos[1]
1 - MackGraphe – Graphene and Nanomaterials Research Center Mackenzie Presbyterian
University, São Paulo, SP, Brazil
2 – Centre for Advanced 2D Materials (CA2DM) National University of Singapore, Singapore Daniel.grasseschi@gmail.com

Black phosphorus (BP) is a lamellar allotrope of phosphorus, which has recently been added to the family of bidimensional crystals.[1,2] Like the carbon atoms in graphene, each P atom in BP is bound to three adjacent P atoms forming a six membered ring. However BP forms a two-dimensional puckered structure, which possesses reduced symmetry that is reflected by their properties. Due its reduced symmetry BP presents an unique optical response, which is highly polarization- dependent. The angular dependence of Raman scattering, for example, of the totally symmetric modes is rather unusual and can be explained by considering a complex polarizability tensor.[3] Twisted BP layers can occur naturally in BP crystal, in result of the synthetic procedure. Preliminary (and unpublished) ellipsometry data, on mechanical exfoliated BP crystal, reveals deviations of up 11 degrees in the superimpostion of different, relatively thick (20-40 nm), layers in the same BP flake, Figure 1. It is expected that this deviations leads to deviations in the Intensity of the totally symmetric Raman modes, as well as in a number of other electronic, mechanical and optical properties. This works studies the properties of twisted BP layers, mainly by Raman spectroscopy to achieve a better understatement of the band structure, electron-radiation interaction and electron-phonon coupling in this material, which is of great importance for the understanding of BP electronic properties. We intent to use high resolution transmission electronic microscopy and electron diffraction to confirm the presence of twisted black phosphorus structures and possible defects generated by layers superimposition, complementing the study done so far by ellipsometry.



ROI	Orientation (degrees)	Thickness (nm)
0	11	31
1	22	48
2	15	93

Figure 1: *(A) Optical microscopy in a reflection mode. (B) Regions of interest selected and analyxed in the ellipsometer. (C) Table with the values of orientation and thickness of the regions of interest.*

The financial support from FAPESP, Mackgraphe and CA2DM are gratefully acknowledged.

[1] F. Xia, H. Wang, Y. Jia, *Nat. Commun.* **2014**, *5*, DOI 10.1038/ncomms5458.
[2] V. Tran, R. Soklaski, Y. Liang, L. Yang, *Phys. Rev. B - Condens. Matter Mater. Phys.* **2014**, *89*, DOI 10.1103/PhysRevB.89.235319.
[3] H. B. Ribeiro, M. A. Pimenta, C. J. S. de Matos, R. L. Moreira, A. S. Rodin, J. D. Zapata, E. A. T. de Souza, A. H. Castro Neto, *ACS Nano* **2015**, *9*, 4270.

Influence of cryogenic temperature on the artificial aging behavior of AA6061 Al alloy processed by Severe Plastic Deformation

Danielle Cristina Camilo Magalhães[1]; Vitor Luiz Sordi[1]; Maurizio Ferrante[1]

[1] Federal University of São Carlos, São Carlos – São Paulo Corresponding author: danielle_camilo@yahoo.com.br

In this work AA6061 aluminum alloy samples were deformed by conventional rolling and Equal-Channel Angular Pressing (ECAP) at 298 K and 77 K. The ability of these processes in obtaining ultra-fine grained microstructures and substantially change the mechanical properties after aging heat treatment was investigated. Equivalent strain levels were taken up to ε = 2.0 and heat treatments were performed at 373 K in an oil bath, for times from 0.5 to 48 hours. The samples were analyzed by optical metallography and Vickers hardness measurements (100 gf, 15 sec) in the longitudinal direction. Tensile tests are performed at the Instron machine with strain rate of 10^{-3} s^{-1}. The Transmission Electron Microscopy (TEM) investigations were conducted in a Phillips CM120 operated at 120 kV. For TEM preparation the samples were mechanically ground up to 0.07 mm thickness using 1200 grit size emery papers and subsequently thinning by electron-polishing using Tenupol-3. The electrolyte with 25% of HNO_3 and 75% of methanol was used at -40 ºC and 20 V. Fig 1 shows the behavior of AA6061 Al alloy in solution annealing condition submitted to tensile tests at 298 K and 77 K. Preliminary results indicate that the cryogenic deformation promotes a partial suppression of dynamic recovery mechanisms leading to an increase in the dislocation storage capacity [1, 2]. Fig. 2 shows a microstructure obtained by TEM analysis for AA6061 alloy before and after deformation by ECAP (ε = 1,4 or two passes in B_c route) at room temperature. It can to observe a small grains and subgrains on the microstructure. It is expected that the microstructural refinement will be more intense due to the reduced deformation temperature [2]. In addition, the artificial aging kinetics of this alloy may be accelerated by the increase in the number of nucleation sites [1, 2]. It is expected that with the TEM technique it is possible to quantify and identify such nanosize precipitates dispersed in the aluminum matrix.

The authors would like to thank the Department of Materials Engineering of UFSCar and FAPESP (project grant no. 2014/15091-4) by the infrastructure and financial support. D. C. C. Magalhães acknowledge to the CNPq for her scholarship.

[1] FU, M. W. et al. Materials Science and Engineering A, 526, 84-92, 2009.

[2] PANIGRAHI, S. K.; JAYAGATHAN, R. Journal of Alloys and Compounds, 470, 285-288,2009.

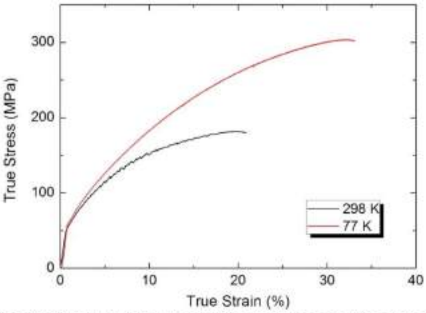


Fig. 1 - Curves of tensile tests of AA6061 Al alloy in solution annealing condition. The tests were performed at 298 K and 77 K, with strain rate of 10^{-3} s^{-1}.

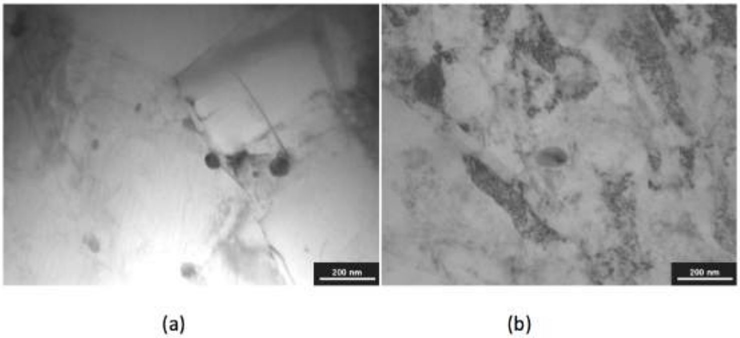


Fig. 2 - Bright field TEM micrographs of AA6061 Al alloy: (a) as-received material, with large grains and low dislocation density; and (b) sample after two passes in ECAP at room-temperature in B_C route with significant grain refinement (new grains and subgrains).

Silver nanoparticles synthesis to application as nano biosensors

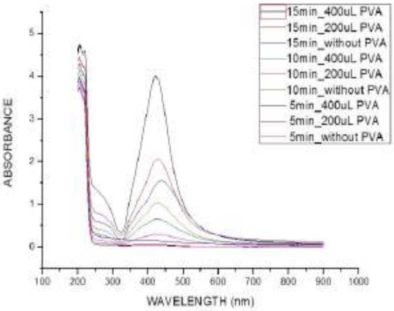
Danilo Soares Costa[1], Jairo Pinto de Oliveira[2], Bárbara Altoé Milaneze[2], Wanderson Juvencio Keijok[2], Adilson Ribeiro Prado[2], Maria José Pontes[2], Moises Renato Nunes Ribeiro[2], Breno Valentim Nogueira[2] e Marco Cesar Cunegundes Guimarães[2]
[1,2] Federal University of Espírito Santo, Vitória, Espírito Santo, Brazil jairo_cbb@hotmail.com

Nanoscience is a new interdisciplinary science, which can be defined as a whole knowledge on fundamental properties of nano-size objects [1]. Silver nanoparticles (AgNP's) have unique optical, electrical, and thermal properties and are being incorporated into products that range from photovoltaics to biological and chemical sensors have stimulated different areas of research in recent years. The optical properties of AgNP's are dictated by the geometrical parameters such as size and shape. The same material composition can be determined with different physical and chemical characteristics just modifying characteristics such as size, self- organization, crystalline structure and shape, the point of the material in the nanometer range show distinct physical and chemical properties of materials on the macroscopic scale [2]. Thus, this work aimed to optimize the synthesis of AgNP's using sodium citrate as reduction method, assessing concentrations of this reducing agent and the synthesis time. The attempt is to develop a route to generate nanoparticles from a precursor and facilitate the use of these nanomaterials in biosensors to detect antigens.

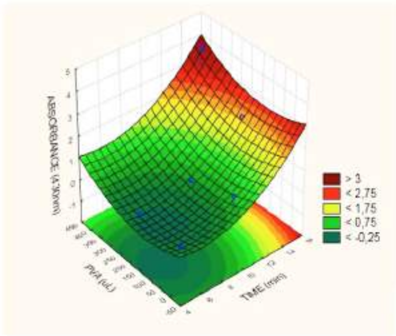
To check the effect of variables on conversion of the reaction, as well as finding the conditions that maximized the synthesis of AgNP's, one factorial design (3^2) with 3 levels and 2 variables was performed. The variables evaluated were: concentration of stabilizing agent (PVA) and the time synthesis (5, 10 and 15 min). These intervals were defined to cover most of the studies described on the literature [3,4,5].

Samples AgNP's were collected after the step for synthesis and had their optical properties assessed by spectrophotometer UV-vis (UV-3600 UV-VIS-NIR, Shimadzu Inc., Japan). The size and morphology of AgNP's were examined by transmission electron microscopy (JEM1400, JEOL Inc., Japan). The outcomes provided byeach equipment are depicted in figures 01-A, 01-B and figure 02.

A



B



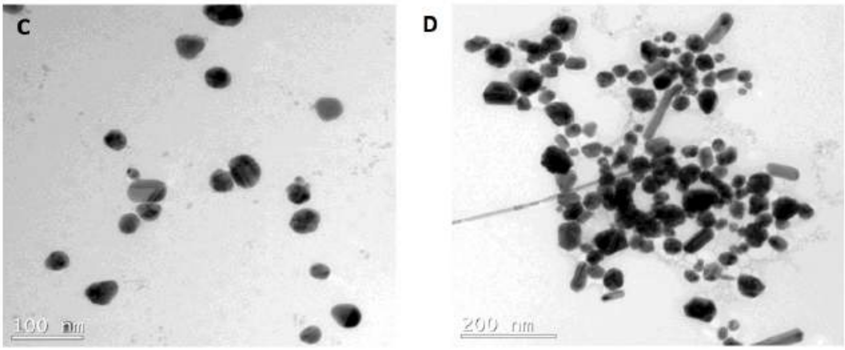


Figure 01. UV-Vis electronic spectrum showing the different absorbance levels of absorbance of the conditions evaluated (A). Estimating the absorbance of the nanoparticles by absorbance (430nm) as a function of the variables (C). TEM images, Time (15 min) and PVA (400uL (D); Time synthesis (15 min) and without stabilizing agent PVA.

1. *Sergeev G.B. Cryochemistry of Metal Nanoparticles. Journal of Nanoparticle Research, 2003, Volume 5, Issue 5-6, pp 529-537.*
2. *Page, K.; Proffen, T.; Terrones, H.; Terrones, M.; Lee, L.; Yang, Y.; Stemmer, S.; Seshadri, R.; Cheetham, A. K.; Chem. Phys. Lett. 2004,393,385.*
3. *Morones, J. R.; Elechiguerra, J. L.; Camacho, A.; Holt, K.; Kouri, J. B.; Ramirez, J. T.; Yacaman, M. J. "The bactericidal effect of silver Nanoparticles", Nanotechnology, 2005, 16, 2346.*

Synthesis and structural analysis of $CoFe_2O_4$:$BaTiO_3$ nanocomposites

D. Alanis[1*], P.N. Oliveira[1], R.D. Bini[1], D.M. Silva[1], G.S. Dias[1],I.A. Santos[1], L.F. Cótica[1]
[1]Department of Physics, State University of Maringá
Av. Cololmbo, 5790, Maringá, Paraná, Brazil 87020-900
*e-mail: denise_a89@hotmail.com

Multiferroic materials have attracted interest due to the presence of more than one ferroic order, for example magnetic and electric orders, in the same phase. This particular coupling phenomenon is known as magnetoelectric (ME) effect. However, it is difficult to obtain significant ME effect in single-phase materials, since magnetic and electric dipoles have to coexist in the same asymmetric structure. Thus, in order to enhance the ME effect, piezoelectricmagnetostrictive

composites have been exploited. Among some different configurations to prepare composite materials, the core-shell nanoparticles are also investigated as a beneficial starting material for magnetoelectric nanocomposite (MENC) materials. This structure provides direct and large surface contact of phases and preserves the individual piezoelectric and magnetostrictive properties of each phase. Particularly, ferrite-barium titanate in a core-shell configuration has been investigated due to appropriate individual (magnetostrictive and piezoelectric) properties of the components at room temperature. In addition, their chemical and mechanical stability and nontoxic properties are also important in applications regarding the environment and biological applications. This work aims to prepare MENC's in a core-shell configuration with a narrow size distribution. A combination of polymeric and citrate methods was used for the MENC's syntheses. MENC's were prepared in the 1:1, 3:2 and 7:3 ($CoFe_2O_4$:$BaTiO_3$) molar ratios, respectively. The structural characterizations of the obtained MENC's were performed by X-ray diffraction and Fourier transform infrared spectroscopy (FTIR). These analyses showed a combination of a cubic $CoFe_2O_4$ and a tetragonal $BaTiO_3$ composite. A core-shell morphology of MENC's was observed by transmission and scanning electron microscopies. The MENC's atomic compositions were confirmed using energy dispersive X-ray spectroscopy. Finally, the ferrimagnetic character of the MENC's was observed in the magnetic characterizations obtained in a vibrating sample magnetometer.

We are thankful to CAPEs, CNPq and FINEP.

[1] L. F. Cotica, et al., Journal of Nano Research, 28 (2014) 131.

[2] L. F. Cotica, et al., Journal of Magnetism and Magnetic Materials, 324 (2011) 559.

Relation between the crystal structure interfaces of NiTi/Co, NiTi/Ni and FeRhPd films with their magnetic behavior

Diana L. Torres[1] and Daniel R. Cornejo[1]
[1] São Paulo University, Physics Institute, São Paulo, SP, Brazil
dianats@if.usp.br

Magnetic control at the nano-scale is interesting for technological applications. Nowadays, several ways to obtain this control have been reported and the development of new materials to improve it is growing up. For instead, it can be observed in ferromagnetic films coupled with materials which show temperature- or field-driven structural phase transition, as well as, ferromagnetic films which show first order phase transitions trough changes in temperature. More specifically, we study the magnetic behavior of the NiTi/Co and NiTi/Ni films through the structural phase transition of the nearly equiatomic NiTi layer. The films have been grown on silicon (100) substrates by DC magnetron sputtering. In this structure, the magnetization of the ferromagnetic layer may be modified through changes in the stress field at the interface, when the structural phase transition in the non-magnetic layer is carried-out. Also, we study FeRhPd films deposited on MgO (001) which show a first magneto-structural phase transition. All these functional structures are characterized by X-ray diffraction (XRD) and Rutherford backscattering spectrometry (RBS) to obtain the crystal structure and chemical composition respectively. Magnetic measurements as a function of temperature or magnetic field are performed by using a superconducting quantum interference device (SQUID) and a vibrating sample magnetometer (VSM) to study anisotropy behavior, coercivity, magnetic phase transitions, etc. Finally, we expect to use High resolution-TEM analysis to get a more precise relation between the structure in interfaces of the films and their magnetic behavior.

ZnO Semiconductor Nanowires Gas Sensors

E.S.H. de Menezes[1]*, C. L. Sombrio[1], B.Canto[1], R. Reis[2] and D. L. Baptista[1],
[1]Instituto de Física, UFRGS, Porto Alegre, Rio Grande do Sul, Brazil
[2]National Center for Electron Microscopy, Berkeley, California, USA
eduardoserralta@hotmail.com

Zinc Oxide nanowires have a good potential for fast and selective gas sensing applications [1-4]. When in contact with a small gas concentration the nanowire electrical resistance changes drastically. Therefore it is possible to use such behavior to detect very low gas concentrations through a nanowire-based sensing device. Additionally, the nanowire surface can be modified to change the sensor selectivity. The purpose of this project is to develop different gas sensing devices and characterize the electrical response to different gases. The electrical behavior of the nanowire is related to the lattice structure and defect characteristics. In this work, we present the project perspectives and techniques that will be applied to develop nanowire-based gas sensors. Previous as-grown ZnO nanowires samples were characterized using advanced electron microscopy (FEG-SEM, HRTEM, HAADF-STEM) and spectrum-imaging (EDX, EELS) techniques (Fig 1-2). The determination of growth polarity was also achieved by CBED analysis. HRTEM/STEM analyses were performed using a XFEG Cs-corrected FEI Titan 80/300 microscope.,. The ZnO nanowires were grown by vapor-liquid-solid (VLS) mechanism using sapphire as substrate and Au as catalyst. Dense and vertically aligned ZnO nanowires forest was grown epitaxially on sapphire substrates as showed in Fig. 1 (a). The nanowires were about 50 nm in diameter and its length up to 5 µm. A spatial distribution of Au catalyst nanoparticles at the ZnO/substrate interface is clearly observed in Fig. 1 (b) by HAADF-STEM and EDX-SI. The experimental and simulated CBED patterns presented in Fig. 1 (c-d) indicate a Zn-polar growth (e). New samples with different growth conditions will be synthesized and electron microscopy will be utilized to characterize it.

[1] P. Yang et al., Adv. Funct. Mater., 12 (2002) 323.
[2] M.-T. Chen et al., Nano Lett., 10 (2010) 4387.
[3] C. Soci et al., Nano Lett., 7 (2007) 1003.
[4] A. Janotti et al., Phys. Rev. B, 76 (2007) 165202.

The authors thanks the Materials Metrology Division (DIMAT) for the use of Electron Microscopy facilities at INMETRO. This work was partially supported by Brazilian agencies CNPq and CAPES

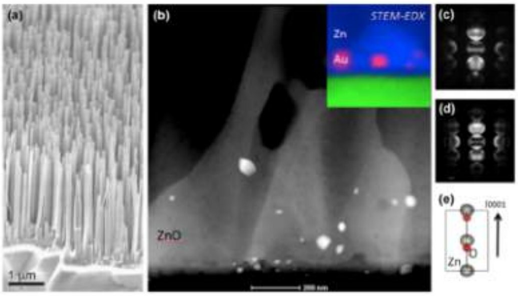


Fig. 1. Characterization of the as-grown ZnO nanowires. (a) SEM micrograph of an epitaxially grown ZnO forest on c-plane sapphire substrate. (b) HAADF-STEM image of the ZnO/substrate interface and an EDX spectrum image showing the presence of Au seeds at the base of nanowires. (c) Experimental and (d) simulated CBED patterns indicating the Zn-polarity (e) of the ZnO structure.

Using Transmission Electron Microscopy (TEM) to assess the microstructure of thermomechanical processed Advanced High Strength Steels

Edwan Anderson Ariza[1], Arthur Seiji Nishikawa[1], André Paulo Tschiptschin[1,2]

[1] Metallurgical and Materials Engineering Department, University of São Paulo (USP)

[2] National Nanotechnology Laboratory (LNNano) – National Center for Research in Energy and Materials – (CNPEM). andersonariza@usp.br

The use of Transmission Electron Microscopy (TEM) to identify and assess the microstructure of thermomechanical processed Advanced High Strength Steels (AHSS) is discussed. Thermomechanical simulation of hot stamping, quenching and partitioning processes (HSQ&P) of a high-strength TRIP800 steel were carried out in a Gleeble machine coupled to the XTMS Synchrotron X-ray diffraction line at the National Nanotechnology Laboratory [1]. The microstructures and mechanical properties were analyzed using Light Optical Microscopy (LOM), Field Emission Gun Scanning Electron Microscopy (FEG- SEM), X-ray diffraction (XRD), Electron backscatter diffraction (EBSD), Nanoindentation (NI) and TEM. The microstructure after Q&P and HSQ&P treatments consists predominantly of ferrite, bainite, retained austenite and martensite. The TEM analysis of the bainitic-morphology packets is used to identify if they consist of a lath ferrite phase separated by an interlath carbon- enriched retained austenite. In order to obtain an accurate understanding of the processing-microstructure-properties relations of these materials requires detailed analysis by TEM. TEM is also used to confirm if fine carbides had been precipitated during partitioning treatment. Another important aim to use TEM technique is the identification of the different types of retained austenite formed after Q&P and HSQ&P processes. Usually three types of retained austenite with different size and morphology can be found in microstructures treated by Q&P. One type is the blocky retained austenite distributed in bainite ferrite matrix. Other type is the ultra-fine retained austenite films (~20 nm thick) located between bainitic ferrite plates. And another retained austenite is the chunks- type (100–300 nm width) located between martensite laths. The different carbon enriching processes of these three types of austenite could lead to the different sizes and morphologies [2]. The distribution, morphology and stability of retained austenite play a critical role in the mechanical properties of the TRIP- assisted steels.

Acknowledgements to FAPESP process nº 2014/11793-4 for the financial support. The authors also acknowledge the Brazilian Nanotechnology National Laboratory – LNNano for the use of the XTMS installation at the XRD-1 beamline.

[1] LNNano - lnnano.cnpem.br/laboratories/cpm/facilities/xtms/

[2] Gao, G., et al., A carbide-free bainite/martensite/austenite triplex steel with enhanced mechanical properties treated by a novel quenching–partitioning–tempering process. Materials Science and Engineering: A, 2013. 559: p. 165-169.

Microstructural analysis of nanoquartz by transmission electron microscopy.

Schenkel[1], E. A., Santos[1], M. F. M., Fujiwara[1,2], E., Suzuki[1], C. K.
1- Laboratory of Photonic Materials & Devices, Department of Manufacturing and Materials Engineering, Faculty of Mechanical Engineering, State University of Campinas
2-Department of Integrated Systems, Faculty of Mechanical Engineering, State University of Campinas

Nanoquartz are nanoparticles obtained by hydrothermal syntesis of silica [1] or high-energy milling of crystal quartz bulk [2, 3]. This material has importance from a scientific point of view, to understand quartz phase transitions [4] and geological process [5], such as from a technological point of view, to manufacture specialty glasses [6], ultrafiltration membranes [7] and concrete additives [8]. In the case of the nanoquartz obtained by high-energy milling, the XRD analysis shows a loss of crystallinity by a fraction of the material [3]. A proposed model is that nanoparticles have an amorphous shell and a crystalline core [3, 9, 10]. The aim of this of this work is to obtain images by TEM in order to confirm or refute the core- shell model. If this model is confirmed, will be trying to measure the thickness of the amorphous shell and verify that the results obtained are consistent with XRD analysis. For this, nanoquartz samples obtained from two different geological origins (Belmonte-BA and Soledade-PB) will be analyzed. These particles were obtained by high energy-ball milling and separated by decantation in an aqueous solution [3]. Using the LNNANO microscope TEM-HR JEOL 3010, atomic resolution images will be acquired and analyzed using the ImageJ software[11]. The results will be compared with the XRD patterns obtained at Laboratory of Photonic Materials & Devices diffractometer and XRD1 beam line in LNLS and [3].

Magnetic nanoparticles coupled with β-cyclodextrin as a delivery system for doxorubicin

Evelyn Christyan da S. Santos[1], Célia M. Ronconi[1]
[1] Universidade Federal Fluminense, Niterói, Rio de Janeiro, Brasil
cmronconi@id.uff.br

Cancer is currently the most investigated class of diseases, which is known by out-of-control abnormal cell growth. The common treatments consist in the surgical, chemotherapy and radiotherapy approaches, where the second is the most applied in the cases [1]. However, this treatment, which is based on the use of drugs are often aggressive to the body of the patient, because it affects not only the target cells but also the healthy ones, leading to many side effects [2]. Thus, the development of new devices aiming to minimize these effects caused by the use of traditional drugs is fundamental. In order to overcome these problems, a delivery control system of drugs must be designed. Herein, the preparation and characterization of magnetic iron oxide nanoparticles (MNPs) coupled with β-cyclodextrins (β-CDs) as drug delivery system for doxorubicin (DOX) is reported. The nanodevice was prepared in four steps: (i) monotosylation of the β-CDs in basic solution [3]; (ii) synthesis of Fe_3O_4 nanoparticles *via* coprecipitation of Fe (II) and Fe (III) ions from basic solution [4]; (iii) surface modification with aminopropyl groups; and (iv) coupling of the monotosylated β-CDs with amino-functionalized Fe_3O_4 nanoparticles through tosyl S_N2 nucleophilic substitution [3]. The nanodevice and the precursors were characterized by several techniques. NMR ^1H and ^{13}C spectroscopy confirmed the synthesis of the monotosylated β-CDs. FT-IR spectroscopy showed the presence of β-CDs groups on the surface of iron oxide MNPs. Elemental and thermogravimetric analyses, and DLS (zeta potential and size) revealed the MNPs modification by aminopropyl and β-CDs groups (all these characterizations were made at UFF). Further investigation about the structure (XRD and Raman), size (TEM) and magnetic measurements will be carried out, as well as the DOX release by UV-Vis spectroscopy under hyperthermia conditions.

The authors gratefully acknowledge FAPERJ (JCNE), CNPq (Jovens Pesquisadores em Nanotecnologia grant number 550572/2012-0 and ECSS fellowship), CAPES (T. C.S. fellowship) and FINEP (0113031500) for the financial support. We also thank the Multiuser Laboratory of Material Characterization (http://www.uff.br/lamate/) and Multiuser Laboratory of Spectroscopy (http://www.uff.br/lame/).

[1] W. Guo et al. Dalton Trans., 43, 18056 (2014). [2] F. Zhang et al. Nano Lett., 12, 61 (2012).
[3] G. H. G. Ahmed et al. Microchim Acta, 181, 941 (2014). [4] B. Atashkar et al. Catal. Sci. Technol., 3, 2140 (2013).

Real time study of growth mechanism of luminescent CdTe@3-MPA nanocrystal using a CCD camera

Fernando Menegatti de Melo[1], Daniel Grasseschi[2], Henrique Eisi Toma[1*]

[1] Institute of Chemistry, University of São Paulo, São Paulo, SP, Brazil

[2] Mackgraphe-Graphene and Nanomaterials Research Center, Mackenzie Presbyterian University, São Paulo, SP, Brazil fernando.menegatti.melo@usp.br

Semiconductor QDs have been intensively studied due to their interesting characteristics both from the views of fundamental research and practical application[1]. In the past two decades, significant advances have been made towards the synthesis of colloidal semiconductor QDs, particularly II–VI compound such as CdSe, CdS and CdTe. This work aims to study in real time the influence of the ligand concentration (mercaptopropionic acid – MPA) in the growth mechanism of luminescent CdTe semiconductor nanocrystal, a promising class of visible-active nanocrystals due to high emission quantum yields and a wide useful spectral range, using a CCD camera and analyzing the RGB components to confirm size-dependent band gap. Fig.1 shows images obtained by Transmission Electron Microscopy **(TEM JEOL JEM 2100)** of luminescent CdTe quantum dots in the ratio 1:2.3 (Cd: 3-MPA). Fig.2 confirms size-dependent band-gap using a CCD camera and a fluorimeter in different refluxing times. The measurements were taken in a Supramolecular Nanotech Lab (LNS) and Analytical Center of Institute of Chemistry – USP.

We greatly acknowledge the Institute of Chemistry of University of São Paulo and the support from FAPESP (Grant 2013/24725-4) and CNPq (Grant 482383/2013-5).

[1] C. B. Murray et al., Annu. Rev. Mater. Sci., 30, 545 - 610 (2000).

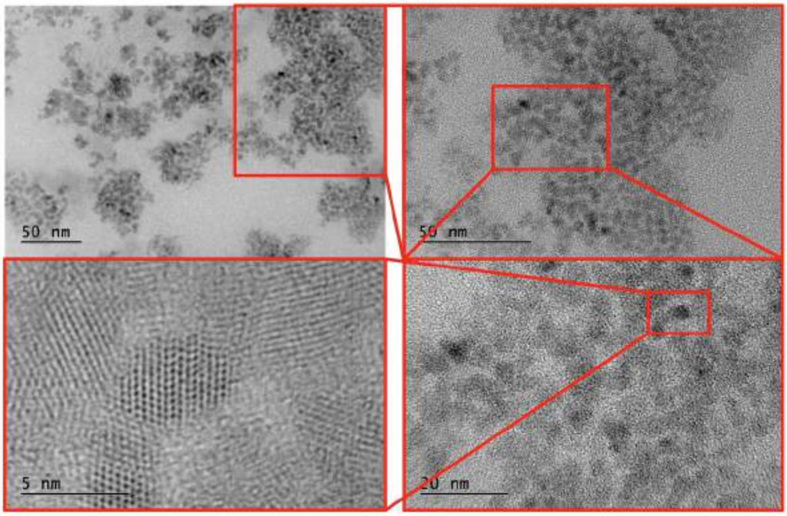


Fig. 1: Images obtained by Transmission Electron Microscopy **(TEM JEOL JEM 2100)** of luminescent CdTe quantum dots in the ratio 1:2.3 (Cd: 3-MPA)

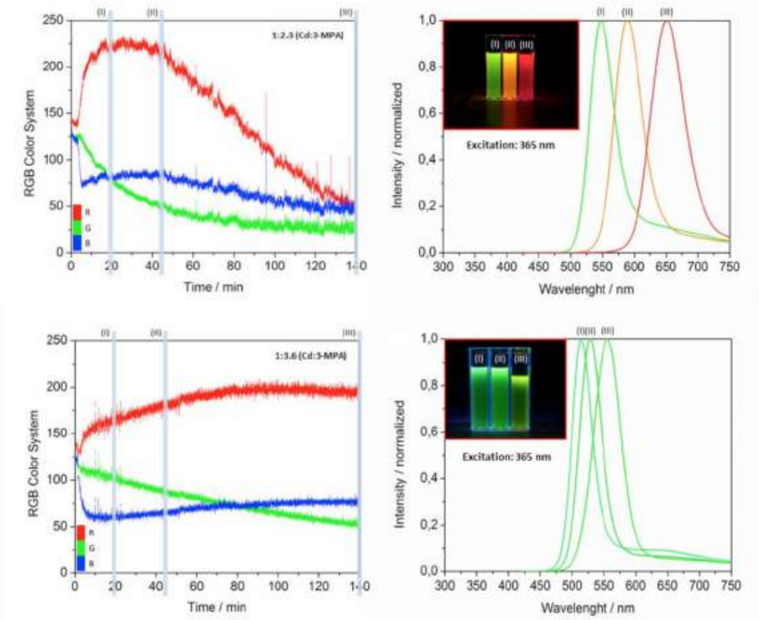


Fig. 2: (Left) Analysis of RGB components for two different ratios (Cd:3-MPA). **(Right)** Emission spectra for three different refluxing times (18, 50, 140 minutes respectively).

FeCo-N_X/C Composite as Electrocatalyst for the Oxygen Reduction Reaction in Direct Formate Fuel Cells

Francisca E. R. Oliveira[1], Fabio H. B. Lima[1]
[1]Institute of Chemistry of São Carlos, University of São Paulo, São Carlos, São Paulo, Brazil
elenicequimica@gmail.com

The major challenge for development of the fuel cells has been related to the discovery of electrocatalysts that show high activity, stability and selectivity [1,2]. In this study, we have investigated the synthesis and electrocatalytic activity of FeN_x/C, CoN_x/C and $FeCoN_x/C$ composites for the ORR and their tolerance to the presence of formate ions. The catalysts were prepared using a simple procedure that involves the chelation of Fe(II) and Co(II) with imidazole, followed by a heat-treatment process in N_2 atmosphere at 700 °C for 10 h[3]. XPS, XRD and TEM measurements were performed in order to characterize the materials. TEM image was recorded on a JEOL JEM 2100 LaB_6 microscope operating at 200 kV installed in the Electron Microscopy Laboratory of the IQSC-USP. The electrochemical measurements were performed using a regular three- electrode cell, in N2 or O2-saturated 1.0 M KOH electrolyte and in the absence and presence of formate ions. The catalysts were deposited glassy carbon rotating disk electrode. Fig.1 shows the TEM image of the $FeCoN_x/C$ as it can be observed heterogeneous distribution of fine particles over the entire carbon support surface with formation of clusters. The results of the ORR, presented in Fig.2, show that the $FeCoN_x/C$ composite present a synergic effect, possessing the higher onset potential and the current density. Indeed, the activity of this material, noted by its ORR half-wave potential, is close to that for the state-of-the art Pt/C. The high activity of the non- precious metal catalyst is discussed in this work based on the MN_4/C or MN_2/C active sites, as identified via experiments of XPS. Further, the Fig.3, this electrocatalyst has a remarkable tolerance to the presence of formate ions. This is ascribed to its activity for the catalysis of the ORR, and its inactivity for the catalysis of the electrochemical oxidation of formate ions. Therefore, this is a promising cathode electrocatalyst for direct formate fuel cells.

[1] YU, X., *et al.* **Applied Catalysis B: Environmental** 165, 63 – 67, 2015. [2] BEZERRA, C. W. B., *et al.* **Electrochimica Acta** 53, 4937– 4951,2008. [3] MA, Y., *et al.***Electrochimica Acta** 55, 7945-7950,2010.

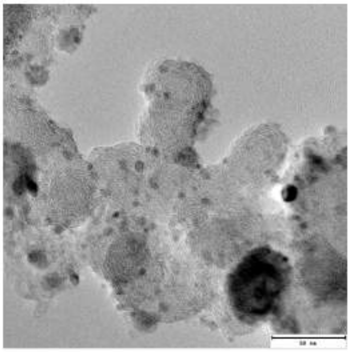


Fig. 1: TEM image of FeCoN$_x$/C

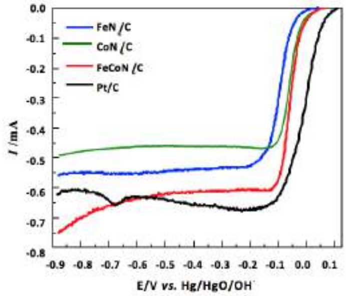


Fig. 2: ORR polarization curves for FeNx/C, CoNx/C and FeCoNx/C catalysts in comparison to that of commercial Pt/C at 1600 rpm in 1 M KOH oxygen-saturated solution.

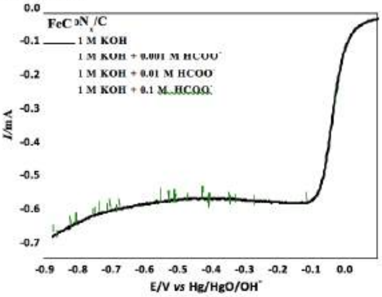


Fig. 3: ORR polarization curves for FeCoNx/C catalyst in the presence of 0.001 M, 0.01 M and 0.1 M formate ion at 1600 rpm in 1 M KOH oxygen-saturated solution.

Synthesis and characterization of Ni supported on Nb_2O_5 catalyst to apply in cellulose conversion reaction

Glauco F. Leal[1,2], Dean H. Barret[1], Silvia F. Moya[1],
Antonio A. S. Curvelo[2,3], Cristiane B. Rodella[1].[1] Brazilian Synchrotron Light Laboratory (LNLS), Brazilian Center for Research in Energy and Materials (CNPEM), Campinas, São Paulo, Brazil.[2] Institute of Chemistry of São Carlos (IQSC), University of São Paulo (USP), Departament of Physical Chemistry, São Carlos, São Paulo, Brazil[3] Brazilian Bioethanol Science and Technology Laboratory (CTBE), Brazilian Center for Research in Energy and Materials (CNPEM), 13083-970, Campinas, São Paulo, Brazil. glaucoferro@gmail.com

The catalytic conversion of cellulose to biofuels and other value added chemicals is one of the most promising routes for the development of economically viable biorefineries. However, the challenge of developing green chemical methods for renewable energy generation based on heterogeneous catalysis relies on a thorough investigation of the physical and chemical properties of the catalyst [1]. Moreover, the correlation of these properties to the functional behavior of the catalyst within the cellulose valorization reaction. Cellulose processing firstly requires hydrolysis to obtain glucose followed by the transformed of glucose to fuels and chemicals [2, 3]. Thus, this PhD project aims to synthesize a new class of bifunctional catalysts composed of Ni and Co dispersed on Nb_2O_5 for cellulose conversion to obtain platform chemicals such as, sorbitol, HMF and levulinic acid among other products. Solid acid catalysts, such as Nb_2O_5 can be effective for cellulose hydrolysis. On the other hand, transition metals, such as Ni and Co are catalysts for hydrogenation and hydrogenolysis reactions. The structural, electronic, surface and textural properties will be investigated using *ex situ* and *in situ* synchrotron-based techniques (XRD and XAS) as well as N_2 physisorption and XPS. Acidic properties of the catalysts will be analyzed by TPD – NH_3 and FT-IR using adsorbed pyridine. Physical and chemical characteristics of the catalyst will be correlated with the catalytic performance. It is clear that transmission microscopy is a fundamental technique to study heterogeneous catalysts and it will not be different in this PhD project. TEM will be a powerful technique to investigate morphology, particle size and distribution of the Co, Ni and Nb_2O_5 from the preparation steps to the post catalytic reaction. These results will be correlated with XRD, XAS and XPS as well as catalytic properties. This will be a step forward in understanding and optimizing the catalyst and reaction parameters to improve specific product yields.

The authors are grateful for the CNPq scholarship and the financial support from the LNLS/CNPEM as well as from IQSC-USP-São Carlos, LNLS and CTBE and to their staff.

[1] R. Rinaldi, F. Schüth, ChemSusChem. 2, 1096-1107 (2009).
[2] I. Nowak, M. Ziolek, Chem. Rev. 99, 3603-3624 (1999).
[3] D. M. Alonso, J. Q. Bond, J. A. Dumesic, Green Chem. 12, 1493-1513 (2010).

Development of New Metal Matrix Composites (MMCs) with Superior Resistance to Creep and Fatigue

Volpato GM[1], Lemos G[2], Pyczak F[3], Tetzlaff U[4], Fredel MC[5]
[1] Federal University of Santa Catarina (UFSC), Florianópolis, SC, Brazil
[2] Federal University of Santa Catarina (UFSC), Florianópolis, SC, Brazil
[3] Helmholtz Zentrum Geesthacht (HZG), Geesthacht, SH, Germany
[4] Technische Hochschule Ingolstadt (THI), Ingolstadt, BY, Germany
[5] Federal University of Santa Catarina (UFSC), Florianópolis, SC, Brazil
Guilherme.volpato@grad.ufsc.br

Nickel-Chromium superalloys are materials designed to fulfill a demand for great resistance to mechanical and chemical deterioration in high-temperature applications (e.g. gas turbines). Its microstructure is constituted by matrix-oriented precipitates, which grant the alloy first-rate properties at its ideal thermodynamic surroundings. However, superalloys characteristics' development is not following properly the advancement of engine technology, which currently shows the need for higher Turbine Entry Temperatures (TETs) [1]. The addition of a new ceramic phase reinforcement to the superalloys' microstructure would create a Metal Matrix Composite (MMC), allowing the development of a material capable of substituting existent alloys by combining the characteristics of the ceramic and the superalloy itself [2]. This intersection of both material classes may create an advanced set of superalloys, more resistant to both creep and fatigue, while still affordable commercially. Specific ceramic phases would expand the steady-state creep, what would decelerate the microstructure deterioration process and extend the alloy lifetime. Moreover, Ni based MMCs present a low specific density (decreasing an aircraft's total mass) and a diminished Ni mass percentage, reducing the cost of the component [3]. However, in order to achieve this set of desirable thermomechanical properties, the interface between matrix and ceramic reinforcement has to be studied appropriately [4]. Among the various characterization techniques, Transmission Electron Microscopy (together with associated micro-spectrometry [5]) is a powerful way of achieving a greater understanding of it: tripod polishing, ion milling and possibly Focused Ion Beam (FIB) are techniques likely to be used as to avoid interface deterioration.

Conselho Nacional de Desenvolvimento Científico e Tecnológico
(CNPq 206464/2014-2)

[1] Reed R. The Superalloys: Fundamentals and Applications. 1st ed. New York: Cambridge, 2006.
[2] Chawla N, Chawla K. Metal matrix composites. 1st ed. New York: Springer, 2006. [3] M Haël et al., Advanced Engineering Materials, no. 6, p. 319–326 (2000).
[4] U.S. Congress. Office of Technology Assessment. Advanced Materials by Design 1st ed. Washington: U.S Government Printing Office, 1988.
[5] Williams DB, Carter CB, Transmission Electron Microscopy: A Textbook for Materials Science. 2nd ed. New York: Springer, 2009.

Gold nanoparticles obtained by the influence of ultrasound and their potential for enzyme immobilization

Heloise Ribeiro de Barros[1], Mary Conceição dos Santos[1], Leandro Piovan[1], Izabel C. Riegel-Vidotti[1]

[1] Universidade Federal do Paraná, Curitiba, Paraná, Brazil heloisebarros1@gmail.com

Gold nanoparticles (AuNPs) are of great interest due their optic, electronic and magnetic intrinsic properties.[1] The chemical reduction method is widely employed for the synthesis of AuNPs since the synthesis is relatively easy to achieve. On the other hand, the use of ultrasound to obtain nanoparticles can induce changes in the material properties such as morphology, composition and reactivity.[2] The goal of this study is to evaluate the effect of ultrasound in obtaining AuNPs either in the presence or in absence of the stabilizing agent gum arabic (GA). The variables were the time and the amplitude of the ultrasonic irradiation. Also, the as-synthesized particles were tested for the immobilization of free Candida antarctica lipase (CALB). Transmission Electronic Microscopy (TEM) images were obtained using a JEOL 1200EX-II microscope at Centro de Microscopia Eletrônica (CME-UFPR). It was observed that AuNPs synthesized in presence of GA are mainly spherical and exhibit narrow size distribution, whereas bare-AuNPs are larger, asymmetric, and have a broader size distribution. In addition, for enzyme immobilization, lipase could act either as stabilizing agent for AuNPs since it was not observe the presence of large aggregates as seen by TEM images (Figure 1). Besides, CALB was more effectively immobilized when added before the reducing agent NaBH4 and in the absence of GA. Moreover, these AuNPs remained stable for days whereas in the synthesis adding CALB after NaBH4 the particles precipitate within 24 hours. Therefore, the CALB acts as a stabilizing agent since the enzymes are present in the nucleation and growing stages of nanoparticles. On the other hand, in the presence of GA, the step at which CALB was added was not the determinant variable in the adsorption of the enzyme, since GA is acting as the stabilizing agent. Therefore, this detailed study contributes to understanding about the driving forces of interactions and further to control the AuNPs stability.

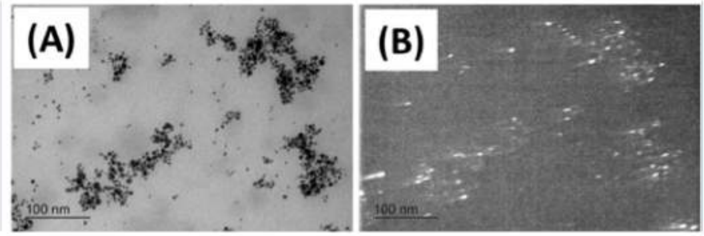


Figure 1. TEM images of lipase-AuNPs obtain in (A) bright field and (B) dark field acquirement.

The authors are very grateful to the Centro de Microscopia Eletrônica of UFPR (CME-UFPR) for the TEM images. The authors acknowledge the support given by the Brazilian National Counsel of Technological and Scientific Development (CNPq) mainly through the grants 577232/2008-8, 477467/2010-5 and 564741/2010-8 (Rede Nanoglicobiotec). Also, authors acknowledge to CAPES for the fellowships.

[1] Astruc, D. et al., Chemical Review, 104, 293-346 (2004). [2] Lourenço, R. et al., Cerâmica, 56, 28-38, (2010).

Sistemas Microfluídicos Para A Incorporação De *Small Interfering Rna* (Sirna) Em Lipossomas Catiônicos E Para Transfecção *In Vitro* De Células De Mamíferos Em Microcanais Destinados À Terapia Gênica

Ismail Es[1], Tiago Albertini Balbino[1], Meryem Ok[2], Adriano Rodrigues Azzoni[3], Lucimara Gaziola de la Torre[1*]

[1]Department of Material and Bioprocess Engineering, Faculty of Chemical Engineering, University of Campinas (UNICAMP), Campinas, São Paulo, Brazil

[2]Department of Biological Engineering, Massachusetts Institute of Technology, Cambridge, MA, United States of America

[3]Department of Chemical Engineering, São Paulo University, São Paulo, Brazil

*Corresponding Author: lucimaratorre@gmail.com

This research project aims the technological development of microfluidic systems to incorporate small interfering RNA (siRNA-silencer) inside of nano-scaled cationic liposomes (CLs), in order to get non-viral vectors for applications in gene therapy. Gene therapy is a promising technique that introduces a correct copy of the defective gene for the treatment of genetic diseases. The production of CLs-siRNA complexes by using microfluidics technology, which processes fluids in small amounts, enables the continuous operation as a single-phase system. The project will be divided into three stages: In the first stage, microfluidic device will be designed and the electrostatic complexation between conventional CLs and siRNA in microchannels will be studied and compared to bulk process, which is a conventional technique to produce CLs/siRNA complexes. In the second stage, the liposome composition will be modified with the inclusion of lipid derivatives that contain polyethylene glycol- distearoyl phosphatidylethanolamine with folate (DSPE-PEG-Folate) in order to generate Stealth liposomes with specific targeting to cells with folate receptors on their surface. The efficiency of the new liposome composition will be compared with the conventional ones. At the end of the first two stages, the physicochemical and biochemical properties of the complexes (conventional LCs, LCs-STEALTH, incorporated siRNA in LCs) using Transmission Electron Microscope (TEM) will be evaluated. For a better statistical analysis on size and morphology, lower magnification on images will be used to provide a sufficient number of particles that can be measured to generate statistics. High magnification on images will be used to provide a close-up image of particle morphology, surface and position of siRNAs.

Financial support and scholarship by Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) are deeply acknowledged.

Study of ionic irradiation effects on nuclear materials cavity system

Fichtner, P.F.P. [1]; **Timm, M.** [1]; **Oyarzabal, I.M.** [1]; **Pasini, W. M.** [2]; **Oliveira, F. M.** [1]
[1] Physics Institute of Federal University of Rio Grande do Sul (UFRGS)
[2] Metallurgical Engineering Department of Federal University of Rio Grande do Sul (UFRGS)

Our project focuses on analyzing changes in microstructure due to neutron irradiation (emulated by ion irradiation) in cladding materials of nuclear reactors for Brazilian Navy submarines. These changes include formation and growing of nanocavities and nanobubbles (voids filled with gas atoms), in addition to precipitates. In order to analyze them, electron microscope images are necessary. Considering TEM has the resolution to analyze in nanoscale, especially in z direction, it is extremely necessary to our project. Despite the fact that we are, at the present moment, generating the defects on our samples (stainless steels AISI 347 and AISI 348) by ion implantation, and, for this reason, do not have any TEM image yet, we intend to achieve it and improve our future images with the knowledge acquired with the TEM Summer School. Considering the researches of fourth generation reactors are just in its beginning, it is understandable that some part of the knowledge in this particular area comes from adapting information from previous generations, and we use it to predict the behavior of the materials under these new operational conditions. Therefore, the knowledge and images acquired in LNNano would be very important in order to help us to get better image precision and resolution and complement our analyses.

Odette, G. R. Recent Progress In Developing and Qualifying Nanostructured Ferritic Alloys for Advanced Fission and Fusion Applications. The Journal of the Minerals, Metals & Materials Society, (2014) Vol. 66, pp. 2427-2441.

Ran, G.; Xu, J.;Shen, Q.; Zhang, J.;Li, N.;Wang, L. In situ TEM Observation of Growth Behavior of Kr Bubbles in Zirconium Alloy during Post-Implantation Annealing. Nuclear Instruments and Methods in Physics Research B, (2013) Vol. 307, pp. 516-521.

IDREES Y., Yao Z., KIRK M.A., DAYMOND M.R. In situ study of defect accumulation in zirconium under heavy ion irradiation, Journal of Nuclear Materials, v. 433 (2013) 95-107.

Bacterial Nanosensor Based in Gold Nanoparticles

J. P. Oliveira1, A. R. Prado[2], R.H.A. Pereira[1], D.M. Ferreira[1], W.J.Keijok[1], R. Schuenck[3] M.J. Pontes2, M.R.N. Ribeiro2, B.V. Nogueira1, M. C. C. Guimarães[1*]

[1] Laboratório Ultraestrutura Celular Carlos Alberto Redins - LUCCAR, Departamento de Morfologia, CCS, Universidade Federal do Espírito Santo, Vitória – ES, Brasil

[2] Laboratório de Telecomunicação, Departamento de Engenharia Elétrica, Centro Tecnológico, Universidade Federal do Espírito Santo, Vitória – ES, Brasil

[3] Laboratório de Microbiologia, Departamento de Patologia, Centro de Ciências da Saúde, Universidade Federal do Espírito Santo, Vitória – ES, Brasil

* marco.guimaraes@ufes.br

Recently, advances in nanotechnology have brought new perspectives and had been stimulate different areas of research. In perspective, metal nanoparticles due to optical, electronic and magnetic properties has allowed a wide variety of application such as nanosensors, drug delivery system, lubricants, solar cells, catalysis and others [1]. A novel and sensitive colorimetric method to detect Escherichia coli was developed as a model for Gram-negative bacteria by a trypsin modified gold nanoparticles (AuNP's) sensor. Trypsin (Sigma Aldrich) molecule bound with E. coli via adhesion between positive and negative electricity of trypsin and E. coli respectively. AuNP's with different sizes were prepared by reduction and simultaneous stabilization with trisodium citrate. Tetrachloroauric acid (HAuCl4, Merk) was used as precursor of AuNP's and the dihydrate of trisodium citrate (Na3C6H5O7•2H2O, Merck) as reducing agent. All glassware and equipment were cleaned with a solution of aqua regia (HCl:HNO3 = 3:1) and washed with ultrapure water. To prepare AuNP's, the trisodium citrate was added to gold precursor solution at 100ºC. The solution was kept under stirring by the time determined by the experimental design [2]. Samples were collected immediately after synthesis and their optical properties were evaluated by UV-vis spectrophotometry (FEMTO 800 XI). The size and morphology were examined by transmission electron microscope (JEM-1400, JEOL, USA). After simple mixing of the trypsin and AuNP's solution the average diameter is 20 nm under enzyme friendly conditions (pH 8.0). The interaction between trypsin and AuNPs was quantified by measuring the absorbance at 280 nm [3] (Figure 1). Upon addition of increasing concentration of E. coli, as discussed above, an increase in the extinction in 625 nm region along with the concomitant decrease in the intensity of adsorption peak at 520 nm was observed. Besides the spectroscopy UV - visible, the electron microscopy images showed changes in the size of nanopaticulas and interactions of nanoparticles with bacteria (Figures 2 and 3). This bioassay was efficient and promising for bacteria detection.

[1] M.-C. Daniel, D. Astruc. Chem. Rev., 104 (1) (2004), pp. 293–346
[2] Oliveira et al. BMC Proceedings 2014, 8(Suppl 4):P249.
[3] Hinterwirth H1, Lindner W, Lämmerhofer M. Anal Chim Acta. 2012 Jul 6;733:90-7.

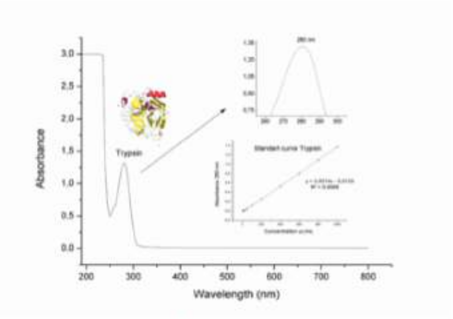


Figure 1 - UV-Vis spectrum and standart curve of trypsin.

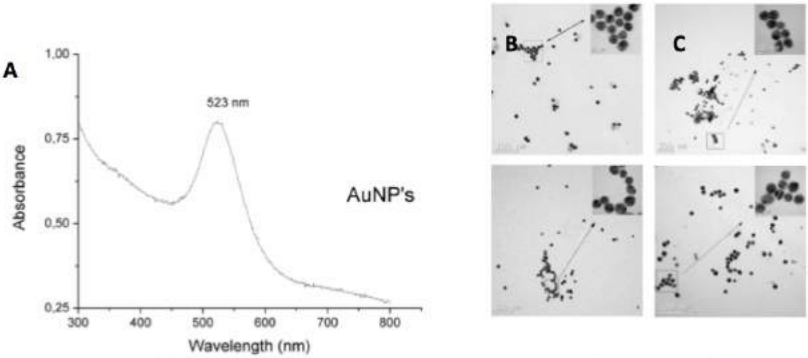


Figura 2: UV-Vis spectrum of gold nanoparticles (A) and images of AuNP's by TEM (120KV) (B,C,D,E).

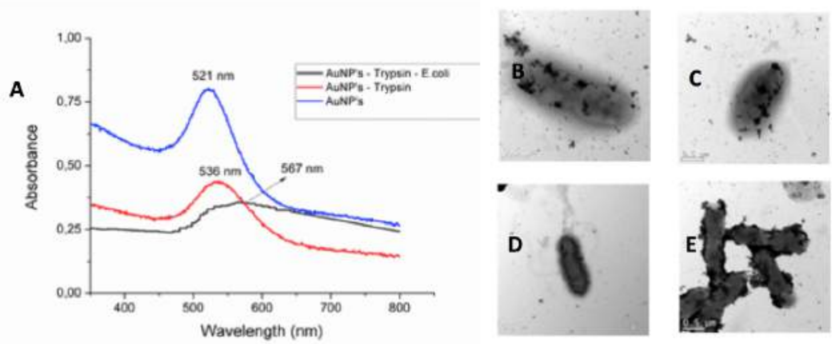


Figura 3: UV-Vis spectrum of gold nanoparticles, with trypsin and trypsin – *E.coli* (A) and images of nanoparticles complex with *E. coli* by TEM (120KV) (B,C,D,E).

MAGNETOSOMES SINTHESIZED BY MAGNETOTACTIC BACTERIA IN DIFFERENT CONDITIONS

Jefferson Cypriano[1*], Marcos Farina[2], Ulysses Lins[1]
[1]Instituto de Microbiologia Paulo de Góes, UFRJ
[2]Instituto de Ciências Biomédicas, UFRJ
*Jeff.tm@gmail.com

Magnetotactic bacteria synthesize nano-sized magnetite (Fe_3O_4) and/or greigite (Fe_3S_4) crystals enveloped by a membrane comprising a structure called magnetosome [1]. Recent works indicates that changes in environmental factors or culture conditions such as pH, temperature, carbon source and iron can influence nanoparticles formation [2;3]. In particular, we observed variations between magnetosome of bacteria growing under different conditions, displaying an amount of defects and twinning. Thus, this project aims to use high-resolution transmission electron microscopy associated with electron energy loss spectroscopy (EELS) in order to determining nature of changes in crystalline microstructure and elemental composition of magnetosome derived from cultivation or/and natural condition, and determine iron oxidation state of magnetite crystals. Electron energy loss near-edge fine structure was successfully employed for the study of abiotic magnetite but has never been used on magnetotactic bacteria magnetosomes. Thus, we will be tentatively use this approach to study possible variations in iron oxidation states of magnetosomes crystals.

This work is supported by CNPq, CAPES and FAPERJ.

[1] FAIVRE, D. *et al.*, Angew. Chemie. Int. 46:8495-8499, 2007.
[2] FAIVRE, D. *et al.*, Am. Mineral. 93:463-469, 2008a.
[3] MOISESCU, C. *et al.*, Front. Microbiol. 5:49, 2014.

Efficiency enhancement of Eu3+ doped tellurite glasses-covered solar cells in the presence of silver nanoparticles

J. A. M. Garcia[1,2], L. R. P. Kassab[1]

[1] Faculdade de Tecnologia de São Paulo, CEETEPS/UNESP, São Paulo, SP, Brazil

[2] Departamento de Engenharia de Sistemas Eletrônicos, Escola Politécnica da USP, São Paulo, SP, Brazil
augusto.magar gmail.com

Different photovoltaic technologies have been explored and the research of new materials is based on the increase of solar cell efficiency. Down conversion and upconversion processes in photonic materials can be used to modify the solar spectrum. In this paper, we explore the modification of the solar spectrum using tellurite glasses doped with rare earth ions and its influence on the efficiency of commercially available silicon and GaP solar cells. So it is studied the efficiency of these commercial solar cells covered with tellurite glasses (TeO_2–ZnO) doped with Eu^{3+} ions, with and without silver (Ag) nanoparticles using electrical characterization. The samples were prepared using the melting quenching technique followed by adequate heat treatment (at the transition temperature) to thermally reduce the Ag$^+$ ions to Ag^0 and to nucleate the silver nanoparticles. This procedure was already reported in previous work [1]. A 200 kV transmission electron microscope (TEM) was used to determine the sizes and shapes of the Ag nanoparticles. For these measurements the samples were milled, mixed with distilled water, and partially decanted. The floating part was taken by using a metallic screen and analysed by TEM. Energy dispersive x-ray spectroscopy was performed during the TEM analysis in order to confirm the presence of Te, Zn and Ag. Spherical Ag nanoparticles with size around 30 nm were found. The efficiency of a commercial solar cell of silicon covered with an undoped glass is increased in ~7 % when covered with a TeO_2-ZnO glass doped with 1 wt% of Eu $^{3+}$; in the presence of Ag nanoparticles (2 wt%) the efficiency enhancement is of 14%. For the case of GaP solar cell, an enhancement efficiency of ~6% is observed when it is covered with the TeO_2-ZnO glass doped with 1wt% of Eu $^{3+}$ and of 33% in the presence of Ag nanoparticles (2 wt%). These results indicate that Eu^{3+} doped TeO_2-ZnO glasses with Ag nanoparticles are potential materials for applications in solar cell.

Thanks to Prof. Dr. Luciana Reyes Pires Kassab by the orientation; to the Faculdade de Tecnologia de São Paulo, by provide the Laboratório de Tecnologia em Materiais Fotônicos e Optoeletrônicos for the realization of this project; to collaborators of the Department of Physics of the Universidade Federal de Pernambuco by the realization of the electrical characterizations using solar cells; and to the National Laboratory of Technology, CNPEM, for providing the use of Transmission Electron Microscope.

[1] CAMILO, M. E.; SILVA, E. O.; KASSAB, L. R. P.; GARCIA, J. A. M.; ARAUJO, .C. B.; Journal of Alloys and Compounds, 644, 155 (2015).

Study of the influence of organic ligands on the catalytic activity of metal nanoparticles

Jhonatan Luiz Fiorio[1], Fernanda Parra da Silva[1], Liane Márcia Rossi[1].
[1] Instituto de Química USP, Av. Prof. Lineu Prestes 748, São Paulo, 05508-000, SP, Brasil (11)30919143
lrossi@iq.usp.br

Preformed palladium NPs were immobilized on the functionalized magnetic support (∼30 nm silica spheres, Figure 1 a,b) by coordination capture method. [1,2,3] The catalyst contains 1% wt% of Pd, as determined by atomic absorption analysis (ICP OES). The sizes of the supported Pd NPs were determined using a transmission electron microscopy (TEM). The Pd NPs (Figure 1 c,d) demonstrated a mean diameter of 3,05 ± 1,46 nm (Pd/Fe_3O_4@SiO_2triamine). In order to study the catalytic activity after the removal of the organic groups, the catalyst were calcined (Figure 1 e,f) at 400 ºC by 2 hours (Pd-TT/F_3O_4@SiO_2triamine). Transmission electron microscopy analysis demonstrated a mean diameter of 4,21 ± 1,64 nm.

The catalytic activity of the Pd catalysts was investigated in the hydrogenation of cyclohexene in solventless conditions. A strong influence of the functional group on the catalytic behavior of the Pd catalyst was observed. The turnover frequency (TOF), for the catalyst functionalized with diethylenetriamine was 7051,86 h^{-1} (Figure 2). After calcination, to remove the organic ligand, the catalytic rate was improved (13534,22 h^{-1}). Both catalysts, synthetized in this work, were reused in 15 successive runs, and the catalytic activity decreased as the catalysts were reused in successive reactions. These results show that the diethylenetriamine grafted on the magnetite surfaces has a strong deactivating effect on the catalytic activity of the Pd NPs when compared with amine groups or ethylenediamine, reported elsewhere.[4,5] The catalyst was calcined its catalytic activity was improved. However calcination causes growth in the nanoparticles.

In summary, we have prepared a magnetically recoverable Pd nanocatalyst with a strong metal-support interaction promoted by ligands grafted on the support surface. The catalytic activity in hydrogenation of olefins was strongly influenced by the organoalkoxysilane present, and the metal-support interaction will be investigated in more detail.

The authors gratefully acknowledge support from FAPESP, CNPq and CAPES.

[1] Jacinto, M. J. et al. M. Appl. Catal. A Gen. 2008, 338, 52.
[2] Rossi, L. M. et al. Appl. Catal. A Gen. 2007, 330, 139.
[3] Silva, T. A. G. et al. Catal. Sci. Technol. 2013, 3, 2993.
[4] Rossi, L. M. et al. Inorg. Chem. 2009, 48, 4640.
[5] Silva, F. P. da et al. Tetrahedron 2013, 70, 3314.

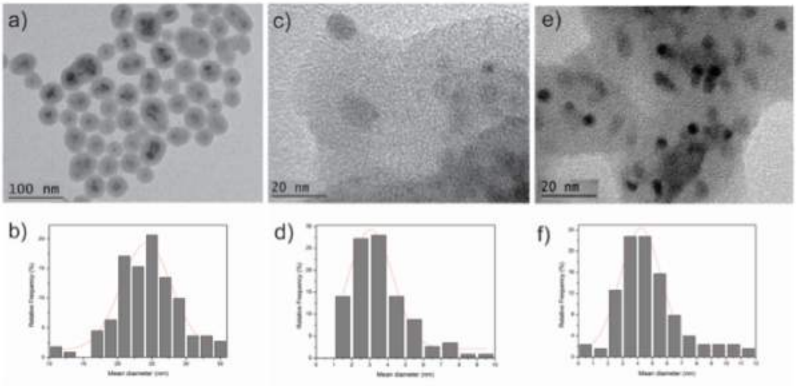


Figure 1. *TEM images of: a) Fe_3O_4@SiO_2triamine, c) Pd/Fe_3O_4@SiO_2triamine and e) Pd-TT/F_3O_4@SiO_2triamine; histogram showing particle size distribution of: b) Fe_3O_4@SiO_2triamine, d) Pd/Fe_3O_4@SiO_2triamine and f) Pd-TT/F_3O_4@SiO_2triamine.*

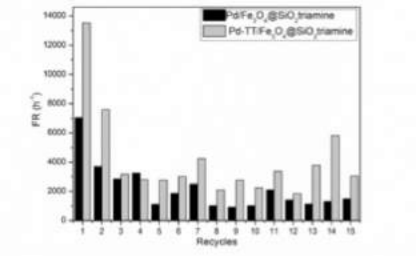


Figure 2. *Catalyst recycling in the hydrogenation of cyclohexene. Conditions: 6 atm H_2, 75 °C, 17,5 mmol of cyclohexene and 50 mg of supported catalyst (2500 mol of substrate/mol of catalyst).*

Study of Decarburization and Oxidation Kinectics in Spring Steels

Jéssica C. C. de Castro[1], Sydney F. Santos[2], Renato A. Antunes[3]
[1] UFABC, Santo André, Brazil
[2] UFABC, Santo André, Brazil
[3] UFABC, Santo André, Brazil
jessica.castro@aluno.ufabc.edu.br

The decarburization is the loss of carbon from the steel to the atmosphere resulting in deleterious impact on the mechanical properties of these alloys. The large silicon content in spring steels favors the decarburization of these materials during manufacturing. In this work, the decarburization process during heat treatment of SAE 9254 spring steel is investigated. Samples of this steel were annealed in electrical furnace in air at different processing conditions, varying the annealing temperature and time, followed by oil quenching. The investigated temperatures ranged from 750 to 950^{o} C under 30 minutes of annealing. Samples were also heat treated at 890^{o} C varying the holding time from 0.5 to 4 h. The microstructure of the obtained samples was analyzed by optical microscopy and confocal laser microscopy. Thermogravimetric analyses were also performed in order to investigate the decarburization kinetics. It was observed that decarburization evolved with the increase of heating time and temperature. After short annealing time a ferrite free layer is formed and the layer depth increases as function of time. . A more complex dependence of decarburization with temperature was observed. At intermediate temperatures the depth of the ferrite free zone is larger. The region between full decarburization (ferrite) and parts of the steel that still have carbon need to be better understood for this reason it is intended to use the Transmission Electron Microscopy (TEM).

The authors would like to thanks PPG-Nano, CNPq, and ThyssenKrupp Bilstein Brasil by supporting this work. JCCC thanks DAI program (UFABC/CNPq) for the PhD scholarship.

[1] C. Zhang et al., Int. J. Miner. Metall. Mater., 19, 2 (2012). [2] Y. Liu et al., ISIJ International, 54, 8 (2014).

Nanocomposites based on alfa-nickel hydroxide and graphene oxide

Josué M. Gonçalves[1], Robson R. Guimarães[1], Alfredo Duarte[1], Cícero V. Nunes Jr[2], Henrique E. Toma[1], Koiti Araki[1]

[1] Universidade de São Paulo, São Paulo, São Paulo, Brazil

[2] Universidade Estadual do Centro-Oeste do Paraná, Guarapuava, Paraná, Brazil.

josuemartins@usp.br

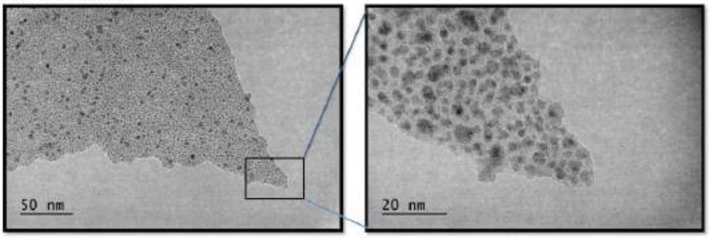
The nickel hydroxide ($Ni(OH)_2$) have been widely studied as electroactive materials for Ni-MH batteries. Many efforts have been made to improve the conductivity, electrochemical reversibility and load capacity of these batteries. The $Ni(OH)_2$ can present polymorphs α and β, where the former has higher load capacity and superior electrochemical properties. However, the α-$Ni(OH)_2$ is not stable and is easily converted to the β form [1]. This is the main reason for non-use of α-$Ni(OH)_2$ as positive electrodes of batteries. The graphene oxide (GO) is a two-dimensional material that contains a variety of functional groups reactive oxygen [2], which makes it a good candidate for many applications. In this context, we propose the synthesis and characterization of nanocomposite α-$Ni(OH)_2$/GO, seeking stabilizing α-$Ni(OH)_2$ for use in batteries.

After synthesis, modified electrodes were prepared with the following materials: α-$Ni(OH)_2$, α1-Ni/GO and α2-Ni/GO. Figure 1 shows images obtained by TEM. The micrographs for the nanocomposite α2-Ni/GO shows a greater distribution of the nanoparticles, probably because the smaller amount of the nanoparticle compared with GO mass.

The result of cyclic voltammetry to α-$Ni(OH)_2$ (Figure 2A) showed a reversible process. It also was observed the current decay of these peaks from 100° voltametric cycle, indicating conversion to β form. The voltammetry of the nanocomposite α1 and α2-Ni/GO (Figure 2 B and C) showed increasing intensity of Ipc and Ipa peaks with increasing number of cycles and higher reversibility when compared to α-$Ni(OH)_2$. Furthermore, there was no decrease in peak currents even after 350 charge and discharge cycles, thereby showing increased stability of the alpha phase by the interaction with GO.

It was observed stabilization of α-$Ni(OH)_2$ via interaction with GO. This was possible due to complete exfoliation of GO allowing maximum interaction with nanoparticles of $Ni(OH)_2$. The results have demonstrate that nanocomposites α- $Ni(OH)_2$/GO shows great potential for use in Ni-MH type battery.

(A) α1-Ni/GO



(B) α2-Ni/GO

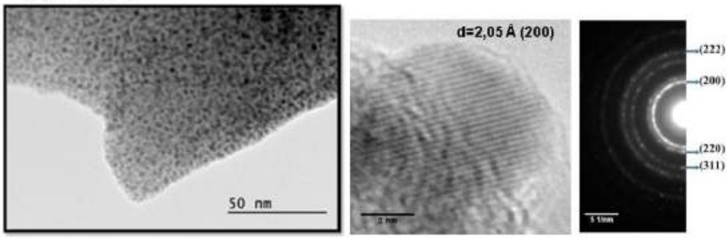


Figure 1 - Images of TEM of materials α1-Ni/GO and α2-Ni /GO.

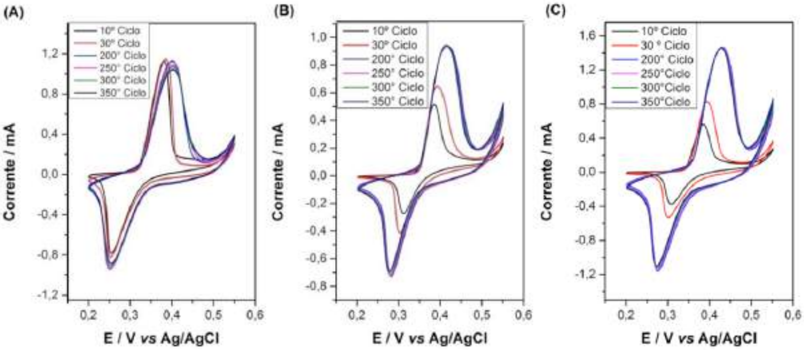


Figure 2: *Cyclic voltammograms of (A) α-Ni(OH)$_2$, (B) α1-Ni/GO (C) α2-Ni/GO, NaOH 1 mol/L, 20 mV/s.*

CNPq and USP.

[1] P. R. Martins et al., RSC Advances, 3, 20261-20266 (2013). [2] Chen, D et al., Chemical Reviews, 112, 6027–6053 (2012).

Brittle behavior of friction stirred welded joints in pipeline steel API-5L-X80

Julián Arnaldo Ávila Díaz[1,2,*], Andre Paulo Tschiptschin[2,3], Antonio José Ramirez[1,2,4].
[1] School of Mechanical Engineering, University of Campinas, Campinas, Sao Paulo, Brazil
[2] Brazilian Nanotechnology National Laboratory, Campinas, Sao Paulo, Brazil
[3] Polytechnic School, University of São Paulo, Sao Paulo, Brazil.
[4] The Ohio State University, Columbus, Ohio, USA
*Corresponding author: julian.diaz@lnnano.cnpem.br.

The fracture toughness of friction-stirred welded (FSW) joints at the temperature range of 0 C to -40 °C is a critical issue for decisions about its application in API-5L-X80 steels; however, brittle fracture behavior of FSW weldments at -20 °C has been reported [1,2]. Previous results from the microstructural characterization of FSW joints have been shown in Figure 1 [3]. The brittle behavior was associated with crack initiation at the second dispersed phases (martensite-austenite microconstituent –M-A) and (TiNb)(C,N)-type inclusions [1]. In addition, the same mechanism involving M-A particles has been associated with brittle fracture initiation and crack propagation in the coarse-grained heat affected zone of arc welding joints [4–5]. However, these microstructural features do not completely explain the brittle behavior within the stirred and hard zones of friction stir welded joints, overall, arc-welded and FSW microstructures within the joint are dissimilar, although they both have the suspect M-A microconstituent and Ti-N inclusions.

The aim of the present proposal is a deeper microstructural characterization that would pinpoint the key factor that are involved in the reported brittle behavior, more specifically at the stirred and hard zones of FSW welded joints in API-5L-X8 steel, see Figure 1. The focus of this proposal is the determination of the crystal structure, distribution, shape and hardness of the different elements belonging to the bainitic matrix and second dispersed phases over those critical regions. Therefore, transmission electron microscopy (TEM) is the most suitable characterization technique for this proposal.

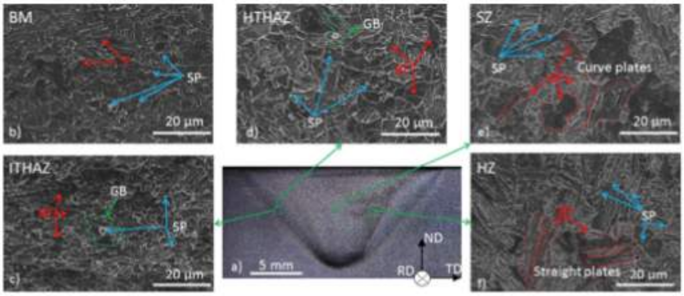


Figure 1: Microstructures of different regions within the friction stirred welded joints: a) Cross section Macro photo of the joint, microstructure of b) BM, Base material; c) ITHAZ, intermediate temperature HAZ; d) HTHAZ, high temperature HAZ; e) SZ, stirred zone and f) HZ, hard zone Etched with Nital 2%. Abreviation: F, ferrite; BF, bainitic ferrite; GB, granular bainite and SP, secondary phases. The arrows indicate the position of some specific microstructure.

FSW, API 5L X80 steel, brittle fracture, welded joints, TEM
The authors would like to acknowledge the financial support of Colciencias by the scholarship No. 512 from 2010. We would like to thank the following institutions: Petrobras and LNNano/CNPEM for providing economic funding and laboratory facilities where this work will be developed; TenarisConfab for the materials donation.

[1] Fairchild D.P. et al., Trends Weld. Res. 9th Int. Conf., 193–200, 2012.
[2] Ávila, J.A.D., Eng. Fract. Mech., October, 147, 176–186, 2015.
[3] Ávila, J.A.D et al., E., Metall. Mater. Trans. A, submitting, xx-xx, 20xx.
[4] Mohseni P., University of Science and Technology, PhD thesis, 2012.
[5] Fairchild D.P., ASTM STP 1058, 117–141, 1990.

Development of nanostructured lipid carriers containing a phenolic monoterpene as an alternative to leishmaniasis treatment

Juliana G. Galvão[1], Raquel L. Santos[1], Tainara Santos[1], Silvio S. Dolabella[2], Rogéria S. Nunes[1]
[1] [1]Pharmacy Department, Federal University of Sergipe, São Cristóvão, Sergipe, Brazil
[2]Morphology Department, Federal University of Sergipe, São Cristóvão, Sergipe, Brazil
Corresponding Author: julianaggalvao@gmail.com

Leishmaniasis consists in a neglected infectious disease caused by protozoa of the genus *Leishmania* in the family Trypanosomatidae. It is estimated that occurs 1.3 million new cases and 20,000 to 30,000 deaths every year in the world. Since the control of insect vector is difficult and no effective vaccine exists, chemotherapy is the main means of dealing with this disease. In the past 70 years, pentavalent antimonials, amphotericin B and miltefosine have been used as gold standard treatment of leishmaniasis. However, the leishmaniasis conventional treatment presents some undesirable adverse effects such as gastrointestinal disorders, kidney and liver toxicity. Since these drugs are too expensive and Leishmania species have been demonstrated resistance against these drugs, natural products can provide an important alternative to leishmaniasis treatment. A phenolic monoterpene (natural product obtained from essential oils) has been recently reported as a potent leishmanicidal agent. Furthermore, some studies also have been reported the use of nanostructured lipid carriers as drug delivery systems of leishmanicidal drugs. Thus, the aim of this project focuses on the development of Nanostructured Lipid Carriers (NLCs) containing a phenolic monoterpene as an alternative leishmaniasis treatment. Firstly, the NLCs with and without monoterpene will be obtained by solvent diffusion method and evaluated for particle size, polidispersity index, zeta potential. NLCs were characterized by DSC, XRD and Transmission electron microscopy (TEM) as well. Moreover, the analytical methodology for quantify the monoterpene by high performance liquid chromatography (HPLC/UV) will be validated. Afterwards, it will be determined the encapsulation efficiency and *in vitro* release profile of the drug from the NLCs. Finally, it will be performed the cytotoxicity assay, promastigote viability, as well as, antiamastigote activity evaluation.

The authors acknowledge CAPES and CNPq for supporting funds.

[1] WHO. Leishmaniasis Fact Sheet N° 375 Updated February 2015.
[2] TIUMAN et al., International Journal of Infectious Diseases, 15, 525-532 (2011).
[3] PASTOR et al., Acta Tropica, 145, 31-38 (2015).
[4] DOMINGO et al. Analytica Chimica Acta, 744, p. 8–22 (2012).

Development and application of high-resolution imaging techniques for morphological characterization of microfossils

Lara Maldanis[1,2], Douglas Galante[1]
[1] Brazilian Synchrotron Light Laboratory, CNPEM, Campinas, SP, Brazil
[2]São Carlos Institute of Physics, University of São Paulo, São Carlos, SP, Brazil
lara.maldanis@lnls.br

Microfossils are the most ancient morphological life traces on earth. Their affinity, otherwise, are quite disputed because of the difficulty on identifying biogenic structures in very processed and billion years old rocks[1,2]. A deep understanding and the ability of characterize the first known life forms of the planet are a crucial step for the systematic search of life in other places within the universe. Imaging techniques are non-destructive and largely applied approaches in fossil characterization, and can provide valuable information of internal structures. Particularly in the case of microfossils, sub-micrometric resolution is required for the identification of cellular structures, that can help to attest biogenicity and to identify and differentiate prokaryotes and eukaryotes. In this project we focus in developing and applying high resolution imaging techniques to microfossils, including HRTEM, micro-CT and ptychography. HRTEM has already been applied in fossil studies, showing that it is a powerful approach in paleontological studies[3,4]. Our objective is to make a systematic study with different sample preparations, and to analyze the capability of these different techniques to resolve intracellular structures in microfossils. Data treatment and filters development will be performed for each case, aiming to maximize the resolution and contrast of intracellular features. Increasing the quality of imaging information of microfossils in non-destructive ways, we expect with this work to contribute to the astrobiological and paleontological community, through stablishing feasible methodologies that could contribute to the biogenicity problem of the oldest presumed fossils of earth, besides to allow a better classification of eukaryotes and prokaryotes samples.

1. Schopf, J. W. Science 260, 640–646 (1993).
2. Brasier, M. D. et al. Nature 416, 76–81 (2002).
3. Wacey, D., et al. Nature Geoscience. 4, 698-702 (2011).
4. Cady, S. L., et al. Astrobiology 3, 351-368 (2003).

Facile Approach to Preparation of Optical and Magnetic Nanocomposites Containing $Fe_3O_4@SiO_2$ Grafted with Rare Earth Complexes

Latif U. Khan[1], Diego Muraca[2], Hermi F. Brito[1], Kleber R. Pirota[2]

[1]University of Sao Paulo, Institute of Chemistry, Department of Fundamental Chemistry, Av. Prof. Lineu Prestes, 748, 05508-000, São Paulo-SP, Brazil.
[2]Institute of Physics "Gleb Wataghin" Condensed Matter Physics Department, State University of Campinas (UNICAMP), 13083-859 Campinas-SP, Brazil.
E-mail: latifkhn@iq.usp.br

The fabrication of bifunctional nanocomposites, co-assembling two different photonic (RE^{3+}) and magnetic (Fe_3O_4) features into single entity nanostructures is reported. Their preparation is accessible through a facile method of multistep syntheses, using Fe_3O_4 as core nanoparticles, which were coated with SiO_2 shell and further grafted with Eu^{3+} and Tb^{3+} complexes. The sophisticated structural features and morphologies of the core-shell $Fe_3O_4@SiO_2$-(TTA-RE-L) nanomaterials (Figure 1) containing aggregation of Fe_3O_4 core nanoparticles were studied by Small-angle X-ray Scattering (SAXS). The core mean size $\langle D_{SAXS} \rangle$, shell thickness ΔR, cluster size ξ and fractal dimension D_F were determined by fitting the experimental SAXS data, corroborating through Transmission Electron Microscopy (TEM) images (Figure 2). The DC magnetic properties at temperatures of 2 and 300 K were explored in support to the structural conclusions from SAXS and TEM analyses, and investigated the influence of SiO_2 coating and RE^{3+} complexes on the M-H and ZFC/FC magnetization curves. The paramagnetic contributions of the RE^{3+} ions to the whole magnetizations of the Eu^{3+} and Tb^{3+} nanocomposites were also discussed. The photoluminescence properties of the Eu^{3+} and Tb^{3+} nanocomposites based on the emission spectral data and luminescence decay curves were studied. The experimental intensity parameters (Ω_λ), lifetimes (τ), emission quantum efficiencies (η) as well as radiative (A_{rad}) and non-radiative (A_{nrad}) decay rates were calculated and discussed.

The authors are grateful for financial support from the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES, Brazil), Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq, Brazil), Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP, Brazil), Instituto Nacional de Ciência e Tecnologia de Nanotecnologia para Marcadores Integrados (inct-INAMI, Brazil), CNPEM-LNLS synchrotron, Campinas-SP, Brazil under Proposal Nos. SAXS1–14355 (7959), CNPEM-LNNano, Campinas-SP, Brazil under Proposal Nos. TEM-MSC 14828 (7959).

[1] Khan, L. U. etal. *Inorg. Chem.* **2014**, *53*, 12902–12910.
[2] Bünzli, J.-C. G. *Coord. Chem. Rev.* **2015**, *293-294*, 19–47.
[3] Guinier, A.; Fournet, G. Small-angle scattering of X-rays. New York: John Wiley & Sons, Inc. 1955.

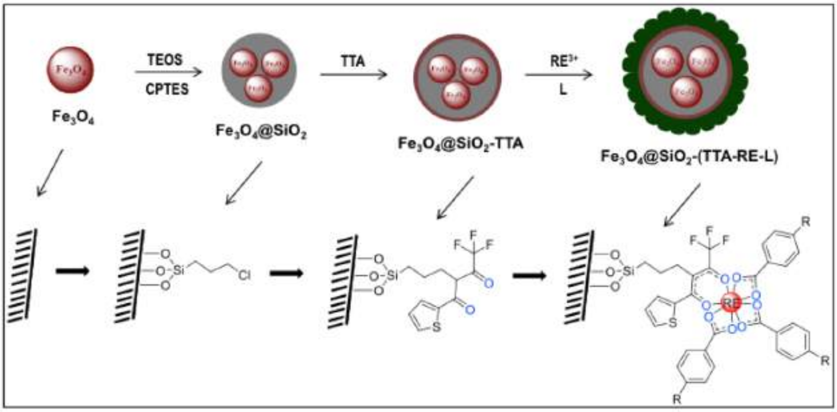


Figure 1. Preparation route of magnetic and luminescent nanocomposites; including synthesis of $Fe_3O_4@SiO_2$ nanoparticles, chemical modification with TTA and further syntheses of RE^{3+} complexes on the surface of $Fe_3O_4@SiO_2$-TTA nanostructures - $Fe_3O_4@SiO_2$-(TTA-RE-L).

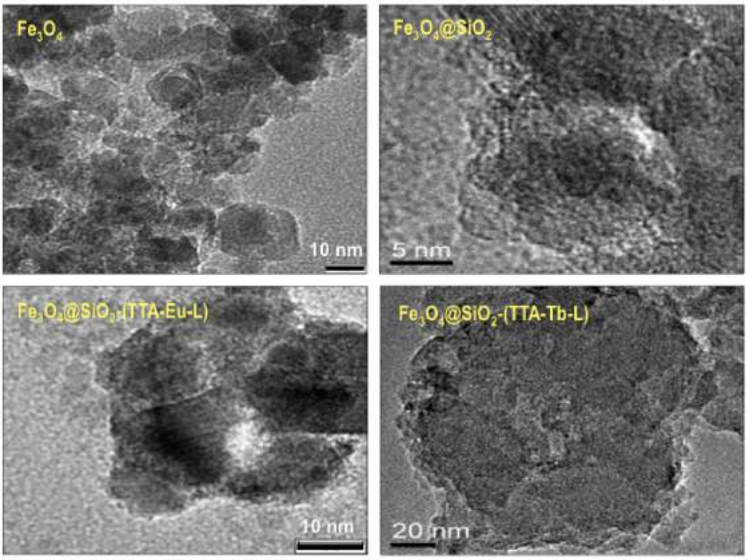


Figure 2. TEM and High-resolution TEM images (clockwise from top left) of Fe_3O_4, $Fe_3O_4@SiO_2$, $Fe_3O_4@SiO_2$-(TTA-Eu-L) and $Fe_3O_4@SiO_2$-(TTA-Tb-L) nanomaterials.

Interaction of single and multi-layer graphene oxide with fetal bovine serum: understanding the protein corona formation

Franqui, L. S.[1,2]; Soares, J. R. F.[1]; Martinez, D. S. T.[1,2].
[1]Brazilian Nanotechnology National Laboratory – Brazilian Center for Research in Energy and Materials, Campinas, São Paulo, Brazil
[2]School of Technology – State University of Campinas, Limeira, São Paulo, Brazil
lidiane.franqui@yahoo.com.br

When in contact with biological systems, nanomaterial surface adsorbs biomolecules from the biological medium mainly proteins, yielding a coating called protein corona, which affects the biological response of nanomaterials (i.e. toxicity). Several factors can influence on the protein corona formation, such as nanomaterial physicochemical properties and the nature of biological medium (e.g.; composition, exposure time; temperature, etc). Thereby, the aim of this study was to compare the single-layer (GO- SL) and multi-layer (GO-ML) graphene oxide behavior after interaction with DMEM cell culture medium containing fetal bovine serum (FBS). Our previous results showed that GO-SL adsorbs more proteins than the GO-ML. Furthermore, the presence of FBS proteins in the medium have significantly increased the dispersion stability of GO-SL and GO-ML. Although GO-ML adsorbed fewer amount of proteins on its surface, there was no significant difference in the dispersion stability between both samples. Thus, the number of GO layers can influence its interaction with FBS proteins, with implications for cytotoxicity assessment and biomedical applications of these nanomaterials. The next step is characterize the bare GOs as well as FBS protein corona–coated-GOs, in order to understand the role of morphology. According to literature, TEM is a key technique to solve this problem. For example, Park, *et al.* (2015)[1] and Sun, et al. (2012)[2] employed HRTEM to visualize and determine the number of GO layers. Kelly, *et al.* (2015)[3], Wang, *et al.* (2013)[4] and Miclăuș, *et al.* (2014)[5] reported the use of different TEM techniques to characterize the protein corona. Finally, TEM techniques are crucial to understanding the nanobiointeractions towards biomedical and toxicological applications of graphene-based materials.

We thank the "Rede Brasileira de Nanotoxicologia" (CIGENANOTOX, Campinas, Brazil), Process 552120/2011-1, and "Coordenação de Aperfeiçoamento de Pessoal Nível Superior" (CAPES) for their financial support.

[1] Park, E-J. et al., Archives of Toxicology, 89, 1557-1568 (2015).
[2] Sun, J. et al., Chemical Communications, 48, 8126–8128 (2012). [3] Kelly, P. M. et al., Nature Nanotechnology, 10, 472-479 (2015).
[4] Wang, L. et al., Journal of the American Chemical Society, 135, 17359–17368
(2013).
[5] Miclăus, T. et al., Nano Letters, 14, 2086–2093 (2014).

Nanomechanical characterization of composites based on PLLA-*b*-PEO-*b*-PLLA copolymer and nanohydroxyapatite

Livia M. D. Loiola, Laura C. E. Da Silva, Laura A. Fasce, Patricia M. Frontini, Maria do C. Gonçalves, Maria I. Felisberti
Institute of Chemistry, University of Campinas – UNICAMP, P.O. Box 6154, 13083-970, Campinas, São Paulo, Brazil.
Universidad Nacional de Mar del Plata, Instituto de Investigaciones en Ciencia y Tecnología de Materiales, INTEMA, J.B. Justo 4302 - B7608 FDQ - Mar del Plata, Argentina.

Composites combining biocompatible polymers and nanohydroxyapatite (nHAp) are unique materials regarding mechanical properties and bioactivity. Poly(L-lactide) (PLLA) is a bioabsorbable polyester with a hydrophobic surface and highly crystalline nature that limit its biomedical application. The copolymerization of PLLA with a hydrophilic and amorphous poly (ethylene oxide) (PEO) block, and the subsequent addition of nHAp to the copolymer matrix were performed to design injection molded composites. PLLA blocks were attached to PEO through ring-opening polymerization of L-lactide to obtain the PLLA-*b*-PEO-*b*-PLLA copolymer. Moreover, nHAp surface was functionalized with PEO (nHAp@PEO) in the attempt to improve nHAp dispersion into the polymeric matrix.

Reduced elastic modulus (E_R) and indentation hardness (H) of PLLA-*b*-PEO-*b*-PLLA and nanocomposites were determined by depth sensing indentation tests. The incorporation of nHAp slightly increased both E_R (~22%) and H (~15%) of the PLLA-*b*-PEO-*b*-PLLA matrix. The addition of nHAp@PEO resulted in a lower increment of mechanical parameters (~3% for E_R and ~15% for H). The expected increase in elastic modulus due to the stiffening effect of the incorporation of nHAp or nHAp@PEO particles was compensated by the reduction in the crystalline level of the composite matrix.

Transmission electron microscopy (TEM) was used to further investigate the lower increase in elastic modulus. Figures 1a,b show that PLLA-*b*-PEO-*b*-PLLA presents phase segregation "grape-like" of the PEO middle block. As it is shown in Figure 1c, this phase segregration is not observed in the nHAp nanocomposite. This may be due to the interaction between PEO block and nHAp surface and could contribute to the lower increase in elastic modulus since allows an increase in chain mobility. nHAp@PEO nanocomposite (Figure 2) presents leached out PEO spread throughout the polymeric matrix, which is confirmed by the carbon (Figure 2b) and calcium (Figure 2c) maps.

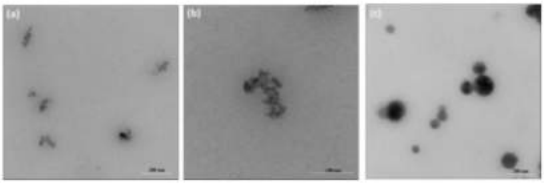


Figure 1. TEM bright field micrographs of (a, b) PLLA-*b*-PEO-*b*-PLLA copolymer and (c) nHAp nanocomposite after processing.

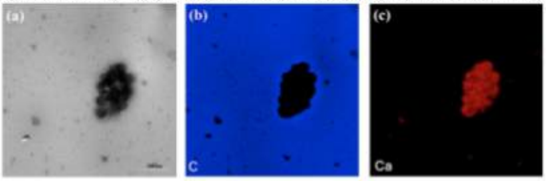


Figure 2. TEM bright field micrograph of nHAp@PEO nanocomposite (a) and its calcium (b) and carbon

(c) maps.

Morphological study of lignocellulose residues from agriculture, sugarcane and orange bagasse, during enzymatic degradation

Lucimara Lopes da Silva, Ph.D.
Pos doctoral researcher at University of Campinas, Institute of Chemistry.

The fractionation of lignocellulosic biomass for second-generation ethanol production is a dynamic research area nowadays and the process commonly used to achieve this involves: pretreatment of the lignocellulosic substrate, followed by enzymatic hydrolysis to obtain fermentable sugars and then fermentation to ethanol-2G. Enzymatic hydrolysis is the limiting step of this process due to the high cost of enzymes and the possibility of their inactivation during saccharification. A promising approach to understand the action mechanisms of these biocatalysts on the cell wall is to evaluate employed enzymes efficiency accounting for different substrates, together with the evaluation of cell wall corresponding morphological changes. However, such studies are still very scarce and limited. Thus, the aim our proposal is to study the morphological changes taking place on agriculture wastes, such as sugarcane and orange bagasse, and on a model cellulosic substrate (paper filter Whatman n° 1), all submitted to enzymatic hydrolysis. Bagasse samples previously pretreated at conditions well established will be used and the released sugars by hydrolyses will be quantified using high performance liquid chromatography (HPLC). The use of atomic force microscopy (AFM), transmissiom electronic microscopy (TEM) and scanning electron microscopy (FESEM) is proposed for the morphological bagasse analyses. Also, the micro and nanostructures originating from hydrolyzed biomass, mainly nanocellulose, and composites and nanocomposites obtained by mixing these nanostructures with polymers will be characterized by using these microscopic techniques. The results should contribute to the comprehension of the mechanisms involved in enzymatic degradation of lignocellulosic substrates, enabling the proposal of new approaches for the conversion of plant biomass into fermentable sugars.

Key words: cellulose, enzymes, hydrolysis, microscopic analysis, conversion of plant biomass.

Study of BiSI nanostructures synthesis for application in ionizing radiation detectors

Maia Mombrú[1], *Ivana Aguiar*[1], *Laura Fornaro*[2]

[1] *Grupo de Desarrollo de Materiales y Estudios Ambientales, Cátedra de Radioquímica, Facultad de Química, Universidad de la República, Montevideo, Uruguay*

[2] *Grupo de Desarrollo de Materiales y Estudios Ambientales, Departamento de Desarrollo Tecnológico, CURE, Universidad de la República, Rocha, Uruguay* maiam@fq.edu.uy

BiSI belongs to the $A^{V}B^{VI}C^{VII}$ chalcohalides group of compounds. These compounds show several interesting properties such as ferroelectricity, piezoelectricity along the c axis, and photoelectricity, among others [1-2]. In this work we present BiSI nanostructures synthesized by solvothermal method with the intention of using them for room-temperature ionizing radiation detection, due to its high density, high absorption coefficient, and high atomic number of constituting elements. The solvent and capping agent were varied to study their influence in morphology and particle size. Four samples were prepared, using either water or ethylene glycol as solvents and oxalic acid or octadecanethiol as capping agents. The nanostructures obtained were characterized by XRD to determine reaction completeness (Rigaku ULTIMA IV diffractometer at Facultad de Química); TEM to observe nanostructures morphology (Jeol JEM 2100 with 200 kV of voltage acceleration at CURE), size and growth orientation; and finally IR Diffuse Reflectance to study the capping agent-nanostructure union (Shimadzu spectrometer with PIKE accessory). BiSI synthesized with water presented Bi_2S_3 phase according to the XRD spectra, so the reaction was incomplete. Crystalline nanorods in the range of 100-200 nm mean width were present in all samples, and crystalline round nanoparticles around 5 nm in diameter were also detected in samples where ethylene glycol was the solvent, according to TEM observations (Figure 1). IR spectra showed in all cases that the capping agent is present in the samples but with successive washes it disappears, showing that if there is a bond between nanostructure-capping agent, it is weak. In the future, nanostructures with ethylene glycol as solvent will be used to fabricate pellets to construct detectors and study their ionizing radiation detection properties.

We wish to acknowledge Alvaro Olivera from CURE-Rocha, for high resolution images of TEM; CadifraX, DETEMA for XRD spectra, and Cátedra de Fisicoquímica, Facultad de Química, for enabling us the use of the diffuse reflectance accesory.

[1] S. Kvedaravicius et al., Ferroelectrics, 177, 181-190 (1996).
[2] R. Rern; J. Phys. Chem. Solids, vol 23, 249-253 (1962).

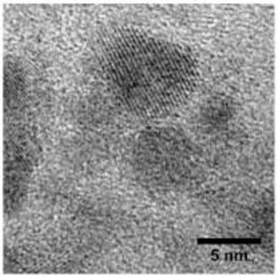


Figure 1. BiSI nanoparticles obtained through solvothermal synthesis using ethylene glycol as solvent and octadecanethiol as capping agent.

Microstructure and residual stresses in CrAlN / CrN multilayer deposited by the HIPIMS process.

M.C.R. Guimarães[1], *C. H. Cunha*[1], *W. R. Correr*[1], *P. Mordente*[2], *J. A. Araujo*[3], *H.C. Pinto*[1]

[1]*Escola de Engenharia de São Carlos, Universidade de São Paulo, 13566-590 São Carlos, Brazil*

[2]*MAHLE Metal Leve, Brazil*

[3]*Departamento de Engenharia Metalúrgica e Materiais, Universidade de São Paulo, Av. Prof. Mello Moraes 2463, 05508-030 São Paulo, SP, Brazil*

Multilayer ceramic coating has been developed with high wear for tribological application in lubricated sliding motion. The process is known as Impulse Magnetron Sputtering High Power (HIPIMS) which is an ionized physical vapor deposition technique based on conventional direct current magnetron sputtering. The coating materials to be investigated are designed in interspersed (Cr1-x, Alx) N and CrN layers, which will be deposited in martensitic stainless steel rings with 17% Cr.

The X-ray diffraction of the CrAlN/CrN multilayer coating shows reflections corresponding to the (111), (002), (022), (113) and (222) planes characteristic of CrN pattern; (111) is the most intense diffraction peak. The deconvolution of the diffraction lines was carried out based on the formalism of Segmüller and Blakeslee for determining the multilayer periodicity. A central peak is observed in $2\theta = 96{,}8°$ and satellite peaks at both sides of the central peak, thus revealing a periodicity of 5 nm for the coating. The residual stress was analyzed by x-ray diffraction and the results reveal 500 MPa for the transversal direction and

550 MPa for the circumferential direction. The surface hardness of the film was measured by nanoindentation tests, with 20 mN load, approach speed 2 µm/min and creep of 15 seconds. The test indicated a hardness value around 18 GPa. SEM images show a homogeneous layer without droplets. To continue the characterization of the samples will be necessary the use of the TEM techniques that will provide the lattice parameter in each of the constituent layers, structural analysis of the multilayers and assessment of their relative thicknesses.

The availability of well-defined satellite peaks is indicative of epitaxial growth of the

sub-layers within the coating, as well as of chemical modulation in the multilayer. The previous results exhibited a coating with high hardness, absence of droplets and excellent homogeneity.

ZnO nanostructures directly grown on paper and bacterial cellulose substrates.

Saionara Vilhegas Costa[a,b], Talita Mazon[b] and Ana Flávia Nogueira[a].

[a] *University of Campinas, Laboratório de Nanotecnologia e Energia Solar.*

[b] *Center for Information Technology Renato Archer – CTI.*

Zinc oxide (ZnO) is an optoelectronic material with a plethora of applications in electronic and optoelectronic devices. The interest in growing nanostructures on paper or paper-like substrates is mainly because of their low cost, environmentally friendly properties, biodegradability, recyclability, mechanical flexibility and compatibility with most printing processes. In this report, hierarchical ZnO nano- and microstructures were directly grown for the first time on a bacterial cellulose substrate and on two additional different papers by hydrothermal synthesis without any surface modification layer. Compactness and smoothness of the substrates are two important parameters that allow the growth of oriented structures. Hence, in this work we studied the influence of three papers substrates: photographic paper (PP), chromatography paper (CP) and bacterial cellulose (BC) on the morphological properties of ZnO nano and microstructures grown by hydrothermal synthesis. These papers were chosen due to their suitable mechanical strength, purity, porosity and their relatively low cost. All papers utilized in this work have succeeded in the growth of ZnO nano- and microstructures that were spread non- uniformly over the entire substrate. We can visualize the formation of different morphologies such as microrods, scattered nanorods and microflowers (Fig. 1a to i). Bright-field transmission electron micrographs (Fig. 1j and k) confirm lattice spacings of 0.52 nm and 0.28 nm in the <0001> and <01$\bar{1}$0> directions, respectively, consistent with the lattice constants of wurtzite ZnO. In Fig. 1j it was possible to visualize a thin layer of amorphous ZnO on the nanorod surface. The inset in Fig. 1k shows typical selected area electron diffraction (SAED) pattern of the corresponding ZnO nanorods.

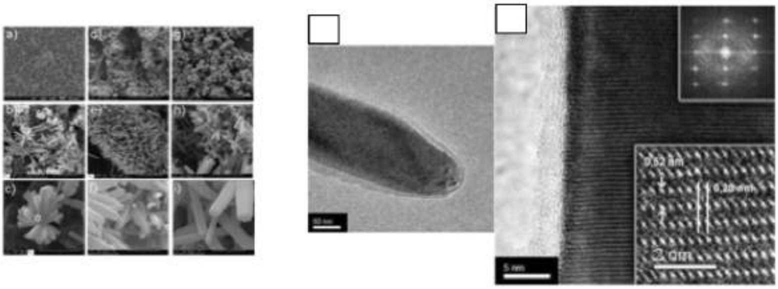


Fig. 3 FEG-SEM images of (a)–(c) ZnO microflowers, microrods and nanorods grown on photographic paper (PP); (d)–(f) microrods and nanorods grown on chromatography paper (CP); (g)–(i) microrods and nanorods grown on bacterial cellulose (BC); (j) and (k) HRTEM image of ZnO nanorods grown on CP.

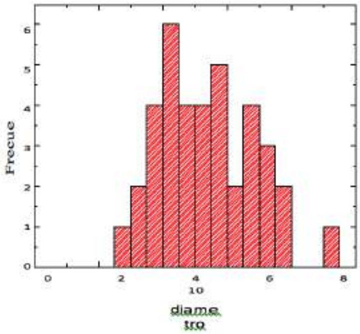
D. Vanmaekelbergh, L. K. V. Vugt, Nanoscale, 2011, ***3****, 2783*

STUDY OF INTERFACIAL EFFECT OF THE MIXTURE OF a MAGNETIC SEMICONDUCTOR AND MANGANESE FERRITES $FeIn_{0.8}Cr_{1.2}S_4/MnFe_2O_4$

USING TEM

Yeni Sánchez[1], Yannick Guari[2], Joulia Larionova[2], Jerome Long[2] and Pedro Silva[1]
1: Laboratorio de Física de la Materia Condensada, Centro de Física, Instituto Venezolano de Investigaciones Científicas (IVIC), Apartado 20632, Caracas 1020-A, Venezuela.
2: Laboratoire de Chimie Moleculaire et Organization du Solide, Universite Montpellier 2, UMR
5637, Place E. Bataillon, Montpellier cedex 5 34095, France.
email: yesanche@ivic.gob.ve

In last decades the miniaturization has been one of the most important goals in the manufacturing of electronic devices. Many attempts have been made in this direction and the use of the Magnetic nanoparticles in the design of new devices may improve the characteristics of them. In this work, we study the interfacial effect of the mixture of a magnetic semiconductor (SM) and manganese ferrites Nanoparticles using transmission electron microscopy (TEM). The synthesis of the magnetic nanoparticles (MNPS) of $MnFe_2O_4$ were realized by using hydrothermal method at 160° C for 2.5 h and the synthesis of magnetic semiconductor (SM) $FeIn_{0.8}Cr_{1.2}S_4$ using the Chemical Transport Vapor (*CVT*) method with $CrCl_3$ as transport agent. The structural characterization of the samples was realized using x-ray diffraction (*XRD*) and *TEM*. Clusters of spherical nanoparticles, with sizes between 2 and 150 nm, were obtained. The semiconductor was knackered by mechanic grinding in an agate mortar and needle-shaped grains were obtained from size 8 nm of diameter and then the mixed $FeIn_{0.8}Cr_{1.2}S_4/MnFe_2O_4$ was realized by mechanic grinding. The DRX pattern shows the presence of spinel structure for the three samples. The TEM micrograph shows that the NPs are placed around of the semiconductor. The magnetic characterizations of the samples were made using the SQUID magnetometry at 2.5 K. The MNP's shown the typical behavior of the ferrites nanoparticles and the SM shows a spin glass behavior below T=120 K. M(H) curves were made with aim of study the interface effect in the mixtures SM/MNp's. This effect is known as Exchange Bias (EB) effect, which is of origin interfacial in two materials with different magnetic order. This effect is manifested as the shift of hysteresis loops in the field axis.



High-Strength Low-Alloy (HSLA) steels: how parameters of welding affect their microstructure, mechanical properties and corrosion behavior

Mainã Portella Garcia, Gerson Luiz Mantovani, Renato Altobelli Antunes
Universidade Federal do ABC, Santo André, São Paulo, Brazil maina.garcia@ufabc.edu.br

The use of High-Strength Low-Alloy (HSLA) steels allow thickness reduction of vehicle body parts and it leads a decrease of vehicle weight. The HSLA steels contain several alloying elements, which can form various types of precipitates, as precipitation of carbonitrides [1]. When HSLA steel is used in automotive industry, welding is an important process that may change their characteristic. Therefore, the weld joints need to be well controlled due some weld defects such as dilutions and cracks that lead to great decrease of properties of the welded joint [2]. Due the elements in HSLA steels and their nanometers precipitation phases that may appears after welding process, the Transmission Electron Microscopy (TEM) is extremely important as a powerful technique to allow for a detailed characterization of fine microstructural features in the Heat Affected Zone (HAZ) and in the weld fusion zone (FZ). D.C Saha et al. conducted a study of dissimilar welds (dual-phase and HSLA). The formation of bainite and martensite in the dissimilar weld FZ was confirmed by TEM, that confirmed that the bainite structure containing bainitic ferrite laths with intralath and interlath cementite precipitates. The martensite microstructure was composed of several parallel martensite laths (150 nm) separated by thin films of retained austenite. TEM images permitted to see the high density of dislocation in martensite laths. Therefore, TEM analysis permitted the differentiation the microstructural constituents within the dissimilar FZ [3]. The aim of this project is to understand how microstructure changes, in different HSLA steels (500, 700 and 900 MPa), due welding process, affect the mechanical properties and corrosion behavior. Thin specimens will be made by pushing 3 mm discs, which will be twin jet electropolisehd to electron transparency in a mixture of perchloric and glacial acetic acid. TEM studies will be carry out at 200 kV in bright field mode and EDS analysis will used as well.

I would like to thank CNPq, Mercedes-Benz, Fronius and PCP Steels for all supports in this work.

[1] S.K. Mishra (Pathak) et al., Materials Science and Engineering, A323, 285–292 (2002).
[2] S. G Wang et al., Materials and Design, 32, 831-837 (2011).
[3] D.C. Saha et al., Materials Science and Engineering, A607, 445-453 (2014).

Multi-technique TEM characterization of bimetallic Au-Pd nanoparticles for the electrocatalysis of the oxygen reduction reaction.

María Angela Alvarez Manso[1]. Denis Ricardo Martins de Godoi[2], Aldo Alberto Rubert[1], Mariano Hernán Fonticelli[1], Hebe de las Mercedes Villullas[2]

[1] The Research Institute of Theoretical and Applied Physical Chemistry *(INIFTA), Diagonal 113 entre 63 and 64 (1900) La Plata, Argentina.*

[2] *Universidade Estadual Paulista - UNESP, Institute of Chemistry, Department of PhysicalChemistry , Rua Prof. Francisco Degni, 55, 14800-900 Araraquarara-SP, Brasil.*

ma.alvarezmanso@gmail.com

Bimetallic catalysts have garnered considerable interest because they exhibit distinctly different and often superior activity for many chemical transformations as compared to pure monometallic systems.

In particular, Au-Pd bimetallic nanoparticles are the most promising candidates to replace the Pt in catalysts for both H_2O_2 [1] production and the oxygen reduction reaction (ORR) [2]. The electrocatalytic properties of the supported nanoparticles toward the ORR will be studied and analyzed considering the composition, geometric and electronic structure of the systems.

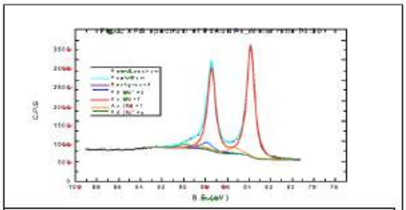
In order to get insight into the relationships between catalytic properties and structure we have synthesized Au-Pd nanoparticles by wet-chemical approaches, we have characterized these materials and tested them towards the ORR. The studies of catalytic activity for the ORR have been carried out using rotating disk electrode (RDE) and rotating ring-disk electrode (RRDE) arrays, in O_2-saturated alkaline solution (See Fig. 3 and 4).

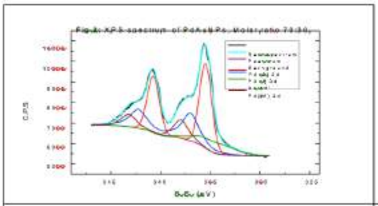
The electronic properties and composition of the Au-Pd nanoparticles on carbon substrates have been studied by conventional source X-ray photoelectron spectroscopy (See Fig. 1 and 2).

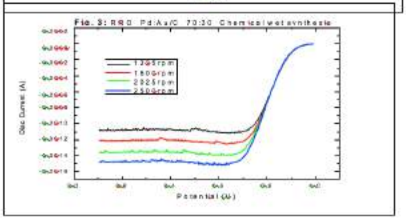
In particular Transmission electron microscopy provides a wide set of useful tools to attempt to study structural aspects of these systems. These techniques will allow me to determinate not only the nanoparticles size distributions, but also the NPs structure using HR-TEM [3] (See **illustration 3**) and electron diffraction patterns, as well as the concentration profiles (alloys and segregated phases) by high-angle annular dark field-scanning transmission electronic microscopy (HAADAF-STEM; see **illustration 2**) and traditional TEM operate mode by EDX analysis [3, 4], before and after electrochemical studies (Identical-location TEM investigations; **See Illustration 1**) [5].

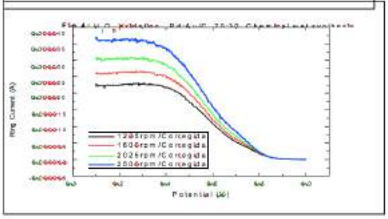
The Research Institute of Theoretical and Applied Physical Chemistry (INIFTA). La Plata. Buenos Aires. Argentina.
National Scientific and Technical Research Council (CONICET) Fundação de Amparo à Pesquisa e Extensão do Estado de São Pablo (FAPESP)
Instituto de quimica de Araraquara-UNESP.SP.Brasil.

[1] J. S. Jirkovský, et al., Journal of the American Chemical Society 133,19432-19441 (2011).
[2] J. B. Xu, et al., International Journal of Hydrogen Energy 35:9693-9700 (2010). [3] Serpell C. J. et al., Nature Chemistry, 3, 478-483 (**2011**).
[4] Taguchi N., et al., Applied Surface Science, 255, 164-166 (2008).
[5] K. Schlögl, et al., J. Electroanalytical Chemistry, 662, 355-360 (2011).









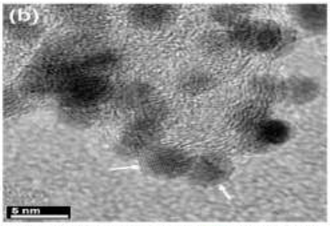


Illustration 1: HR-TEM images of Pd[1.0]- Au. Ref. [5]

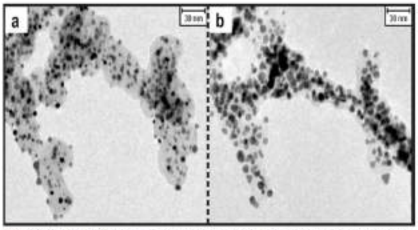


Illustration 3: Identical location – TEM of PtNPs onto carbon support. Ref. [7]

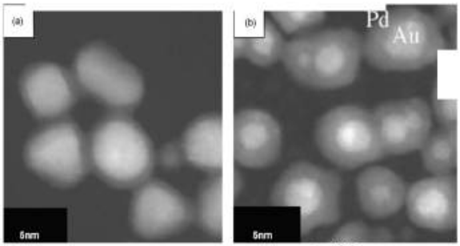


Illustration 4: STEM image of Au-Pd core-shell NPs. Ref. [6]

Study of the Use of Dead *Hypocrea lixii* Biomass for the Production of Copper Nanoparticles

Mariana Marangoni[1], Mariana de Paula Eduardo[2], Cláudio A. Oller do Nascimento[3]
[1] Politechnic School of the University of São Paulo, São Paulo, SP, Brazil
[2] Politechnic School of the University of São Paulo, São Paulo, SP, Brazil
[3] Politechnic School of the University of São Paulo, São Paulo, SP, Brazil
Mari.marangoni@usp.br

A wide variety of nanoparticles production processes has been studied in the past years and a large number of them are bioprocesses. Bioprocesses are developed as a way to reduce the environmental and social impacts caused by traditional processes, such as the use of toxic solvents. Many studies explore the use of fungi biomass to produce nanoparticles, however the use of dead biomass is rarely discussed. A recent study published by Salvadori et al. (2013) indicates that the fungus *H. lixii* has the capacity of synthesizing copper nanoparticles after being autoclaved. Therefore, the focus of this project is to demonstrate the viability of using this fungi biomass in a larger scale. The process variables (pH, temperature, etc.) will be monitored and controlled and their influence on the synthesis process will be studied.

Fungus Hypocrea lixii was isolated from samples of the tailings pond in Sossego copper mine, located in Canaã dos Carajás (PA) northern region of Brazil. A sample of the isolated strain was kindly given by the Institute of Biomedical Sciences (ICB) through Dr. Márcia R. Salvadori.

The fungus is kept in Difco^{TM} PD Agar at 25°C and cultivated in 100mL of Difco^{TM} PD Broth for 5 days in 500mL erlenmeyer flasks at 25°C and 150rpm agitation. After incubation, the biomass is washed with double-deionized water and autoclaved at 121°C for 30 minutes. The wet biomass is then put in contact with 100ppm copper chloride solution for 24h. After that period biomass is filtered through cellulose membranes of 0,45µm pore size and kept in refrigerators at 4°C.

Samples of the filtered biomass were taken, prepared and analyzed in a Zeiss EM900 microscope in the Biology Institute at the University of São Paulo. It is possible to see in Figure 1 the presence of particles inside the cell and close to the cell wall.

We thank FAPESP, Vale and BNDES for supporting this work. We also thank Vinicius Queiroz and Waldir Caldeira for their help with sample preparation and analysis; Dr. Maria Anita Mendes, Dr. Lidiane Andrade and Meriellen D. Dias for their contribution and valuable suggestions.

[1] Salvadori et al., PLoS ONE, volume 8, n.11, p. e80519 (2013).

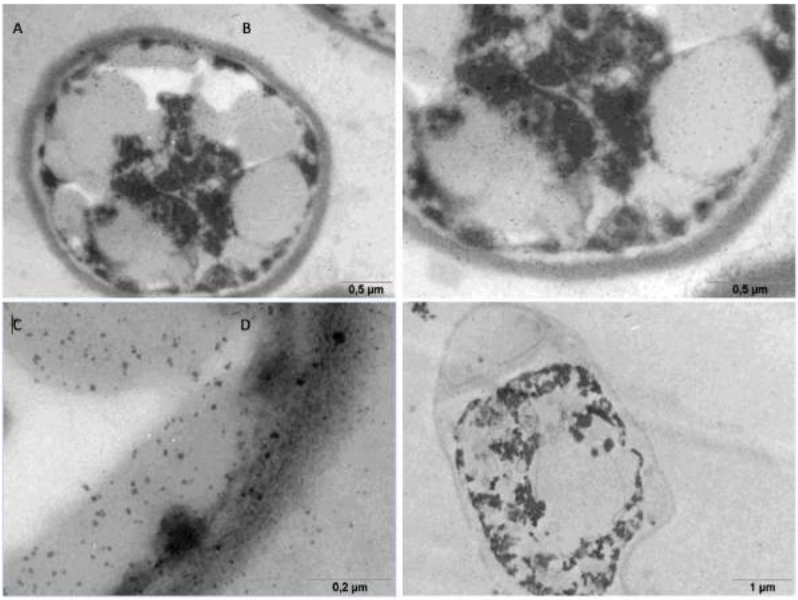


Figure 1 - Samples of fungal biomass before and after contact with copper ions. (A) Fungus cell after contact with copper ions. (B) and (C) Closer images of particles found inside cell and near cell wall. (D) Control sample, before contact with copper ions. (These are partial results)

Study of the alpha phase precipitation mechanisms on pseudospinodal decomposition and classic nucleation in Ti alloys

Mariana G. Mello[1], Rubens Caram[1]
[1] University of Campinas, Campinas, São Paulo, Brazil
marianagm@fem.unicamp.br

The increase in life expectancy and the always necessary healthcare improvements attach great importance to the development of biomaterials. Ti alloys containing β stabilizing elements are prone to be used as biomaterials due to their high specific strength, high corrosion resistance, unusual biocompatibility and low elastic modulus, which is very beneficial to the bone tissues near the implant. This is a study regarding the phase stability in β Ti-Mo-Sn, Ti-Mo-Fe and Ti-Mo-Al alloys processed under different conditions and was carried out through the following steps: study of the effect of third element alloy content (a) on the phase stability in Ti-Mo alloys, (b) on the suppression of α'' and ω phases precipitation; (c) on the precipitation of α phase during aging heat treatments and (d) on the mechanical properties via tensile tests and measurement of the elastic modulus using acoustic techniques. The alloys were prepared by arc melting under controlled atmosphere followed by homogenization heat treatment and hot rolling. Optical microscopy, scanning electron microscopy, X-ray diffraction and differential scanning calorimetry were employed for characterization purposes. Samples were also submitted to solution treatment above β-transus temperature and aging heat treatments under controlled atmosphere. Aiming to understand the influence of the addition of the third alloy element on α phase nucleation in Ti-Mo alloys, TEM techniques have great importance. The α phase precipitation is, in general, very fine laths in β phase matrix, with ω phase precipitates as nucleation sites [1, 2]. TEM can be used for identify the nucleation sites for α phase, consequently, its mechanism. Thus, bright and dark filed can be carried out for concluding the orientation and morphology of the phases. High resolution TEM can be performed to verify the variation of lattice parameters and phase boundaries and STEM/EDS for obtain compositional variations.

The authors are grateful to LME/LNNano/CNPEM for access to the SEM/TEM facilities; the Brazilian research funding

Surface processing as a tool for planar III-V nanowire direction control

M. Zavarize[1], P. Sahoo[1], D. S. Oliveira[1], S. R. Araújo[2], J. Bettini[2] and M. A. Cottta[1]
[1] State University of Campinas, São Paulo, Brazil.
[2] Brazilian Nanotechnology National Laboratory, São Paulo, Brazil.
marianaz@ifi.unicamp.br

Free-standing, out-of-plane semiconductor nanowires have been extensively investigated in the last decade due to their promising application in electronics and photonics. However, their integration into current device processing technologies still poses a challenge. Planar nanowires, on the other hand, show similar advantages with yet a more straightforward integration capability. For this reason, the efforts to control and characterize planar nanowires have grown in the last few years. In this work we study planar InP nanowires grown by the vapor-liquid-solid method, using Au particles deposited on electron-beam defined arrays as catalysts. Substrate surface treatments such as chemical or low energy plasma etchings and thermal annealing prior to growth were explored as tools in order to control the nanowire growth direction.

Scanning electron microscopy was used for statistical analysis of our samples - nanowire length and direction as well as the number of kinks. Our results show that preferential growth directions can indeed be created, depending on the surface treatment. Moreover, the occurrence of kinks can be suppressed. Electron Energy Loss Spectroscopy and cross-section transmission electron microscopy images show that the thickness of the substrate oxide layer in combination with surface roughness, evidenced from atomic force microscopy analysis, play a major role to determine the nanowire initial growth direction and its meandering along the substrate. The atomic force microscopy analysis also gives information about the nanowire cross-section (whole wire) that can be related to the substrate surface roughness and growth direction. Meanwhile, pinning of the catalyst triple phase line at the surface irregularities may be associated with nanowire kinking.

This research is supported by CNPq (grant #479486/2012-3) and FAPESP (grant #2013/02300-1). M.Z. acknowledges financial support from CNPq.

Orange bagasse biomass in the production of ethanol-2G: Immobilization of cellulase and β-glucosidase to the surface and internal structure of mesoporous silicate

Mayra A. Mariño Bohórquez[1], Ljubica Tasic[1].
[1] State University of Campinas, Campinas, São Paulo, Brazil
mayra.bohorquez@iqm.unicamp.br.

In order to adding value to the productive chain of orange bagasse (OB) and for their ethanol-2G in pilot scale, a co-immobilisation strategy for the enzymatic complex from *T. reesei* (Cellublast® 1.5 L) will be developed. It's expected that the immobilisation technique extend the useful life of the enzymes and allow an increase in the enzymatic loading for the hydrolysis, thus reducing operating costs of the process. The immobilization strategy will be developed by modifying the surface of an inorganic nanomaterial (mesoporous silicates) with a magnetic core and hydrophobic cavities. The main goal of this work is the synthesis of this hybrid nanomaterial that will be modified superficially to binding/absorb on cellulase aiming the enzymatic hydrolysis of pre-treated OB. In addition, the internal hydrophobic structure will be tailored for the co-immobilization of β-glucosidase. The magnetic- silica core will be also synthesized, characterized and functionalized previously (in Brazil) for the cellulase immobilization, because they allow an easy separation of the immobilized enzymes from the reaction mixture for its reuse by using a magnet and then coated by sílica to avoid oxidation. The chosen support materials for cellulase and β-glucosidase co-immobilisation will be adapted in fixed-bed to evaluate the reuse of immobilized enzymes during the biomass solubilisation. Particle size distribution, morphology and magnetic core distribution for the nanoparticles coated with silica and silicate mesoporous would be determine by TEM micrographs of a drop onto a 400 mesh copper grid.

The authors would like to express their gratitude to the foundation CAPES and NANOBIOSS.

Novel nanocomposites between functionalized graphene oxide and polypyrrole.

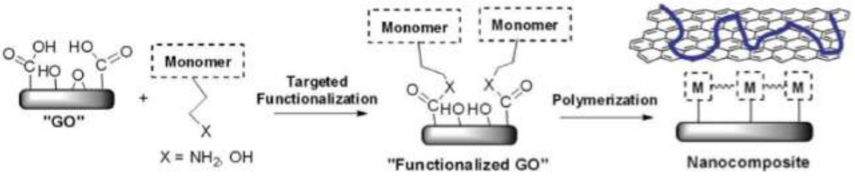
Naiane Naidek, Elisa S. Orth, Aldo J. G. Zarbin.

Universidade Federal do Paraná, Curitiba, Paraná, Brazil
naianenaidek @hotm ail.com

Graphene oxide (GO) has many oxygen groups on its surface and their presence allows covalent bond with functional groups such as monomers, which can lead to novel polymeric nanocomposites of GO. New applications for these materials come due to synergistic properties. Thus, we propose novel nanocomposites of GO covalently linked to polypyrrole, carried out through an innovative method: GO is functionalized with a pyrrole derivative that afterwards is polymerized. The targeted functionalization on the carboxyl sites of GO was performed using 2-(1H-pyrrol-1-yl) ethanamine (PETN) by forming an amide bond.[1] The solid functionalized GO with PETN (GOPETN) obtained was chemically polymerized in aqueous solution containing pyrrole, Scheme 1.[2] The material obtained was characterized by thermal gravimetric analysis (TGA), Raman spectroscopy and infrared and scanning electron microscopy (SEM). The functionalization was confirmed by infrared spectroscopy, Figure 1 by the characteristic amide bands (3292 and 1639 cm^{-1}). TGA analysis showed four mass loss events and one of them corresponds to decomposition of PETN. After the chemical polymerization, it was possible to observe by SEM, the polymer formed on the surface of GOPETN, Figure 2. In addition, characteristics bands of the oxidized polymer was verified by Raman.3However, more structural information is necessary to study the nanocomposite. The analysis of transmission electron microscopy (TEM) will provide valuable on the synthesized nanocomposite. It enables to evaluate the stacking of GO sheets based on the obtained image and the diffraction pattern will estimate the number of graphene sheets. Also, the uniformity of the polymer and overall distribution can be elucidated, which can be related to the mechanism of formation. For example, the functional group is mainly located on the GO sheet edges, and some indications of polymer linking on the edges should be possible by TEM images, that my SEM images is not so evident.

UFPR, CNPq, CAPES, Fundação Araucária, INCT de Nanomateriais de Carbono, Rede Nacional de Pesquisa em Nanotubos de Carbono, NENNAM (F.Araucária/CNPq).

[1] Orth, E.S. et al. Carbon, 61, 543, 2013
[2] Wanga, N et al. Carbohydrate Polymers, 127, 332, 2015. [3] Stempien, Z. et al. Synthetic Metals, 202, 49, 2015.



Scheme 1. Representation of the nanocomposite´s synthesis.

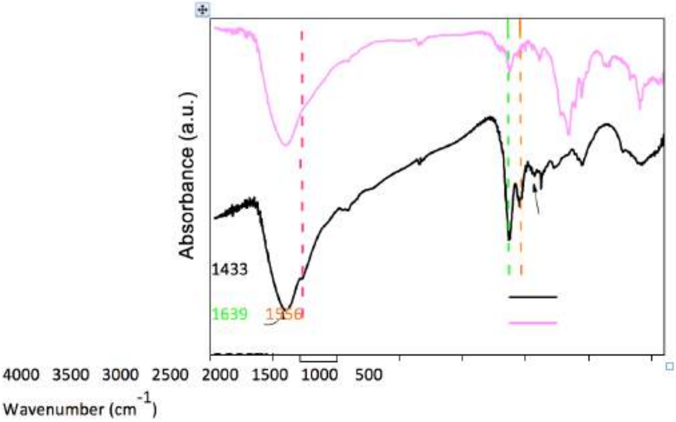


Figure 1. Infrared spectra of GO and GOPETN.

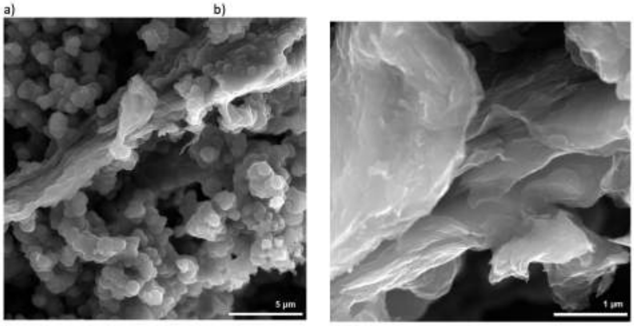


Figure 2. SEM images of nanocomposite.

Production of porous Ti/TiO_2 electrodes for electrochemical devices

Natália de Freitas Daudt[1], Lirio Schaeffer[2], Jocenir Bolta[1]
[1] Universidade Federal de Santa Maria, Cachoeira do Sul, RS, Brazil
[2] Universidade Federal do Rio Grande do Sul, Porto Alegre, RS, Brazil
natalia.daudt@ufsm.br (Corresponding Author: Natália de Freitas Daudt)

Global tendency is to replace the actual power source based on fossil fuel for renewable sources like wind and solar energy. Therefore, high performance electrochemical devices for conversion and storage of energy have had a growing application. In this context, batteries as Li-ion battery, has an important role. Recently, several studies have been focused on development of batteries. However, an increased efficiency and better cycles lives of batteries are required. Porous electrodes provide good access of the electrolyte to the electrode, facilitating charge transfer across the electrode/electrolyte interface [1]. The use of nanostructured materials in electrodes enables to increase the amount of active materials, so that capacity can be increased. Titanium due its electrochemical properties is a candidate for application in electrodes [2]. In our research, innovative porous electrodes produced from nanoparticles of titanium have been manufactured by powder metallurgy. On the electrode surface, a thin film of TiO_2 nanotubes will be grown in order to obtain a functional surface layer. Furthermore, a core-shell structure formed by Ti (core) and TiO_2 nanotubes doped with Ta will be obtained for use as catalyst. The size as well as the crystallinity of TiO_2 play an key role in the electrochemical properties of the porous electrodes [3]. Therefore, transmission electron microscopy (with 120 kV) will be applied to analyze the size distribution of TiO_2 nanotubes and TEM (with 200 kV) will be applied to investigate the crystallinity and atomic plane distribution. Nanostructured materials are promising for improving electrochemical devices efficiency. The results will demonstrate the most suitable Ti/TiO_2 structure in function of crystallinity and particle size for use as electrode in batteries.

The authors want to thank the Brazilian agency CNPq, Universidade Federal de Santa Maria – Campus Cachoeira do Sul and and Laboratory of Mechanical Transformation (LdTM) of Universidade Federal do Rio Grande do Sul (UFRGS).

[1] Vu, A. et al., Adv Energy Mater, v. 2, 1056-1085 (2012).
[2] Zhou et al. J Alloys Compounds, v. 597, 1–7, (2014).
[3] Bi, Z. et al., J Power Sources, v. 222, 461-466, (2013).

Size and shape tunable iron oxide with core-shell nanoparticles for magnetic hyperthermia applications

Navadeep Shrivastava[1], Sarveena[2], Diego Muraca[3], Pedro Mendoza Zélis[4], M. Singh[2], and S. K. Sharma[1*]
[1]Departamento de Física, CCET, Universidade Federal do Maranhão, 65085-580 São Luis, Brazil
[2]Department of Physics, H. P. University, Shimla, 171005, HP India
[3]Instituto de Física Gleb Wataghin - Universidade Estadual de Campinas (UNICAMP) 13083-970 São Paulo, Brazil
[4]Departamento de Física, Instituto de Física La Plata CONICET 49 y 115 (1900) La Plata, Argentina
*surender76@gmail.com

The present work describes the size and shape controlled synthesis and ageing effect of iron oxide nanoparticles obtained through thermal decomposition of Fe-precursors in a high boiling point organic solvent. A mixed phase iron oxide nanoparticles with narrow particle size distribution has been observed when the sample annealed in vacuum instead of Argon atmosphere. Further, it has been observed that a controlled oxidation in the presence of Au nanoseeds not only facilitate the self-organization of iron oxide nanoparticles, but also to switch these nanocomposites into core-shell structures. Controlled reaction time and oxidation temperature facilitate a systematic improvement in the core and shell shape. Spherical and spherical triangle shaped core-shell structures have been synthesized at an optimum oxidation temperature of 125°C and 150°C for 30 minutes. However, with the further increase in the oxidizing temperature as well as ageing time fully grown core-shell structures were achieved. Due to its superparamagnetism and biocompatibility as well as multipurpose biomedical potential these are best suited to pharmaceutical and industrial application. The prepared nanoparticles were checked for their utility in hyperthermia applications by measuring their specific absorption rate (SAR) value. The observed SAR values were largely dependent upon the shape anisotropy of the particles. These core shell nanoparticles have been thoroughly characterized using x-ray diffraction (XRD), high-resolution transmission electron microscopy (HR-TEM), Mössbauer spectroscopy and superconducting quantum interference device (SQUID) magnetometer.

The financial support from the FAPEMA is greatly acknowledged.

[1] S. K. Sharma et. al., Unusual magnetic damping effect in a silver–cobalt ferrite hetero nano-system 5, 17117 (2015)

Morphological and rheological study on blends of recycled polypropylene/ground tire rubber devulcanized by microwave

Pamela Sierra Garcia[1], Sandra Andrea Cruz[2], Carlos Henrique Scuracchio[3]
[1] Center of Engineering, Modeling and Applied Social Science - Universidade Federal do ABC, Santo André, São Paulo, Brazil
[2] Department of Chemistry - Universidade Federal de São Carlos, São Carlos, São Paulo, Brazil
[3] Department of Materials Engineering - Universidade Federal de São Carlos, São Carlos, São Paulo, Brazil
pamela.s.garcia@gmail.com

This work describes the effect of adding devulcanized tire rubber by microwave into recycled polypropylene (PPr) in order to make the PPr more ductile. For this purpose, the microwave devulcanization method was applied to the scrap ground tire rubber (GTR) to obtain a material able to flow and to be remolded [1]. The GTR samples were submitted to different microwave exposure periods and after that, they were embedded in the matrix formed by PPr. Firstly, the analysis of the rubber showed that long exposure times to microwave made the rubber more fluid due to the breaking of its sulfur cross-links [2], as seen in Figure 1. Mechanical and morphological properties were examined as a function of devulcanized GTR content (15% wt.) into the PPr (85% wt.). The results showed that the long exposure periods interfered positively in the adherence of the rubber with the PPr. Also, the blends composed of the most devulcanized GTR had a finer dispersion (Figure 2) and exhibited high toughness. Although these blends exhibited better results, it is necessary to understand what chemical and physical changes took place at the interface between the rubber and the PPr. So, some analysis will be performed in the LNLS, where the *infrared nanospectroscopy* will be used with the *atomic-force microscopy*. The transmission electron microscopy (TEM) will be an efficient tool to study the interfaces, mainly because this technique provides sufficiently high resolution images. Thus, it will possible to visualize the increase of interfacial width, if the polymer blend presents a good interface adhesion. In order to comprehend the mechanical properties, mainly the toughening mechanisms, it is necessary to use the TEM technique. The TEM micrographs can reveal the internal cavitation of rubber particles and thermoplastic toughening mechanisms, such as multiple crazing, shear-yielding and micro and nanovoids, being that all those mechanisms can only be seen at nanoscale [3-5].

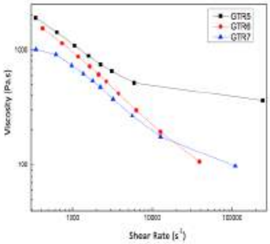


Figure 1. Viscosity versus shear rate for devulcanized samples.

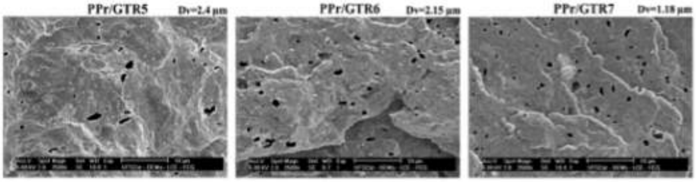


Figure 2. Morphology of blends of PPr/devulcanized GTR and volume average diameter (Dv) of each rubber particle of the different blends studied, where GTR5 represents exposure to microwaves for 5 min; GTR6 for 6 min and GTR7 for 7 min.

The authors are grateful to the Universidade Federal do ABC (UFABC) and Braskem S.A. for financial support and Brazilian Nanotechnology National Laboratory (LNNano) and Brazilian Synchrotron Light Laboratory (LNLS) for assistance in this project.

[1] Karger-Kocsis et al., Journal of Material Science, 48, 1 – 38 (2013).
[2] Garcia et al., Express Polymer Letters, 9, 1015 – 1026 (2015).
[3] Horiuchi et al., Macromolecular Rapid Communications, 28, 915 – 921 (2007).
[4] Song et al., Polymer Journal, 44, 939 – 945 (2012).
[5] Liu et al., Macromolecules, 43, 6058 – 6066 (2010).

Electrocatalytic activity and stability of platinum nanoparticles supported on carbon/molybdenum oxides for the oxygen reduction reaction

Pedro F. B. D. Martins[1], Edson A. Ticianelli[1]
[1] Department of Physical-chemistry, Instituto de Química de São Carlos, Avenida Trabalhador São-carlense, 400, São Carlos, São Paulo, Brazil
pedrofbdmartins@gmail.com

The degradation of Pt based electrocatalysts used in proton exchange membrane fuel cell (PEMFC) cathodes is one of the main issues that restrict wide PEMFC application as energy converter. This work aims to contribute to the improvement of the stability of platinum nanoparticles (Pt NPs) by modification of the support at which they are anchored. Thus, syntheses of catalyst supports based on MoO_x and carbon were carried out, followed by impregnation with Pt NPs. TEM micrographs for all catalysts before and after the 12,000 cycles of the stability tests are shown in Figure 1. For the as-prepared catalysts, a good distribution homogeneity of the Pt NPs on the supports is clearly seen. Results for the Pt/C and Pt/MoO_3-C catalysts after 12,000 cycles evidence the presence of platinum particles with larger sizes, reflecting the expected NPs agglomeration. For Pt/MoO_2*-C the platinum particles also increased, but in minor extent compared to the others. Also, it is seen that all dispersed catalysts present less Pt particles after ageing, although nothing can be said about the Pt element content, due to the growth of the particles. The histograms in Figure 2 show that initially Pt/MoO_3-C and Pt/MoO_2*-C present homogeneous particle size distributions in a small size range, despite the presence of some agglomerates. After 12,000 cycles, an increase in the particle size range is observed for all electrocatalysts, highlighting a raise in the proportion of bigger particles. The Pt/MoO_3-C catalyst showed the highest specific activity toward the oxygen reduction reaction (ORR), and this must be due to metal/support synergistic effects. Regarding the electrochemical stability of the materials, it is observed that, in principle, none of the Mo oxides really decreases the extent of Pt degradation. However, comparing the specific activities towards the ORR before and after electrochemical ageing, it is concluded that Pt/MoO_2*-C is a more stable material compared to Pt/C and Pt/MoO_3-C.

The authors would like to thank the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), the Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP, project number 2013/16930-7), Brazil.

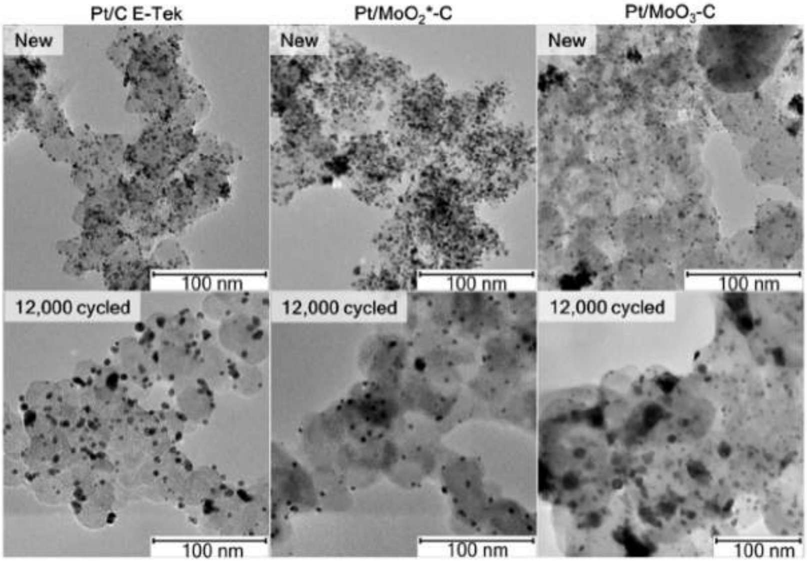


Figure 1. TEM micrographs of each electrocatalyst new and after 12,000 cycles between 0.6 – 1.0 V in 0.5 M H_2SO_4 at ambient temperature in air atmosphere aged.

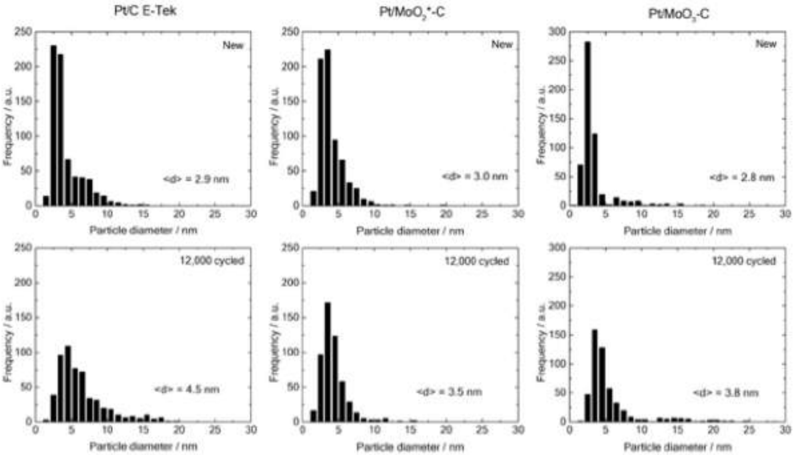


Figure 2. Histograms obtained by TEM micrographs of each electrocatalyst new and after 12,000 cycles between 0.6 – 1.0 V in 0.5 M H_2SO_4 at ambient temperature in air atmosphere aged.

Synthesis and Characterization of New Ni-based Nanomaterials for SOFC Fed with Biofuels

Rafael Machado Reis[1], Edson Antonio Ticianelli[1]
[1] Instituto de Química de São Carlos / USP, São Carlos, São Paulo, Brazil
r af aelmr @iqsc.usp. br (Corresponding Author)

Recently, the effects of global warming combined with fossil fuels usage has received great prominence in the international research. A viable alternative solution that has gained importance relates to the use of biofuels, such as ethanol. However, its direct use in solid oxide fuel cells (SOFC) containing conventional Ni-based anodes causes a rapid deposition of carbon, resulting in poisoning of the cell [1]. In this sense, the main objective was to synthesize bimetallic electrocatalysts containing nickel and a second metal (copper or cobalt) and apply them as a protective layer over conventional nickel anode. Physico-chemical characterization of the synthesized electrocatalysts were performed by XRD and TEM analysis using a FEI CM12-EDX instrument operating at 120 kV and equipped with LaB_6 filament (measurements performed at ITAE/CNR institute, Messina/Italy). XRD showed a good interaction between the two metals and it was obtained an alloy concerning Ni-Cu and Ni-Co, after reduction in H_2 ambient. The crystallite size of both alloys was determined by Scherrer`s equation and it was approximately 35 nm. TEM analysis showed fine particles with a typical size about 5-10 nm, present in both Ni-Cu and Ni-Co materials. However, large aggregates of Ni-Cu nanoparticles were observed, while metallic particles of Ni-Co appeared well distributed at the edges of ceramic particles. In this context, XRD and TEM analysis showed obtaining nanoparticles of Ni-Cu and Ni-Co alloys, thereby indicating both as promising catalysts for SOFC fed with ethanol [2,3].

The authors would like to thank CNPq (proc. 402180/2012-7) and FAPESP (proc. 2013/16930-7) for financial assistances and Dr. M. Lo Faro, from ITAE/CNR institute for TEM analysis. Dr. Rafael M. Reis would like to thank FAPESP (2014/04100-2) for his scholarship.

[1] Sauders, G.J. et al., J. Power Sour, 131, 23-26 (2004).
[2] Lo Faro, M. et al., ChemElectroChem, 1, 1395-1402 (2014). [3] Lo Faro, M. et al., J Appl Electrochem, 45, 647-656 (2015).

Growth of Silver Nanoparticles in Silica Substrate and Anchoring of a Solvatochromic Molecule for Future Application in Optical Sensors.

Rafaela Rigoni Teixeira[1], Marcela Mohallem Oliveira[2]
[1] Federal Technological University of Paraná, Curitiba, Paraná, Brazil
[2] Federal Technological University of Paraná
rafa1307@gmail.com

An important class of nanomaterials are metallic nanoparticles, which stand out for their intensely different and fantastic optical properties[1]. When electromagnetic waves propagate along an interface metal/dielectric medium creates a coupled electromagnetic field of the coherent oscillation of electrons in the conduction band way. Metal nanoparticles in the electric field induces polarization charges, the free electrons in the particle are displaced and the difference in the charge distribution gives rise to a restoring force generating resonance conditions in which the oscillation of free electrons is in phase with the electromagnetic radiation (Plasmon absorption)[2]. These properties (mainly gold, silver and copper nanoparticles in which have absorptions in the visible region of the electromagnetic spectrum[3]) can be very useful for development, for example, optical sensors, which may cause the device a higher sensitivity and selectivity. In this study, we sought growth of silver nanoparticles on a silica substrate and then construct a model system for this growth in a fiber optic sensor. In addition, we intend to add to this system a solvatochromic molecule aiming new features to the material. The samples will be characterized by the following techniques: UV-Vis spectroscopy in which we observe a Plasmon band, Raman spectroscopy in which it probe the existence of functionalizing, X-Ray Diffraction in which it characterize the presence of silver and Transmission Electron Microscopy (TEM), which allow examine size and shape of nanoparticles. As the size and shape of metal nanoparticles directly influence the wavelength of absorption[4] it is necessary to control their distribution and as said the main and the better way to visualize and quantify that is using TEM and that makes this an essential technique for the results of this research.

CAPES, CNPQ, INCT, GQM-UFPR, CME-UFPR, UTFPR, DAQBi and PPGQ.

[1] Franzoi, A. C. et al. Química Nova, v. 34, n. 6, p. 1042 - 1050 (2011). [2] Oliveira, M. M. et al., J. Phys. Chem. B, 110, 17063 (2006).
[3] Shriver and Atkins et al. Inorganic Chemistry. 4th Edition, Editor: Bookman, 2008. [4] Liz-Marzán, L., Materialstoday, ISSN: 1369 7021, p. 26 - 31 (2004).

Toxicological evaluation of nanocomposite membranes applied to nanofiltration of heavy metal ions

Rodrigo Costa Puerari[1], Denice Schulz Vicentini[1], William Gerson
Matias[1]
[1]Laboratory of Environment Toxicology (LABTOX), Department of Sanitary and
Environmental Engineering, Federal University of Santa Catarina, Campus Trindade, CEP:
88040-970, Florianópolis, SC, Brazil. rodrigopuerari@outlook.com

The increase in consumption and pollution of water bodies affect the availability of drinking water. Thus, studies of techniques to treat this resource are necessary. In water treatment field it is common to use polymeric membranes modified with nanomaterials to increase hydrophilicity and prevent fouling[1]. In this work, nanocomposite membranes with polysulfone and chitosan containing silicon dioxide nanotubes pure (SiO_2-NT) and functionalized with 3-[2-(2-aminoethylamino) ethylamino] propyltrimethoxysilane (SiO_2@NH_2-NT) were prepared to remove heavy metals from water[2]. The functionalizing was confirmed by infrared spectroscopy. Results of NT characterization by Transmission Electron Microscopy (TEM) confirmed the tubular morphology of SiO_2-NT with diameters between 50 and 60 nm and different lengths. The surface area analysis (BET method) showed a reduction of surface areas from SiO_2-NT to SiO_2@NH_2-NT of 220.3 $m^2 \cdot g^{-1}$ to 14.3 $m^2 \cdot g^{-1}$, respectively. It is expected that the TEM and SEM analyses show the membrane incorporated with SiO_2-NT in the polysulfone layer and SiO_2@NH_2-NT in the chitosan layer. The toxicological evaluation of the isolated SiO_2-NT and leaching of membranes with embedded SiO_2-NT will be held with the freshwater microcrustacean *Daphnia magna*. The preliminary results of the toxicity test showed $EC_{50,48h}$ equal to 4920 $mg \cdot L^{-1}$ of SiO_2-NT, indicating low toxicity. Analyses for obtaining $EC_{50,48h}$ of SiO_2@NH_2-NT and of leached membrane are in progess, as well the filtration essays to determinate the membrane efficiency. New microscopic analysis will be necessary to complement the characterization of the membranes containing SiO_2@NH_2-NT.

The authors acknowledge Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) (Projeto Universal/2013 - William Gerson Matias/CNPQ 473046/2013-0 Nanocompósitos para aplicação em nanofiltração de sais e íons de metais pesados de águas para abastecimento e efluentes.) for it financial support and LCME/UFSC for the TEM analysis.

[1] Jin, L., et al. Desalination, 298, 34-41 (2012).
[2] Matias, W. G., Vicentini, D. S., Melegari, S. P. Membranas poliméricas contendo nanotubos de SiO_2 funcionalizados aplicadas à nanofiltração de águas e processos de preparação. Registro do Pedido de Patente BR 102015003131 9 em 12/02/2015.

Toxicological evaluation of nanocomposite membranes applied to nanofiltration of heavy metal ions

Rodrigo Costa Puerari[1], Denice Schulz Vicentini[1], William Gerson Matias[1]
[1]Laboratory of Environment Toxicology (LABTOX), Department of Sanitary and Environmental Engineering, Federal University of Santa Catarina, Campus Trindade, CEP: 88040-970, Florianópolis, SC, Brazil. rodrigopuerari@outlook.com

The increase in consumption and pollution of water bodies affect the availability of drinking water. Thus, studies of techniques to treat this resource are necessary. In water treatment field it is common to use polymeric membranes modified with nanomaterials to increase hydrophilicity and prevent fouling[1]. In this work, nanocomposite membranes with polysulfone and chitosan containing silicon dioxide nanotubes pure (SiO_2-NT) and functionalized with 3-[2-(2-aminoethylamino) ethylamino] propyltrimethoxysilane ($SiO_2@NH_2$-NT) were prepared to remove heavy metals from water[2]. The functionalizing was confirmed by infrared spectroscopy. Results of NT characterization by Transmission Electron Microscopy (TEM) confirmed the tubular morphology of SiO_2-NT with diameters between 50 and 60 nm and different lengths. The surface area analysis (BET method) showed a reduction of surface areas from SiO_2-NT to $SiO_2@NH_2$-NT of 220.3 $m^2 \cdot g^{-1}$ to 14.3 $m^2 \cdot g^{-1}$, respectively. It is expected that the TEM and SEM analyses show the membrane incorporated with SiO_2-NT in the polysulfone layer and $SiO_2@NH_2$-NT in the chitosan layer. The toxicological evaluation of the isolated SiO_2-NT and leaching of membranes with embedded SiO_2-NT will be held with the freshwater microcrustacean *Daphnia magna*. The preliminary results of the toxicity test showed $EC_{50,48h}$ equal to 4920 $mg \cdot L^{-1}$ of SiO_2-NT, indicating low toxicity. Analyses for obtaining $EC_{50,48h}$ of $SiO_2@NH_2$-NT and of leached membrane are in progess, as well the filtration essays to determinate the membrane efficiency. New microscopic analysis will be necessary to complement the characterization of the membranes containing $SiO_2@NH_2$-NT.

The authors acknowledge Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) (Projeto Universal/2013 - William Gerson Matias/CNPQ 473046/2013-0 Nanocompósitos para aplicação em nanofiltração de sais e íons de metais pesados de águas para abastecimento e efluentes.) for it financial support and LCME/UFSC for the TEM analysis.

[1] Jin, L., et al. Desalination, 298, 34-41 (2012).
[2] Matias, W. G., Vicentini, D. S., Melegari, S. P. Membranas poliméricas contendo nanotubos de SiO_2 funcionalizados aplicadas à nanofiltração de águas e processos de preparação. Registro do Pedido de Patente BR 102015003131 9 em 12/02/2015.

Non-fullerene acceptor based bulk heterojunction solar cells: Morphology analysis using transmission electron microscopy (TEM)

Sivakumar Gangala,[a] Ana Flavia Nogueira*[a]
[a]Institute of Chemistry, University of Campinas, UNICAMP, Campinas, Sao Paulo, Brazil
Corresponding Author: anaflavia@iqm.unicamp.br

Due to their low-cost fabrication by solution processing, lightweight, and compatibility with flexible substrates, bulk hetero-junction polymer solar cells have emerged as potential economical alternatives to silicon-based solar cells. To obtain efficient bulk hetero-junction polymer solar cells, the exciton diffusion lengths in the Donor/Acceptor should be closely related to the scale of phase separation. The morphology can be controlled by many processing parameters during the production and does influence the final cell efficiency.[1] Transmission electron microscopy (TEM) is one of the important tools to have very good idea about the morphology of the organic thin films. To obtain maximum device performance, formation of domain structure with acceptor and donor materials is most important. TEM study can provide us in depth knowledge of the nano structured morphology of the active material in solar cells, which enable to fabricate device with optimize device structures.

TEM was used to investigate the phase separation morphology; the digital TEM images will be analyzed by carrying out a spatial Fourier transform of the image intensity to obtain the power spectral density (PSD). PSD has been widely used on digital atomic force microscopy (AFM) images to achieve surface roughness information.[2,3] In this project, we will use spatial Fourier transform and PSD as a method for quantitative analysis of TEM images of the polymer of the BHJ materials used in the fabrication of bulk hetero-junction polymer solar cells.

GSK and AFN thank FAPESP for financial support.

1. D. Veldman et al., JACS, 130, 7721-7735(2008)
2. P. Viville et al., J. Phys. Chem. B, 105, 7499-7507 (2001)
3. S. J. Fang et al., J. Appl. Phys., 82, 5891-5898 (1997)

Analysis of the interaction of ZnO nanoparticles with *Phaseolus vulgaris*

Savassa, Susilaine M.[1], Pereira de Carvalho, Hudson W. [1]
[1]Centro de Energia Nuclear na Agricultura – CENA - USP, Piracicaba, São Paulo, Brasil
susisavassa@gmail.com

In recent years has been observed the increasing development of commercial products containing nanomaterials[1,2]. Nevertheless the eco-toxicological implications, assimilation and reactivity of nanomaterials in living organisms are poorly understood[3]. In this context, this project aims at studying the transport, accumulation and chemical transformations undergone by nanomaterials, especially ZnO, absorbed by plants (*Phaseolus vulgaris*, ie. beans). The absorbed nanomaterials will be quantified and the parameters that govern the absorption, such as particle size, concentration and exposure time of root systems will be evaluated. The plant organs will be mapped by micro X-ray fluorescence, revealing in which specialized tissues nanomaterials are stocked. Morphological analyzes, using techniques like electronic scanning microscopy (SEM) and transmission (TEM), will be performed to observe the plant structures at the nanoscopic level uncovering how ZnO nanoparticles affect the cell morphology. The chemical environment of nanomaterials absorbed will be determined by X-ray absorption spectroscopy. Our recent results show that Zn can be accumulated in seeds, for that we have employed bench top EDXRF. Seeds` germination assays were carried out using the following treatments: Zn^{2+} aqueous solution, 300 nm ZnO and 5 nm ZnO aqueous dispersions. Pristine seeds present Zn content around 40 mg kg^{-1}, whereas seeds treated for 12 minutes showed Zn content ranging from 120 to 160 mg kg^{-1} and those treated for 2 hours presented Zn concentration varying from 225 to 300 mg kg^{-1}. Specifically for the seeds treated with 5 nm ZnO for 2 hours the Zn content was 225 mg kg^{-1}(Fig.1). Although this was the lowest value found, this treatment presented no germination at all(Fig.2). Thus our preliminary results indicate that the 5 nm ZnO particles prevent the seed`s germination. The causes of this effect are under investigation and is one of the main branches of the present PhD project.

To post-graduate program CENA -USP, CAPES for the scholarship , the FAPESP for research support (15 / 05942-0)

[1] Khan F. H., Oriental Journal of Chemistry, 29,1399-1408,(2013).
[2] http://vtu.ac.in/nano-technology/
[3] Klaine, S. J., et al., Environmental Toxicology and Chemistry ,27, 1825-1851, (2008).

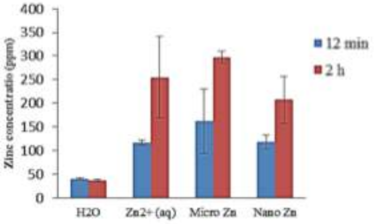


Fig.1: Zinc concentration in seeds.

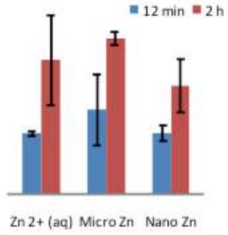


Fig.2: Effect of Zn on the germination of seeds.

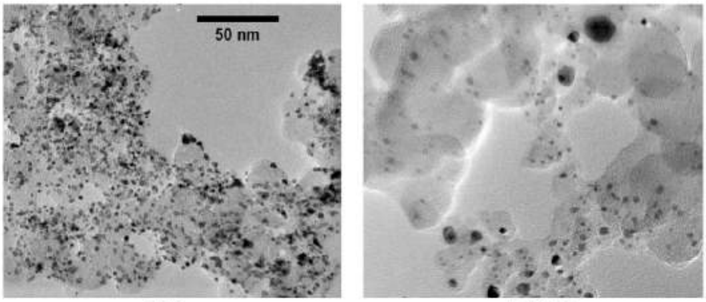
Cryogenic Transmission Electron Microscopy (Cryo-TEM) for studying the morphology of Nanostructured Lipid Carries (NLC) of free phytosterols for food applications

Valeria da Silva Santos[1], Ana Paula Badan Ribeiro[2], Maria Helena Andrade Santana[1].

[1]School of Chemical Engineering, University of Campinas, Campinas, SP, Brazil.
[2]School of Food Engineering, University of Campinas, Campinas, SP, Brazil. santosilvaleria@hotmail.com

Free phytosterols are bioactive compounds related to reduction of cholesterol levels in blood, which is closely related to cardiovascular disease prevention. However, free phytosterols are poorly water soluble substances with difficult application in foods, an alternative, is the incorporation of free phytosterols in NLC. Additionally, NLC has some advantages, such as chemical stability, permeability through the intestine wall and a better incorporation of lipophilic compounds, such as free phytosterols. The aim of this work was to develop and characterize NLC of free phytosterols, using common edible fats and oils (fully hydrogenated soybean oils and soybean oil) as lipid matrix instead of synthetic lipids, generally applied in drugs. The systems were developed by hot high pressure homogenization and characterized by means of particle size at 24 hours and 15 days after. We observed reductions in the particle sizes after 15 days of storage at 25ºC. Actually, we believe it may be related to lipid polymorphic transitions (α→β'→β), which often promote changes in the morphology of the nanoparticles from spherical to platelet-like particles closely related to the stability and expulsion of the active. Therefore the use of Cryo-TEM has great importance in this investigation in order to clarify some structural features of these systems. In this case, the use of freeze-fracture method allows direct investigation of nanoparticles in the vitrified state, very close to their native state without changing the fat polymorphic form. It can provide information about the formation of particles, size and morphology, besides, would be possible to observe the organization of the lamellar triglyceride layers related to the polymorphic form and to clarify the morphologic changes related to lipid polymorphic transitions.

The authors acknowledge the financial support from the Coordination for the Improvement of Higher Education Personnel (Capes, Brazil).



Pt/C

Pt_3Nb/C

Figure 1. TEM images of the base Pt/C and prepared Pt3Nb/C catalysts (same scale for both images).

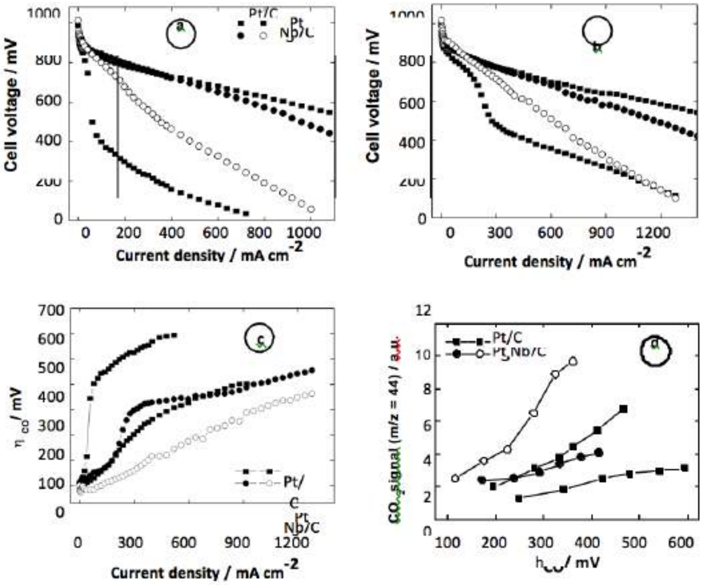


Figure 2. Polarization curves for neat H_2 (solid symbols) and H_2 + 100 ppm CO (hollow symbols) at a) 70ºC, and b) 90 ºC; c) CO overpotential due to the addition of CO to the fuel stream, and d) electrogenerated CO_2 at 70ºC (solid symbols) and 90 ºC (hollow symbols).

Cryogenic Transmission Electron Microscopy (Cryo-TEM) for studying the morphology of Nanostructured Lipid Carries (NLC) of free phytosterols for food applications

Valeria da Silva Santos[1], Ana Paula Badan Ribeiro[2], Maria Helena Andrade Santana[1].

[1]School of Chemical Engineering, University of Campinas, Campinas, SP, Brazil.
[2]School of Food Engineering, University of Campinas, Campinas, SP, Brazil. santosilvaleria@hotmail.com

Free phytosterols are bioactive compounds related to reduction of cholesterol levels in blood, which is closely related to cardiovascular disease prevention. However, free phytosterols are poorly water soluble substances with difficult application in foods, an alternative, is the incorporation of free phytosterols in NLC. Additionally, NLC has some advantages, such as chemical stability, permeability through the intestine wall and a better incorporation of lipophilic compounds, such as free phytosterols. The aim of this work was to develop and characterize NLC of free phytosterols, using common edible fats and oils (fully hydrogenated soybean oils and soybean oil) as lipid matrix instead of synthetic lipids, generally applied in drugs. The systems were developed by hot high pressure homogenization and characterized by means of particle size at 24 hours and 15 days after. We observed reductions in the particle sizes after 15 days of storage at 25ºC. Actually, we believe it may be related to lipid polymorphic transitions ($\alpha \rightarrow \beta' \rightarrow \beta$), which often promote changes in the morphology of the nanoparticles from spherical to platelet-like particles closely related to the stability and expulsion of the active. Therefore the use of Cryo-TEM has great importance in this investigation in order to clarify some structural features of these systems. In this case, the use of freeze-fracture method allows direct investigation of nanoparticles in the vitrified state, very close to their native state without changing the fat polymorphic form. It can provide information about the formation of particles, size and morphology, besides, would be possible to observe the organization of the lamellar triglyceride layers related to the polymorphic form and to clarify the morphologic changes related to lipid polymorphic transitions.

The authors acknowledge the financial support from the Coordination for the Improvement of Higher Education Personnel (Capes, Brazil).

Gold nanoparticle based sensor for early breast cancer detection

Vera Katic[1], Juliano Alves Bonacin[2]
State University of Campinas, UNICAMP, Campinas, State, So Paulo
vera.katic@iqm.unicamp.br

Cancer is a disease that alters health status of cells and ultimately leads to malignant tumors. Late detection of disease increases the number of deaths. Therefore, early detection of cancer can save lives [1]. Our objective is to create highly accurate portable device for early breast cancer detection. The portable device (sensor) would be based on the interaction between gold nanoparticles and biomarkers [2]. Biomarker refers to a measurable indication of biological state or condition. Thus, cancer biomarkers are an indication of cancer and via its detection the existence of specific cancer can be verified. One of the most studied breast biomarkers is CA 15-3, located in the blood. Therefore our focus is to create sensitive sensor for CA 15-3 detection. Initially, shape and size controllable gold nanoparticles will be obtained utilizing photoinduced methods. The following steps will include detailed characterization of aforementioned systems via spectroscopy and electron microscopy. Nanoparticles will be characterized with transmission electron microscopy (TEM) in order to investigate morphological, crystallographic and elemental composition. The final step will be focused on the development of electrochemical and plasmonic sensors.

Thanks to LNNano - Laboratório Nacional de Nanotecnologia CNPEM - Centro Nacional de Pesquisa em Energia e Materiais Campinas - SP – Brasil and CNPq grant number (161819/2014-1)

[1] T. N. Seyfried et al. Carcinogenesis, **35***, 515-527, 2014*
[2] Li et al. Biosensor and Bioelectronics, **43,** *25-29, 2013*
.

Mechanical and microstructural characterization of steels Ultra – High- Strength Thermally and Thermochemically Treated by plasma.

Y. O. Iwaki[1]*, A. S. M. Cardoso*[2]*, D.Y. K. Ranzini*[3]
[1] *Centro Tecnológico da Marinha em São Paulo - CTMSP, Iperó, SP, Brazil*
[2, 3] *Centro Tecnológico da Marinha em São Paulo - CTMSP, São Paulo, SP, Brazil yurika.iwaki@ctmsp.mar.mil.br*

The high strength steel with low alloy and ultra-high strength steel are materials with great industrial application, in which its technology enables strategic innovation. The understanding of the medium carbon steel composition modification SAE 4340 [1] enabled the purchase of the 300M Stainless steel, although in the development application of rocket and energy areas, the Maraging 300 steels were also correlated. To assess and compare the mechanical properties of these steels under different treatments, together with its microstructural correlation, would enable an understanding of the improvements or fragilization, which are decisive in the resistance of such materials. As received the Maraging steel 300M and 300 exhibited high mechanical strength values catastrophic failure in the plastic regime, as well as high threshold in fatigue life compared to steel 4340 [2]. As for the thermochemical nitritation treatment and the properties studied, there was, in steels 4340, significant increase in tensile strength, but decrease in fatigue life. Nevertheless Maraging steels 300M and 300 declined in strength in tensile tests and fatigue life, however exhibited higher hardness values and corrosion resistance. The 300M and Maraging steel showed unfavorable results in fatigue and stretching. Scholars have noted that thermochemical treatments such as nitritation at certain temperatures (acting as tempering / aging in the inner region of the material), can weaken steel with high grades of silicon and titanium [3].

Centro Tecnológico da Marinha em São Paulo and Marinha do Brasil.

[1] MESQUITA, R. A. et al., Tecnologia em Metalurgia e Materiais, v.4, n.4, p. 7-15, (2008).
[2] CARDOSO, A. S. M. et. al, Advanced Materials Research, Vol. 891-892, p. 1507-1512 (2014).
[3] GARRISON JR, W.M., Materials Science and Technology, v. 3, n. 4, p. 256-259 (1987).

Synthesis and characterization of $Sr_{1-x}Cu_xTiO_3$ and $SrTi_{1-x}Cu_xO_3$ compounds applied to catalysis of the water-gas shift reaction

Vitor C. Coletta[1], Francielle C. F. Marcos[2], Francisco G. E. Nogueira[2], Maria I. B. Bernardi[1], Alain Michalowicz[3], Renato V. Gonçalves[1], Elisabete M. Assaf[2], Valmor R. Mastelaro[1]
[1]São Carlos Institute of Physics, University of São Paulo, São Carlos, São Paulo, Brazil
[2]São Carlos Institute of Chemistry, University of São Paulo, São Carlos, São Paulo, Brazil
[3]Universite Paris-Est Creteil Val de Marne – ICMPE-CNRS, Thiais, France
vitor.coletta@usp.br

The water-gas shift reaction is carried out in the production of H_2 free from CO, necessary in applications such as the use in proton exchange membrane (PEM) fuel cells. [1] Oxides with perovskite structure containing copper are promising for catalysis of this type of reaction for presenting a good chemical stability. [2] This research consists in performing the synthesis and characterization of nanoparticles of composition $Sr_{1-x}Cu_xTiO_3$ and $SrTi_{1-x}Cu_xO_3$ looking for the application as catalysts for the water-gas shift reaction. The synthesis was done through the polymeric precursors method with calcination in N_2 atmosphere followed by a heat treatment in O_2 for carbon removal, resulting in nanoparticles with large surface area in comparison to the conventional method. [3] X-ray diffraction results showed that the copper atoms are segregated from the perovskite phase for $x \geq 0.06$ in form of CuO phase. The composition $SrTi_{0.80}Cu_{0.20}O_3$ presented the better activity with 74% of CO conversion at 350°C. Thus, our TEM analyses, at the Chemistry Institute of Unesp, Araraquara, begun with this sample compared to the undoped $SrTiO_3$. Figure 1 shows a high-resolution TEM image of a crystallite of the $SrTiO_3$ sample. The distance of 0.27 nm between the observed crystallographic planes corresponds to that between (110) planes of $SrTiO_3$ cubic phase (PDF 35-0734). As expected from the X-ray diffraction results, the $SrTi_{0.80}Cu_{0.20}O_3$ sample has $SrTiO_3$ as the main phase and also regions rich in CuO phase on the surface as showed in Figure 2a. The high-resolution image of the region in Figure 2b shows planes spaced with a distance close to that reported for (11-1) of CuO phase (PDF 48-1548). The presence of the phase is also confirmed by the EDS spectrum in the region (Figure 2c). The next steps of our TEM characterization will involve analyzing the difference between substituting strontium and titanium sites for copper in the morphology and copper segregation.

The authors are grateful for the financial support provided by São Paulo Research Foundation – FAPESP (grant 2013/09573-3) and National Council for Scientific and Technological Development – CNPq (grants 304498/2013-0 and 140631/2013-5). The authors are also grateful to Marcelo O. Orlandi for the use of the transmission electron microscope.

[1] Gradisher, L. et al. Applied Energy, 139, 335-349 (2015).
[2] Maluf, S. S. et al. Applied Catalysis A: General, 413-414, 85-93 (2012).
[3] da Silva, L. F. et al. Materials Chemistry and Physics, 125, 168-173 (2011).

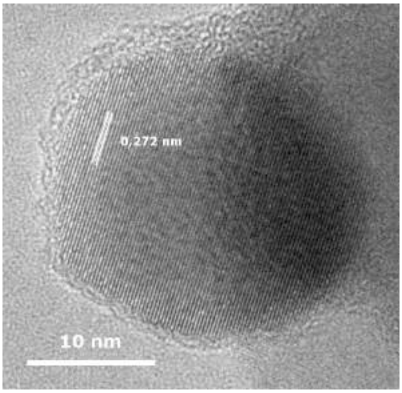


Figure 1 – High-resolution TEM image of $SrTiO_3$ *sample.*

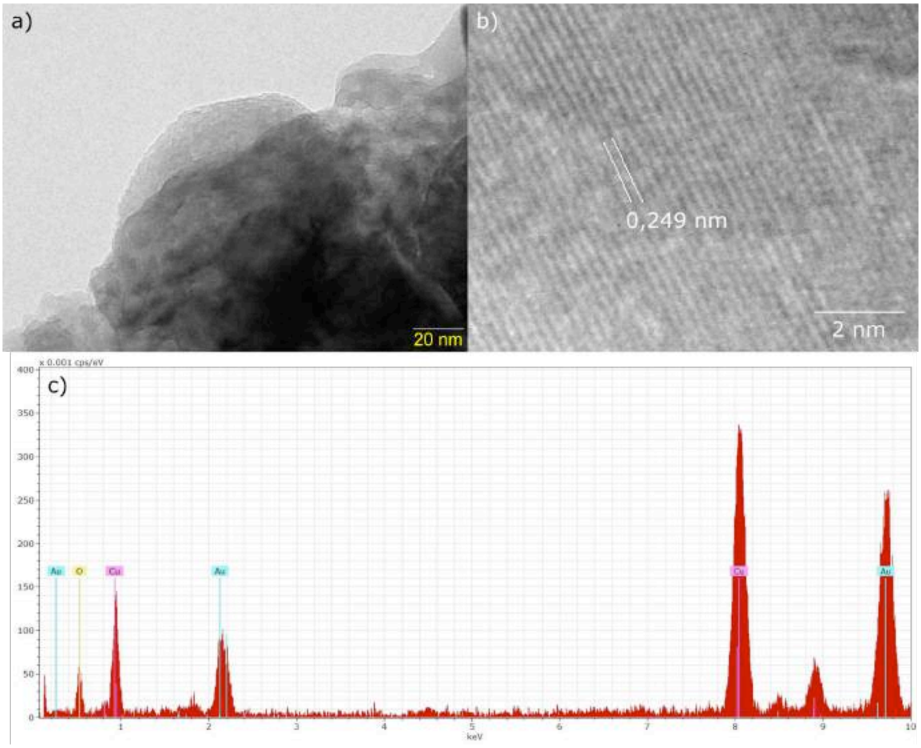


Figure 2 – (a) TEM image of $SrTi_{0.80}Cu_{0.20}O_3$ *sample. (b) high-resolution image and (c) EDS spectrum of the region on the surface.*

Identification of secondary precipitates present at grain boundaries of Co based superalloy

A.M.S. Costa[1], E. S.N. Lopes[2], A. P. Tschiptschin[1,3]
[1]Brazilian Nanotechnology National Laboratory, Campinas, Sao Paulo, Brazil
[2]Faculty of Mechanical Engineering of Unicamp, Campinas, Sao Paulo, Brazil
[3]Department of Metallurgical and Materials Engineering at Polytechnic School of USP
alex.costa@lnnano.cnpem.br

In this study was focused on the characterization of fine precipitates formed on grain boundaries in Co based superalloys. When the precipitates are presented in metallic materials they could improve materials properties such a mechanical, electrical, magnetic and chemical stability as well. Depending on the dimension in size and shape the precipitates can acting such a reforcement of grain boundaries and helps to prevent grain sliding during high temperature performance. In this way is imperative to know which the chemistry composition, what kind of phase it is (intermetallics, carbides, borides and so on), orientation relationship with the matrix phase, where they could be identified on the microstructure. The transmission electron microscopy technique provides a lot of important information about the more located microstructural characterization what is the main goal of this study. The samples have been studied in this work were prepared by focused ion beam (FIB) technique at the Center for Electron Microscopy and Analysis (CEMAS). The features of the samples were analysed by high resolution transmission electron microscope JEOL model JEM 3010 at LME. It was captured bright field images from grain boundaries region. Figure 1 shows the sample that was prepared by FIB technique. Figure 2 shows a couple of details about the microstructure of the material. It is observed the matrix is microconstituted of γ-Co austenitic phase having (A1) FCC structure and coherent $L1_2$ structure precipitates of γ'-$Co_3(Al,W)$ inside it. Fine precipitates of minor secondary phase are found at the grain boundaries are showed Figure 2. Because of the additions of C, B, Ni and Al certain kind of precipitates could be formed during the cooling of the material that was processed by arc melting technique. Chemical analysis using XEDS together electron diffraction technique should help to do a proper identification of which kind of phase are decorating grain boundaries.

This study has been supported by The São Paulo Research Foundation (Fapesp – Process Number 2014/13772-4). I would like to thank Dr. Eder Lopes for preparing FIB samples and Dr. Carlos Ospina for acquisition of TEM images.

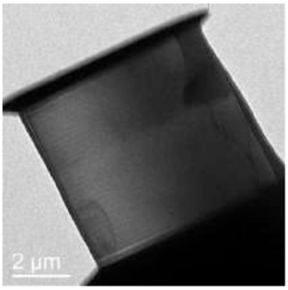


Figure 1- The sample of Co based superalloy prepared by FIB technique.

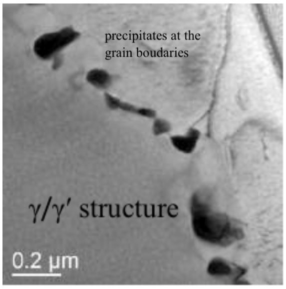


Figure 2- Microstructure of Co based superalloys showing matrix structure and secondary minor phases precipitated at the grain boundaries.

Vanadium interaction with biological systems

B. C. Costa[1], P. N. Lisboa-Filho[2]
[1] Programa de Pós-Graduação em Ciência e Tecnologia de Materiais – Universidade Estadual "Júlio de Mesquita Filho" - UNESP, Bauru, São Paulo, Brazil
[2] Departamento de Física, Universidade Estadual "Júlio de Mesquita Filho" - UNESP, Bauru, São Paulo, Brazil

brunah@fc.unesp.br

Among the most commonly used metallic materials as prosthetic implants are titanium-based alloys, specifically Ti-6Al-4V system, whose use corresponds to 45% of the total production of titanium as biomaterial [1].

In general, metallic materials may suffer corrosion when implanted, leading to release of metal compounds or *debris* (fragments) into the body. Furthermore, the human body is predominantly composed by water, polymers (proteins) and ceramics (bones) and metals are elements found as necessary only in very small quantities [2]. Thus, when a metallic material is implanted in the human body, the toxicity of their constituents elements should be evaluated before its application. Regarding to the evaluation of toxicological potential of elements of the Ti-6Al-4V system, aluminum may present acute toxicity at high doses, and is reported as an element related to neurological disorders and mitigating factor of various diseases. Vanadium plays a role that is still poorly understood in the human body and may present ambiguous cellular responses. Furthermore, vanadium compounds may have interactions with proteins within a living organism, changing its functionality [3].

In this context, the present proposal is based on the possibility of long-term exposure to an implant based on Ti-6Al-4V alloy, the adverse effects of *debris* release from its corrosion in a living system and also the studies related to toxicity of these alloying elements, and the importance of the interaction of this element, especially in its nanostructured form, regarding proteins.

In this way, the *in situ* liquid TEM technique may allow the orientation and conformation analysis of proteins under the surface of this project samples (Ti-6Al-4V and vanadium *debris* obtained from tribocorrosion tests and V_2O_5 powder), and this is the key-role to understanding the interaction and toxicity mechanisms of vanadium in live systems. So a better understanding of this powerful technique is extremely recommended.

The authors would like to thank CAPES and CNPq - Brazilian Funding Agencies for the financial support.

[1] DAVIES, J.R. Handbook of Materials for Medical Devices, Ohio, ASM International, Materials Park, 2003.
[2] CHEN, Q. et al., Materials Science and Engineering R, 87, 1 – 57 (2015).
[3] MUKHERJEE, B. et al., Toxicology Letters, 150, 135 – 143 (2004).

Effect of impurity segregation on intermediate temperature, ductility-dip cracking (DDC) in high-Cr, Ni-base alloys

Carolin Fink, John C. Lippold
The Ohio State University, Columbus, Ohio, USA

fink.242@osu.edu

The chemical composition of the filler metal has proven to be one of the most important factors controlling DDC in Ni-base weld metals. Alloying elements, such as Nb, determine the precipitation behavior at the end of weld metal solidification, mitigating DDC by grain boundary (GB) pinning and boundary "tortuosity" [1]. On the other hand, impurities and interstitials are also considered to play an important role in DDC susceptibility. Both hydrogen and oxygen embrittlement in Ni-base alloys has been reported [2, 3]. Both elements are known to have a detrimental effect on resistance to DDC. A possible contribution due to a GB decohesion effect or local oxidation at the grain boundary is considered possible [4]. However, on the atomic scale, there is very limited knowledge regarding interactions between interstitial elements at the GBs and at the interface between intergranular precipitates and the matrix. These interactions may not be the primary cause of DDC but may promote further intergranular embrittlement in the DDC susceptible temperature range, potentially helping to explain the variability in susceptibility within the same filler metal specification.

The proposed work will elucidate such interactions using electron microscopy (SEM, TEM) coupled with EDS and EELS measurements to understand their role on the cracking mechanism. Gleeble-based thermo-mechanical simulation will be performed with additions of either hydrogen or oxygen (via shielding gas or enriched atmosphere) for weld metal sample preparation. Samples for electron microscopy will be prepared from GB and crack-tip regions and analyzed for oxygen segregation, oxide formation or oxidation of GB particles. To determine the role of hydrogen migration to the GBs additional in-situ TEM analysis could be performed to study its influence on strain localization. This could be done by in-situ TEM tension [5] to observe and analyze the dynamic process of dislocation motion and crack nucleation.

[1] Ramirez, A.J. et al., Materials Science and Engineering A, 380(1-2), pp. 245-258 (2004).
[2] Woodford, D.A., Energy Materials, 1(1), pp. 59-79 (2006).
[3] Collins, M.G. et al., Welding Journal, 82(10), pp. 288s-295s (2003).
[4] Zheng, L. et al., Critical Reviews in Solid State and Materials Sciences, 37, pp. 181-214 (2012).

Low Energy Ion Implanting of Silver or Copper Ion for antimicrobial activity

Cesar Henrique Wanke[*], Tatiana Pacheco Soares, Andreia Valim de Souza, Carlos Alejandro Figueroa, Otávio Bianchi, Cesar Aguzzoli
University of Caxias do Sul, Caxias do Sul, Rio Grande do Sul, Brazil
[*]chwanke@ucs.br

In modern medicine, biomaterials have been widely used as implants. However, orthoses and prostheses infected with post-implanted microorganisms require surgeries and medical interventions that are costly and treatment can take months. To combat infections associated with implants, the best strategy is to prevent them from occurring. One strategy is the silver ion implantation in these biomaterials [1-4]. As the antimicrobial efficacy of the nanoparticle depends on the shape and size of them [5], this can be confirmed by studying the inhibition of bacterial growth by differentially shaped and size nanoparticles. In this work, silver or copper ions were implanted at low energies in medical titanium with the goal to render bactericidal substrate surface and therefore, inhibit biofilm formation. The implantation was done using the Ion Plating equipment. After ion implantation, the samples were analyzed by Rutherford Backscattering Spectrometry (RBS), Glow-Discharge Optical Emission Spectroscopy (GD-EOS) and X-Ray Diffraction. The RBS analysis was performed at the Federal University of Rio Grande do Sul. The results show that the silver was implanted at depths of until 10 nm, corroborating with simulation data. In addition, preliminary tests of antimicrobial activity show that the approach adopted in this work has been effective. However, for a better understanding of how the nanoparticles are distributed in the outer surface, i.e. if are sprayed or in the cluster form, are necessary to use techniques that enable to evaluate this distribution. The most widely used technique for this is the transmission electron microscopy. It is intended to verify how nanoparticles are distributed on the surface (Figure 1a) as well as its distribution in depth (Figure 1b). For this, it needs to analyze the surface and cross section. These analyses will be used to correlate with the process parameter of the equipment and thermal treatment of samples after ion implantation.

We are indebted to the Brazilian agency CAPES, University of Caxias do Sul and Ion Implantation Laboratory (Institute of Physics, Federal University of Rio Grande do Sul, Porto Alegre, RS, Brazil).

[1] L. Zhao et al., Biomaterials, 32, 5706 - 5716 (2011).
[2] A. Melaiye and W. J. Youngs, Expert Opinion on Therapeutic Patents, 15, 125 - 130 (2005).
[3] D. R. Monteiro et al., International Journal of Antimicrobial Agents, 34, 103 – 110 (2009).
[4] K. Hori and S. Matsumoto, Biochemical Engineering Journal, 48, 424 – 434 (2010).
[5] M. Rai et al., Biotechnology Advances, 27, 76 – 83 (2009).

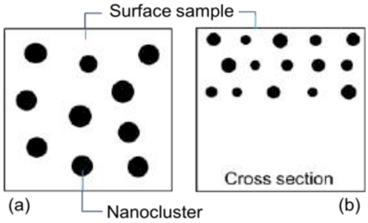


Figure 1. Representation of the formation of nanoclusters of the silver of copper nanoparticles on surface (a) and its distribution in depth (b).

Synthesis and structural analysis of $CoFe_2O_4$:$BaTiO_3$ nanocomposites

D. Alanis[1*], P.N. Oliveira[1], R.D. Bini[1], D.M. Silva[1], G.S. Dias[1],I.A. Santos[1], L.F. Cótica[1]
[1]Department of Physics, State University of Maringá
Av. Cololmbo, 5790, Maringá, Paraná, Brazil 87020-900
*e-mail: denise_a89@hotmail.com

Multiferroic materials have attracted interest due to the presence of more than one ferroic order, for example magnetic and electric orders, in the same phase. This particular coupling phenomenon is known as magnetoelectric (ME) effect. However, it is difficult to obtain significant ME effect in single-phase materials, since magnetic and electric dipoles have to coexist in the same asymmetric structure. Thus, in order to enhance the ME effect, piezoelectricmagnetostrictive composites have been exploited. Among some different configurations to prepare composite materials, the core-shell nanoparticles are also investigated as a beneficial starting material for magnetoelectric nanocomposite (MENC) materials. This structure provides direct and large surface contact of phases and preserves the individual piezoelectric and magnetostrictive properties of each phase. Particularly, ferrite-barium titanate in a core-shell configuration has been investigated due to appropriate individual (magnetostrictive and piezoelectric) properties of the components at room temperature. In addition, their chemical and mechanical stability and nontoxic properties are also important in applications regarding the environment and biological applications. This work aims to prepare MENC's in a core-shell configuration with a narrow size distribution. A combination of polymeric and citrate methods was used for the MENC's syntheses. MENC's were prepared in the 1:1, 3:2 and 7:3 ($CoFe_2O_4$:$BaTiO_3$) molar ratios, respectively. The structural characterizations of the obtained MENC's were performed by X-ray diffraction and Fourier transform infrared spectroscopy (FTIR). These analyses showed a combination of a cubic $CoFe_2O_4$ and a tetragonal $BaTiO_3$ composite. A core-shell morphology of MENC's was observed by transmission and scanning electron microscopies. The MENC's atomic compositions were confirmed using energy dispersive X-ray spectroscopy. Finally, the ferrimagnetic character of the MENC's was observed in the magnetic characterizations obtained in a vibrating sample magnetometer.

We are thankful to CAPEs, CNPq and FINEP.

[1] L. F. Cotica, et al., Journal of Nano Research, 28 (2014) 131.
[2] L. F. Cotica, et al., Journal of Magnetism and Magnetic Materials, 324 (2011) 559.

Relation between the crystal structure interfaces of NiTi/Co, NiTi/Ni and FeRhPd films with their magnetic behavior

Diana L. Torres[1] and Daniel R. Cornejo[1]
[1] São Paulo University, Physics Institute, São Paulo, SP, Brazil
dianats@if.usp.br

Magnetic control at the nano-scale is interesting for technological applications. Nowadays, several ways to obtain this control have been reported and the development of new materials to improve it is growing up. For instead, it can be observed in ferromagnetic films coupled with materials which show temperature- or field-driven structural phase transition, as well as, ferromagnetic films which show first order phase transitions trough changes in temperature. More specifically, we study the magnetic behavior of the NiTi/Co and NiTi/Ni films through the structural phase transition of the nearly equiatomic NiTi layer. The films have been grown on silicon (100) substrates by DC magnetron sputtering. In this structure, the magnetization of the ferromagnetic layer may be modified through changes in the stress field at the interface, when the structural phase transition in the non-magnetic layer is carried-out. Also, we study FeRhPd films deposited on MgO (001) which show a first magneto-structural phase transition.

All these functional structures are characterized by X-ray diffraction (XRD) and Rutherford backscattering spectrometry (RBS) to obtain the crystal structure and chemical composition respectively. Magnetic measurements as a function of temperature or magnetic field are performed by using a superconducting quantum interference device (SQUID) and a vibrating sample magnetometer (VSM) to study anisotropy behavior, coercivity, magnetic phase transitions, etc. Finally, we expect to use High resolution-TEM analysis to get a more precise relation between the structure in interfaces of the films and their magnetic behavior.

Use of TEM for Metallurgical Engineering research on hydrogen embrittlement

D. Pérez Escobar[1], E. Wallaert[2], L. Duprez[3], K. Verbeken[2], A. Atrens[4], M. Andrade[11] ISI of Metallurgy and Special alloys, CIT Senai – Campus Cetec, Belo Horizonte, MG, Brazil
[2] Department of Materials Science and Engineering UGent, Zwijnaarde, OW, Belgium
[3] ArcelorMittal Global R&D Gent, TechnologiePark 935, Zwijnaarde, OW, Belgium
[4] Materials Science, University of Queensland, Santa Lucia, Qld 4072, Australia
diana.perezescobar@gmail.com (Corresponding Author)

Transmission Electron Microscopy was performed in cast material in order to study the distribution of TiC precipitates in as-cast steels. The study was performed aiming to study the interaction of hydrogen interaction with this precipitates during my doctorate. One paper was published on international journal: *D. Pérez Escobar, E. Wallaert, L. Duprez, K. Verbeken, A. Atrens. Thermal desorption spectroscopy study of the interaction of hydrogen with TiC precipitates. Metals and Materials International 19 (2013) 741-748*

After casting, the steel (containing (0.025 wt%C-0.09%Ti) was annealed in a furnace protected with hydrogen atmosphere at temperatures between 550 °C and 800 °C in order to produce different ranges of precipitate sizes. Each sample of cold rolled steel sheet was heated in a furnace at 200 °C/h to an annealing temperature of 550 °C, 650 °C, 725 °C or 800 °C; held 2660 min at the annealing temperature; and cooled to room temperature. 100 precipitates in carbon replicas were analyzed using TEM to determine the size distribution of the precipitates and by energy dispersive X-ray analysis (EDX) in order to determine the chemical composition. To prepare the carbon replicas, each sample was polished to 1 µm to a mirror polish, etched for 10 s with 10% nital, washed with methanol, dried with compressed air, a carbon film was deposited on the surface in a carbon evaporator in vacuum, and the sample with the carbon layer was submerged in 4% nital until the carbon replica peeled off the steel surface. Using a Cu TEM-grid and tweezers, the carbon replica was washed in methanol for ~10 min.

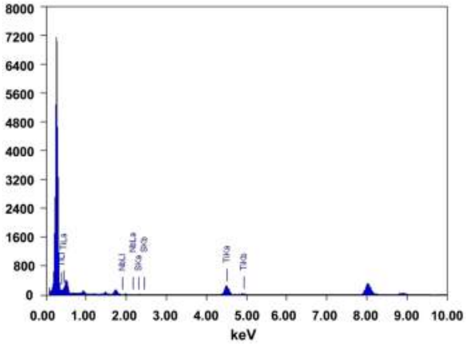


Fig. 3. Typical EDX chemical analysis of a TiC particle in a carbon replica.

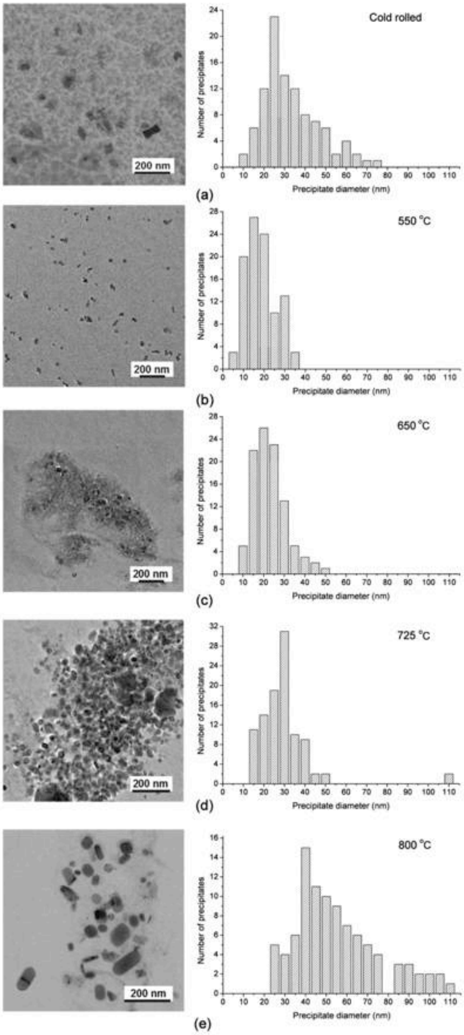


Fig. 2. Typical appearance of the TiC precipitates in the carbon replicas, and the TiC size distribution in the steel (a) cold rolled, and after annealing at (b) 550 °C, (c) 650 °C, (d) 725 °C, and (e) 800 °C.

The authors would like to thank the technical staff at the department of Material Science and Engineering at UGent and OCAS, where the TEM samples were prepared and analyzed.

[1] D. Pérez Escobar, E. Wallaert, L. Duprez, K. Verbeken, A. Atrens. Thermal desorption spectroscopy study of the interaction of hydrogen with TiC precipitates. Metals and Materials International 19 (2013) 741-748.

ZnO Semiconductor Nanowires Gas Sensors

E.S.H. de Menezes[1]*, C. L. Sombrio[1], B.Canto[1], R. Reis[2] and D. L. Baptista[1],
[1]Instituto de Física, UFRGS, Porto Alegre, Rio Grande do Sul, Brazil
[2]National Center for Electron Microscopy, Berkeley, California,USA
eduardoserralta@hotmail.com

Zinc Oxide nanowires have a good potential for fast and selective gas sensing applications [1-4]. When in contact with a small gas concentration the nanowire electrical resistance changes drastically. Therefore it is possible to use such behavior to detect very low gas concentrations through a nanowire-based sensing device. Additionally, the nanowire surface can be modified to change the sensor selectivity. The purpose of this project is to develop different gas sensing devices and characterize the electrical response to different gases. The electrical behavior of the nanowire is related to the lattice structure and defect characteristics. In this work, we present the project perspectives and techniques that will be applied to develop nanowire-based gas sensors. Previous as-grown ZnO nanowires samples were characterized using advanced electron microscopy (FEG-SEM, HRTEM, HAADF-STEM) and spectrum-imaging (EDX, EELS) techniques (Fig 1-2). The determination of growth polarity was also achieved by CBED analysis. HRTEM/STEM analyses were performed using a XFEG Cs-corrected FEI Titan 80/300 microscope.. The ZnO nanowires were grown by vapor-liquid-solid (VLS) mechanism using sapphire as substrate and Au as catalyst. Dense and vertically aligned ZnO nanowires forest was grown epitaxially on sapphire substrates as showed in Fig. 1 (a). The nanowires were about 50 nm in diameter and its length up to 5 μm. A spatial distribution of Au catalyst nanoparticles at the ZnO/substrate interface is clearly observed in Fig. 1 (b) by HAADF-STEM and EDX-SI. The experimental and simulated CBED patterns presented in Fig. 1 (c-d) indicate a Zn-polar growth (e). New samples with different growth conditions will be synthesized and electron microscopy will be utilized to characterize it.

[1] P. Yang et al., Adv. Funct. Mater., 12 (2002) 323.
[2] M.-T. Chen et al., Nano Lett., 10 (2010) 4387.
[3] C. Soci et al., Nano Lett., 7 (2007) 1003.
[4] A. Janotti et al., Phys. Rev. B, 76 (2007) 165202.

The authors thanks the Materials Metrology Division (DIMAT) for the use of Electron Microscopy facilities at INMETRO. This work was partially supported by Brazilian agencies CNPq and CAPES

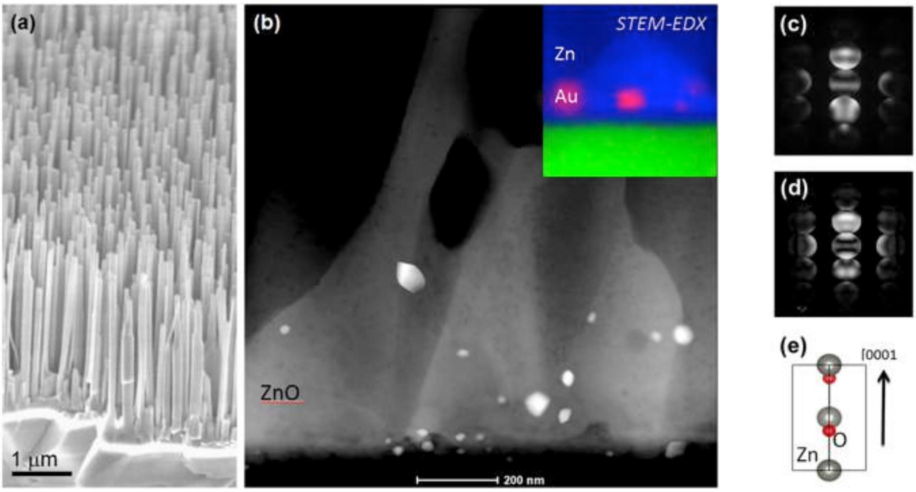


Fig. 1. Characterization of the as-grown ZnO nanowires. (a) SEM micrograph of an epitaxially grown ZnO forest on c-plane sapphire substrate. (b) HAADF-STEM image of the ZnO/substrate interface and an EDX spectrum image showing the presence of Au seeds at the base of nanowires. (c) Experimental and (d) simulated CBED patterns indicating the Zn-polarity (e) of the ZnO structure.

Synthesis and characterization of Ni supported on Nb_2O_5 catalyst to apply in cellulose conversion reaction

Glauco F. Leal[1,2], Dean H. Barret[1], Silvia F. Moya[1],
Antonio A. S. Curvelo[2,3], Cristiane B. Rodella[1].
[1] Brazilian Synchrotron Light Laboratory (LNLS), Brazilian Center for Research in Energy and Materials (CNPEM), Campinas, São Paulo, Brazil.
[2] Institute of Chemistry of São Carlos (IQSC), University of São Paulo (USP), Departament of Physical Chemistry, São Carlos, São Paulo, Brazil
[3] Brazilian Bioethanol Science and Technology Laboratory (CTBE), Brazilian Center for Research in Energy and Materials (CNPEM), 13083-970, Campinas, São Paulo, Brazil.
glaucoferro@gmail.com

The catalytic conversion of cellulose to biofuels and other value added chemicals is one of the most promising routes for the development of economically viable biorefineries. However, the challenge of developing green chemical methods for renewable energy generation based on heterogeneous catalysis relies on a thorough investigation of the physical and chemical properties of the catalyst [1]. Moreover, the correlation of these properties to the functional behavior of the catalyst within the cellulose valorization reaction. Cellulose processing firstly requires hydrolysis to obtain glucose followed by the transformed of glucose to fuels and chemicals [2, 3]. Thus, this PhD project aims to synthesize a new class of bifunctional catalysts composed of Ni and Co dispersed on Nb_2O_5 for cellulose conversion to obtain platform chemicals such as, sorbitol, HMF and levulinic acid among other products. Solid acid catalysts, such as Nb_2O_5 can be effective for cellulose hydrolysis. On the other hand, transition metals, such as Ni and Co are catalysts for hydrogenation and hydrogenolysis reactions. The structural, electronic, surface and textural properties will be investigated using *ex situ* and *in situ* synchrotron-based techniques (XRD and XAS) as well as N_2 physisorption and XPS. Acidic properties of the catalysts will be analyzed by TPD – NH_3 and FT-IR using adsorbed pyridine. Physical and chemical characteristics of the catalyst will be correlated with the catalytic performance. It is clear that transmission microscopy is a fundamental technique to study heterogeneous catalysts and it will not be different in this PhD project. TEM will be a powerful technique to investigate morphology, particle size and distribution of the Co, Ni and Nb_2O_5 from the preparation steps to the post catalytic reaction. These results will be correlated with XRD, XAS and XPS as well as catalytic properties. This will be a step forward in understanding and optimizing the catalyst and reaction parameters to improve specific product yields.

The authors are grateful for the CNPq scholarship and the financial support from the LNLS/CNPEM as well as from IQSC-USP-São Carlos, LNLS and CTBE and to their staff.

[1] R. Rinaldi, F. Schüth, ChemSusChem. 2, 1096-1107 (2009).
[2] I. Nowak, M. Ziolek, Chem. Rev. 99, 3603-3624 (1999).
[3] D. M. Alonso, J. Q. Bond, J. A. Dumesic, Green Chem. 12, 1493-1513 (2010).

Bacterial Nanosensor Based in Gold Nanoparticles

J. P. Oliveira1, A. R. Prado[2], R.H.A. Pereira[1], D.M. Ferreira[1], W.J.Keijok[1], R. Schuenck[3] M.J. Pontes2, M.R.N. Ribeiro2, B.V. Nogueira1, M. C. C. Guimarães[1*]
Laboratório Ultraestrutura Celular Carlos Alberto Redins - LUCCAR, Departamento de Morfologia, CCS, Universidade Federal do Espírito Santo, Vitória – ES, Brasil
Laboratório de Telecomunicação, Departamento de Engenharia Elétrica, Centro Tecnológico, Universidade Federal do Espírito Santo, Vitória – ES, Brasil
Laboratório de Microbiologia, Departamento de Patologia, Centro de Ciências da Saúde, Universidade Federal do Espírito Santo, Vitória – ES, Brasil
* marco.guimaraes@ufes.br

Recently, advances in nanotechnology have brought new perspectives and had been stimulate different areas of research. In perspective, metal nanoparticles due to optical, electronic and magnetic properties has allowed a wide variety of application such as nanosensors, drug delivery system, lubricants, solar cells, catalysis and others [1]. A novel and sensitive colorimetric method to detect Escherichia coli was developed as a model for Gram-negative bacteria by a trypsin modified gold nanoparticles (AuNP's) sensor. Trypsin (Sigma Aldrich) molecule bound with E. coli via adhesion between positive and negative electricity of trypsin and E. coli respectively. AuNP's with different sizes were prepared by reduction and simultaneous stabilization with trisodium citrate. Tetrachloroauric acid (HAuCl4, Merk) was used as precursor of AuNP's and the dihydrate of trisodium citrate (Na3C6H5O7•2H2O, Merck) as reducing agent. All glassware and equipment were cleaned with a solution of aqua regia (HCl:HNO3 = 3:1) and washed with ultrapure water. To prepare AuNP's, the trisodium citrate was added to gold precursor solution at 100ºC. The solution was kept under stirring by the time determined by the experimental design [2]. Samples were collected immediately after synthesis and their optical properties were evaluated by UV-vis spectrophotometry (FEMTO 800 XI). The size and morphology were examined by transmission electron microscope (JEM-1400, JEOL, USA). After simple mixing of the trypsin and AuNP's solution the average diameter is 20 nm under enzyme friendly conditions (pH 8.0). The interaction between trypsin and AuNPs was quantified by measuring the absorbance at 280 nm [3] (Figure 1). Upon addition of increasing concentration of E. coli, as discussed above, an increase in the extinction in 625 nm region along with the concomitant decrease in the intensity of adsorption peak at 520 nm was observed. Besides the spectroscopy UV - visible, the electron microscopy images showed changes in the size of nanopaticulas and interactions of nanoparticles with bacteria (Figures 2 and 3). This bioassay was efficient and promising for bacteria detection.

[1] M.-C. Daniel, D. Astruc. Chem. Rev., 104 (1) (2004), pp. 293–346
[2] Oliveira et al. BMC Proceedings 2014, 8(Suppl 4):P249.
[3] Hinterwirth H1, Lindner W, Lämmerhofer M. Anal Chim Acta. 2012 Jul 6;733:90-7.

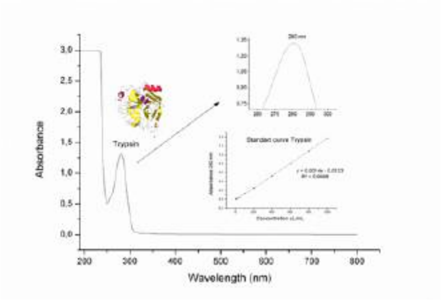


Figure 1 - UV-Vis spectrum and standart curve of trypsin

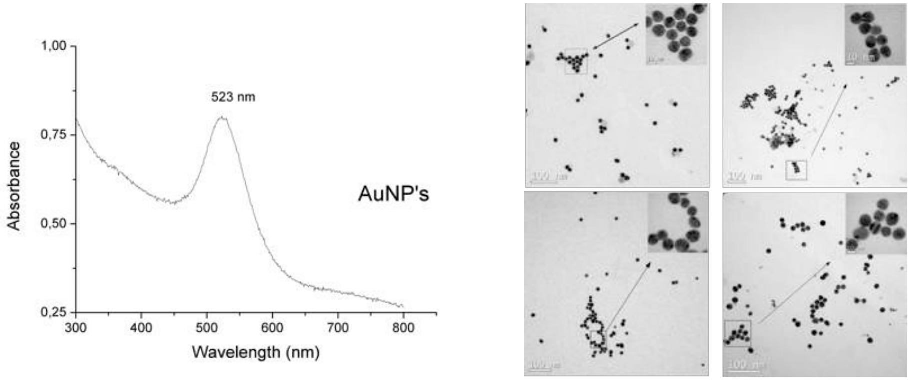


Figura 2: UV-Vis spectrum of gold nanoparticles (A) and images of AuNP's by TEM (120KV) (B,C,D,E).

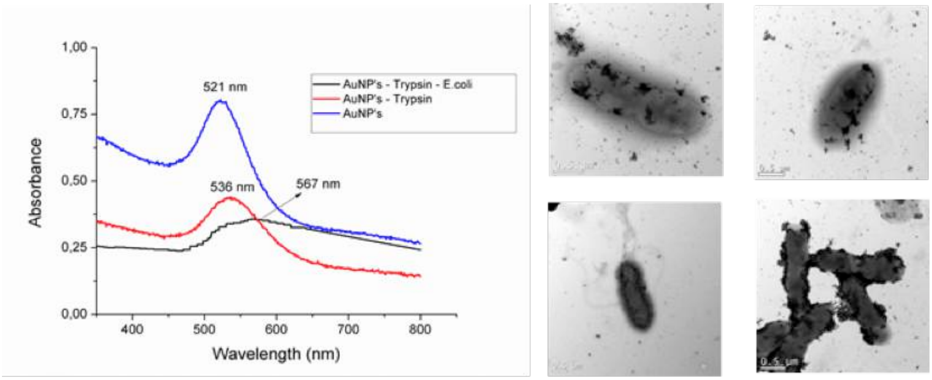


Figura 3: UV-Vis spectrum of gold nanoparticles, with trypsin and trypsin – E.coli (A) and images of nanoparticles complex with E. coli by TEM (120KV) (B,C,D,E).

Study of the influence of organic ligands on the catalytic activity of metal nanoparticles

Jhonatan Luiz Fiorio[1], Fernanda Parra da Silva[1], Liane Márcia Rossi[1].
[1] Instituto de Química USP, Av. Prof. Lineu Prestes 748, São Paulo, 05508-000, SP, Brasil (11)30919143
lrossi@iq.usp.br

Preformed palladium NPs were immobilized on the functionalized magnetic support (˜30 nm silica spheres, Figure 1 a,b) by coordination capture method. [1,2,3] The catalyst contains 1% wt% of Pd, as determined by atomic absorption analysis (ICP OES). The sizes of the supported Pd NPs were determined using a transmission electron microscopy (TEM). The Pd NPs (Figure 1 c,d) demonstrated a mean diameter of 3,05 ± 1,46 nm (Pd/Fe_3O_4@SiO_2triamine). In order to study the catalytic activity after the removal of the organic groups, the catalyst were calcined (Figure 1 e,f) at 400 ºC by 2 hours (Pd-TT/F_3O_4@SiO_2triamine). Transmission electron microscopy analysis demonstrated a mean diameter of 4,21 ± 1,64 nm.
The catalytic activity of the Pd catalysts was investigated in the hydrogenation of cyclohexene in solventless conditions. A strong influence of the functional group on the catalytic behavior of the Pd catalyst was observed. The turnover frequency (TOF), for the catalyst functionalized with diethylenetriamine was 7051,86 h^{-1} (Figure 2). After calcination, to remove the organic ligand, the catalytic rate was improved (13534,22 h^{-1}). Both catalysts, synthetized in this work, were reused in 15 successive runs, and the catalytic activity decreased as the catalysts were reused in successive reactions. These results show that the diethylenetriamine grafted on the magnetite surfaces has a strong deactivating effect on the catalytic activity of the Pd NPs when compared with amine groups or ethylenediamine, reported elsewhere.[4,5] The catalyst was calcined its catalytic activity was improved. However calcination causes growth in the nanoparticles.
In summary, we have prepared a magnetically recoverable Pd nanocatalyst with a strong metal-support interaction promoted by ligands grafted on the support surface. The catalytic activity in hydrogenation of olefins was strongly influenced by the organoalkoxysilane present, and the metal-support interaction will be investigated in more detail.

The authors gratefully acknowledge support from FAPESP, CNPq and CAPES.

[1] Jacinto, M. J. et al. M. Appl. Catal. A Gen. 2008, 338, 52.
[2] Rossi, L. M. et al. Appl. Catal. A Gen. 2007, 330, 139.
[3] Silva, T. A. G. et al. Catal. Sci. Technol. 2013, 3, 2993.
[4] Rossi, L. M. et al. Inorg. Chem. 2009, 48, 4640.
[5] Silva, F. P. da et al. Tetrahedron 2013, 70, 3314.

Figure 1. *TEM images of: a) Fe_3O_4@SiO_2triamine, c) Pd/Fe_3O_4@SiO_2triamine and e) Pd-TT/F_3O_4@SiO_2triamine; histogram showing particle size distribution of: b) Fe_3O_4@SiO_2triamine, d) Pd/Fe_3O_4@SiO_2triamine and f) Pd-TT/F_3O_4@SiO_2triamine.*

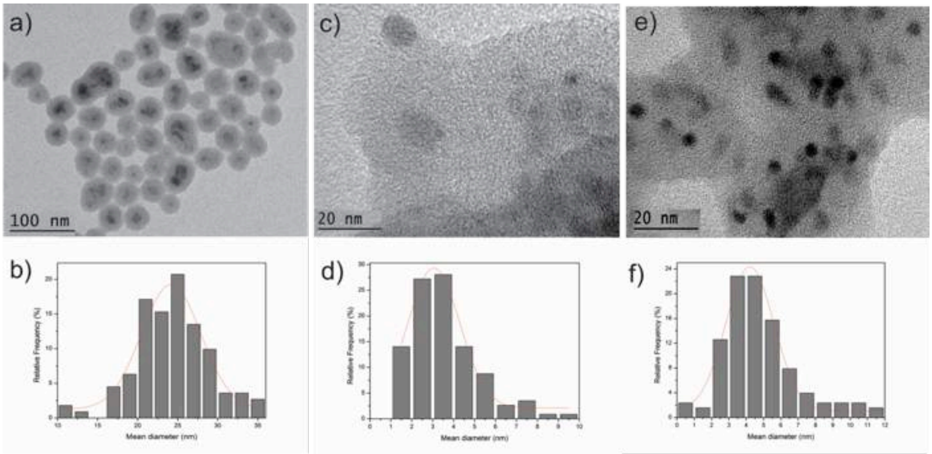
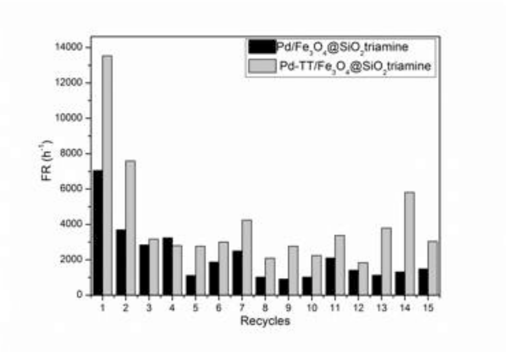


Figure 2. *Catalyst recycling in the hydrogenation of cyclohexene. Conditions: 6 atm H_2, 75 °C, 17,5 mmol of cyclohexene and 50 mg of supported catalyst (2500 mol of substrate/mol of catalyst).*



Brittle behavior of friction stirred welded joints in pipeline steel API-5L-X80

Julián Arnaldo Ávila Díaz[1,2,], Andre Paulo Tschiptschin[2,3], Antonio José Ramirez[1,2,4].*
[1] School of Mechanical Engineering, University of Campinas, Campinas, Sao Paulo, Brazil
[2] Brazilian Nanotechnology National Laboratory, Campinas, Sao Paulo, Brazil
[3] Polytechnic School, University of São Paulo, Sao Paulo, Brazil.
[4] The Ohio State University, Columbus, Ohio, USA
**Corresponding author:* julian.diaz@lnnano.cnpem.br.

The fracture toughness of friction-stirred welded (FSW) joints at the temperature range of 0 C to -40 °C is a critical issue for decisions about its application in API-5L-X80 steels; however, brittle fracture behavior of FSW weldments at -20 °C has been reported [1,2]. Previous results from the microstructural characterization of FSW joints have been shown in Figure 1 [3]. The brittle behavior was associated with crack initiation at the second dispersed phases (martensite-austenite microconstituent –M-A) and (TiNb)(C,N)-type inclusions [1]. In addition, the same mechanism involving M-A particles has been associated with brittle fracture initiation and crack propagation in the coarse-grained heat affected zone of arc welding joints [4–5]. However, these microstructural features do not completely explain the brittle behavior within the stirred and hard zones of friction stir welded joints, overall, arc-welded and FSW microstructures within the joint are dissimilar, although they both have the suspect M-A microconstituent and Ti-N inclusions.

The aim of the present proposal is a deeper microstructural characterization that would pinpoint the key factor that are involved in the reported brittle behavior, more specifically at the stirred and hard zones of FSW welded joints in API-5L-X8 steel, see Figure 1. The focus of this proposal is the determination of the crystal structure, distribution, shape and hardness of the different elements belonging to the bainitic matrix and second dispersed phases over those critical regions. Therefore, transmission electron microscopy (TEM) is the most suitable characterization technique for this proposal.

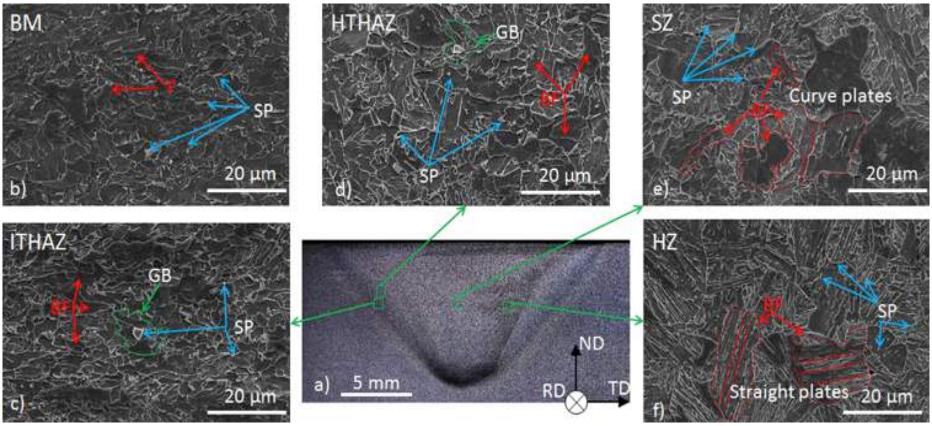


Figure 1: Microstructures of different regions within the friction stirred welded joints: a) Cross section Macro photo of the joint, microstructure of b) BM, Base material; c) ITHAZ, intermediate temperature HAZ; d) HTHAZ, high temperature HAZ; e) SZ, stirred zone and f) HZ, hard zone Etched with Nital 2%. Abreviation: F, ferrite; BF, bainitic ferrite; GB, granular bainite and SP, secondary phases. The arrows indicate the position of some specific microstructure.

FSW, API 5L X80 steel, brittle fracture, welded joints, TEM

The authors would like to acknowledge the financial support of Colciencias by the scholarship No. 512 from 2010. We would like to thank the following institutions: Petrobras and LNNano/CNPEM for providing economic funding and laboratory facilities where this work will be developed; TenarisConfab for the materials donation.

[1] Fairchild D.P. et al., Trends Weld. Res. 9th Int. Conf., 193–200, 2012.
[2] Ávila, J.A.D., Eng. Fract. Mech., October, 147, 176–186, 2015.
[3] Ávila, J.A.D et al., E., Metall. Mater. Trans. A, submitting, xx-xx, 20xx.
[4] Mohseni P., University of Science and Technology, PhD thesis, 2012.
[5] Fairchild D.P., ASTM STP 1058, 117–141, 1990.

Development of nanostructured lipid carriers containing a phenolic monoterpene as an alternative to leishmaniasis treatment

Juliana G. Galvão[1], Raquel L. Santos[1], Tainara Santos[1], Silvio S. Dolabella[2], Rogéria S. Nunes[1]
[1] [1]Pharmacy Department, Federal University of Sergipe, São Cristóvão, Sergipe, Brazil
[2]Morphology Department, Federal University of Sergipe, São Cristóvão, Sergipe, Brazil
Corresponding Author: julianaggalvao@gmail.com

Leishmaniasis consists in a neglected infectious disease caused by protozoa of the genus *Leishmania* in the family Trypanosomatidae. It is estimated that occurs 1.3 million new cases and 20,000 to 30,000 deaths every year in the world. Since the control of insect vector is difficult and no effective vaccine exists, chemotherapy is the main means of dealing with this disease. In the past 70 years, pentavalent antimonials, amphotericin B and miltefosine have been used as gold standard treatment of leishmaniasis. However, the leishmaniasis conventional treatment presents some undesirable adverse effects such as gastrointestinal disorders, kidney and liver toxicity. Since these drugs are too expensive and Leishmania species have been demonstrated resistance against these drugs, natural products can provide an important alternative to leishmaniasis treatment. A phenolic monoterpene (natural product obtained from essential oils) has been recently reported as a potent leishmanicidal agent. Furthermore, some studies also have been reported the use of nanostructured lipid carriers as drug delivery systems of leishmanicidal drugs. Thus, the aim of this project focuses on the development of Nanostructured Lipid Carriers (NLCs) containing a phenolic monoterpene as an alternative leishmaniasis treatment. Firstly, the NLCs with and without monoterpene will be obtained by solvent diffusion method and evaluated for particle size, polidispersity index, zeta potential. NLCs were characterized by DSC, XRD and Transmission electron microscopy (TEM) as well. Moreover, the analytical methodology for quantify the monoterpene by high performance liquid chromatography (HPLC/UV) will be validated. Afterwards, it will be determined the encapsulation efficiency and *in vitro* release profile of the drug from the NLCs. Finally, it will be performed the cytotoxicity assay, promastigote viability, as well as, antiamastigote activity evaluation.

The authors acknowledge CAPES and CNPq for supporting funds.

[1] WHO. Leishmaniasis Fact Sheet N° 375 Updated February 2015.
[2] TIUMAN et al., International Journal of Infectious Diseases, 15, 525-532 (2011).
[3] PASTOR et al., Acta Tropica, 145, 31-38 (2015).
[4] DOMINGO et al. Analytica Chimica Acta, 744, p. 8–22 (2012).

Development and application of high-resolution imaging techniques for morphological characterization of microfossils

Lara Maldanis[1,2], Douglas Galante[1]
[1] Brazilian Synchrotron Light Laboratory, CNPEM, Campinas, SP, Brazil
[2]São Carlos Institute of Physics, University of São Paulo, São Carlos, SP, Brazil
lara.maldanis@lnls.br

Microfossils are the most ancient morphological life traces on earth. Their affinity, otherwise, are quite disputed because of the difficulty on identifying biogenic structures in very processed and billion years old rocks[1,2]. A deep understanding and the ability of characterize the first known life forms of the planet are a crucial step for the systematic search of life in other places within the universe. Imaging techniques are non-destructive and largely applied approaches in fossil characterization, and can provide valuable information of internal structures. Particularly in the case of microfossils, sub-micrometric resolution is required for the identification of cellular structures, that can help to attest biogenicity and to identify and differentiate prokaryotes and eukaryotes. In this project we focus in developing and applying high resolution imaging techniques to microfossils, including HRTEM, micro-CT and ptychography. HRTEM has already been applied in fossil studies, showing that it is a powerful approach in paleontological studies[3,4]. Our objective is to make a systematic study with different sample preparations, and to analyze the capability of these different techniques to resolve intracellular structures in microfossils. Data treatment and filters development will be performed for each case, aiming to maximize the resolution and contrast of intracellular features. Increasing the quality of imaging information of microfossils in non-destructive ways, we expect with this work to contribute to the astrobiological and paleontological community, through stablishing feasible methodologies that could contribute to the biogenicity problem of the oldest presumed fossils of earth, besides to allow a better classification of eukaryotes and prokaryotes samples.

Schopf, J. W. Science 260, 640–646 (1993).
Brasier, M. D. et al. Nature 416, 76–81 (2002).
Wacey, D., et al. Nature Geoscience. 4, 698-702 (2011).
Cady, S. L., et al. Astrobiology 3, 351-368 (2003).

Facile Approach to Preparation of Optical and Magnetic Nanocomposites Containing $Fe_3O_4@SiO_2$ Grafted with Rare Earth Complexes

Latif U. Khan[1], Diego Muraca[2], Hermi F. Brito[1], Kleber R. Pirota[2]

[1]University of Sao Paulo, Institute of Chemistry, Department of Fundamental Chemistry, Av. Prof. Lineu Prestes, 748, 05508-000, São Paulo-SP, Brazil.
[2]Institute of Physics “Gleb Wataghin” Condensed Matter Physics Department, State University of Campinas (UNICAMP), 13083-859 Campinas-SP, Brazil.
E-mail: latifkhn@iq.usp.br

The fabrication of bifunctional nanocomposites, co-assembling two different photonic (RE^{3+}) and magnetic (Fe_3O_4) features into single entity nanostructures is reported. Their preparation is accessible through a facile method of multistep syntheses, using Fe_3O_4 as core nanoparticles, which were coated with SiO_2 shell and further grafted with Eu^{3+} and Tb^{3+} complexes. The sophisticated structural features and morphologies of the core-shell $Fe_3O_4@SiO_2$-(TTA-RE-L) nanomaterials (Figure 1) containing aggregation of Fe_3O_4 core nanoparticles were studied by Small-angle X-ray Scattering (SAXS). The core mean size ΔR , shell thickness ΔR, cluster size ξ and fractal dimension D_F were determined by fitting the experimental SAXS data, corroborating through Transmission Electron Microscopy (TEM) images (Figure 2). The DC magnetic properties at temperatures of 2 and 300 K were explored in support to the structural conclusions from SAXS and TEM analyses, and investigated the influence of SiO_2 coating and RE^{3+} complexes on the M-H and ZFC/FC magnetization curves. The paramagnetic contributions of the RE^{3+} ions to the whole magnetizations of the Eu^{3+} and Tb^{3+} nanocomposites were also discussed. The photoluminescence properties of the Eu^{3+} and Tb^{3+} nanocomposites based on the emission spectral data and luminescence decay curves were studied. The experimental intensity parameters (W_λ), lifetimes (t), emission quantum efficiencies (h) as well as radiative (A_{rad}) and non-radiative (A_{nrad}) decay rates were calculated and discussed.

The authors are grateful for financial support from the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES, Brazil), Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq, Brazil), Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP, Brazil), Instituto Nacional de Ciência e Tecnologia de Nanotecnologia para Marcadores Integrados (inct-INAMI, Brazil), CNPEM-LNLS synchrotron, Campinas-SP, Brazil under Proposal Nos. SAXS1−14355 (7959), CNPEM-LNNano, Campinas-SP, Brazil under Proposal Nos. TEM-MSC 14828 (7959).

[1] Khan, L. U. etal. Inorg. Chem. 2014, 53, 12902–12910.
[2] Bünzli, J.-C. G. Coord. Chem. Rev. 2015, 293-294, 19–47.
[3] Guinier, A.; Fournet, G. Small-angle scattering of X-rays. New York: John Wiley & Sons, Inc. 1955.

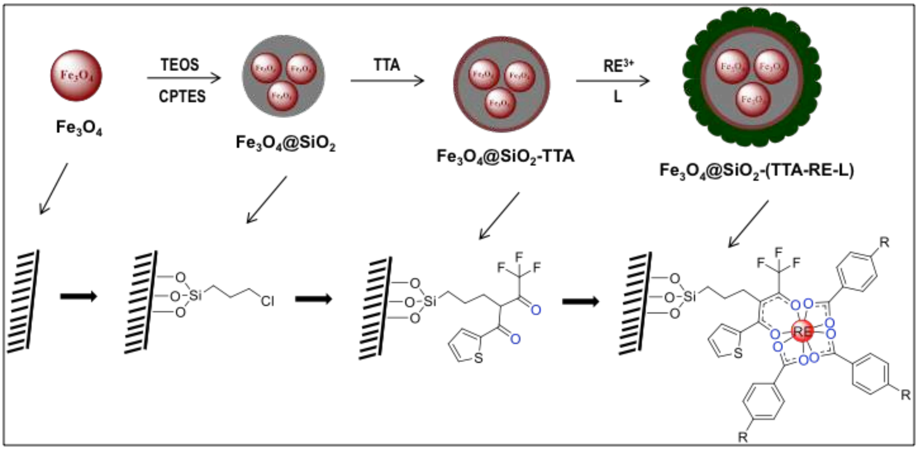


Figure 1. Preparation route of magnetic and luminescent nanocomposites; including synthesis of $Fe_3O_4@SiO_2$ nanoparticles, chemical modification with TTA and further syntheses of RE^{3+} complexes on the surface of $Fe_3O_4@SiO_2$-TTA nanostructures - $Fe_3O_4@SiO_2$-(TTA-RE-L).

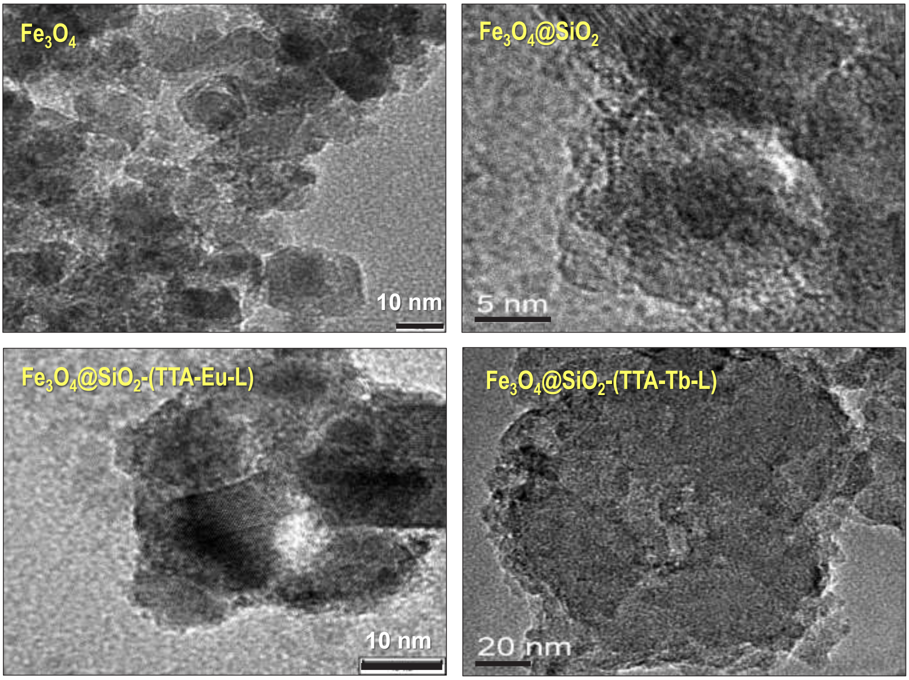


Figure 2. TEM and High-resolution TEM images (clockwise from top left) of Fe_3O_4, $Fe_3O_4@SiO_2$, $Fe_3O_4@SiO_2$-(TTA-Eu-L) and $Fe_3O_4@SiO_2$-(TTA-Tb-L) nanomaterials.

Study of the alpha phase precipitation mechanisms on pseudospinodal decomposition and classic nucleation in Ti alloys

Mariana G. Mello[1], Rubens Caram[1]
[1] University of Campinas, Campinas, São Paulo, Brazil
marianagm@fem.unicamp.br

The increase in life expectancy and the always necessary healthcare improvements attach great importance to the development of biomaterials. Ti alloys containing β stabilizing elements are prone to be used as biomaterials due to their high specific strength, high corrosion resistance, unusual biocompatibility and low elastic modulus, which is very beneficial to the bone tissues near the implant. This is a study regarding the phase stability in β Ti-Mo-Sn, Ti-Mo-Fe and Ti-Mo-Al alloys processed under different conditions and was carried out through the following steps: study of the effect of third element alloy content (a) on the phase stability in Ti-Mo alloys, (b) on the suppression of α'' and ω phases precipitation; (c) on the precipitation of α phase during aging heat treatments and (d) on the mechanical properties via tensile tests and measurement of the elastic modulus using acoustic techniques. The alloys were prepared by arc melting under controlled atmosphere followed by homogenization heat treatment and hot rolling. Optical microscopy, scanning electron microscopy, X-ray diffraction and differential scanning calorimetry were employed for characterization purposes. Samples were also submitted to solution treatment above β-transus temperature and aging heat treatments under controlled atmosphere. Aiming to understand the influence of the addition of the third alloy element on α phase nucleation in Ti-Mo alloys, TEM techniques have great importance. The α phase precipitation is, in general, very fine laths in β phase matrix, with ω phase precipitates as nucleation sites [1, 2]. TEM can be used for identify the nucleation sites for α phase, consequently, its mechanism. Thus, bright and dark filed can be carried out for concluding the orientation and morphology of the phases. High resolution TEM can be performed to verify the variation of lattice parameters and phase boundaries and STEM/EDS for obtain compositional variations.

The authors are grateful to LME/LNNano/CNPEM for access to the SEM/TEM facilities; the Brazilian research funding agencies FAPESP (State of São Paulo Research Foundation) and CNPq (National Council for Scientific and Technological Development) for their financial support.

[1] Zheng, Y. Nucleation Mechanisms of Refined Alpha Microstructure in Beta Titanium Alloys, 2013, 235p. Dissertation. The Ohio State University.
[2] NAG, S. et al. ω-Assisted nucleation and growth of α precipitates in the Ti–5Al–5Mo–5V–3Cr–0.5 Fe β titanium alloy. Acta Materialia, v. 57, n. 7, p. 2136-2147, 2009.

Surface processing as a tool for planar III-V nanowire direction control

M. Zavarize[1], P. Sahoo[1], D. S. Oliveira[1], S. R. Araújo[2], J. Bettini[2] and M. A. Cottta[1]
[1] State University of Campinas, São Paulo, Brazil.
[2] Brazilian Nanotechnology National Laboratory, São Paulo, Brazil.
marianaz@ifi.unicamp.br

Free-standing, out-of-plane semiconductor nanowires have been extensively investigated in the last decade due to their promising application in electronics and photonics. However, their integration into current device processing technologies still poses a challenge. Planar nanowires, on the other hand, show similar advantages with yet a more straightforward integration capability. For this reason, the efforts to control and characterize planar nanowires have grown in the last few years. In this work we study planar InP nanowires grown by the vapor-liquid-solid method, using Au particles deposited on electron-beam defined arrays as catalysts. Substrate surface treatments such as chemical or low energy plasma etchings and thermal annealing prior to growth were explored as tools in order to control the nanowire growth direction.
Scanning electron microscopy was used for statistical analysis of our samples - nanowire length and direction as well as the number of kinks. Our results show that preferential growth directions can indeed be created, depending on the surface treatment. Moreover, the occurrence of kinks can be suppressed. Electron Energy Loss Spectroscopy and cross-section transmission electron microscopy images show that the thickness of the substrate oxide layer in combination with surface roughness, evidenced from atomic force microscopy analysis, play a major role to determine the nanowire initial growth direction and its meandering along the substrate. The atomic force microscopy analysis also gives information about the nanowire cross-section (whole wire) that can be related to the substrate surface roughness and growth direction. Meanwhile, pinning of the catalyst triple phase line at the surface irregularities may be associated with nanowire kinking.

This research is supported by CNPq (grant #479486/2012-3) and FAPESP (grant #2013/02300-1). M.Z. acknowledges financial support from CNPq.

Production of porous Ti/TiO_2 electrodes for electrochemical devices

Natália de Freitas Daudt[1], Lirio Schaeffer[2], Jocenir Boita[1]
[1] Universidade Federal de Santa Maria, Cachoeira do Sul, RS, Brazil
[2] Universidade Federal do Rio Grande do Sul, Porto Alegre, RS, Brazil

natalia.daudt@ufsm.br (Corresponding Author: Natália de Freitas Daudt)

Global tendency is to replace the actual power source based on fossil fuel for renewable sources like wind and solar energy. Therefore, high performance electrochemical devices for conversion and storage of energy have had a growing application. In this context, batteries as Li-ion battery, has an important role. Recently, several studies have been focused on development of batteries. However, an increased efficiency and better cycles lives of batteries are required. Porous electrodes provide good access of the electrolyte to the electrode, facilitating charge transfer across the electrode/electrolyte interface [1]. The use of nanostructured materials in electrodes enables to increase the amount of active materials, so that capacity can be increased. Titanium due its electrochemical properties is a candidate for application in electrodes [2]. In our research, innovative porous electrodes produced from nanoparticles of titanium have been manufactured by powder metallurgy. On the electrode surface, a thin film of TiO_2 nanotubes will be grown in order to obtain a functional surface layer. Furthermore, a core-shell structure formed by Ti (core) and TiO_2 nanotubes doped with Ta will be obtained for use as catalyst. The size as well as the crystallinity of TiO_2 play an key role in the electrochemical properties of the porous electrodes [3]. Therefore, transmission electron microscopy (with 120 kV) will be applied to analyze the size distribution of TiO_2 nanotubes and TEM (with 200 kV) will be applied to investigate the crystallinity and atomic plane distribution. Nanostructured materials are promising for improving electrochemical devices efficiency. The results will demonstrate the most suitable Ti/TiO_2 structure in function of crystallinity and particle size for use as electrode in batteries.

The authors want to thank the Brazilian agency CNPq, Universidade Federal de Santa Maria – Campus Cachoeira do Sul and and Laboratory of Mechanical Transformation (LdTM) of Universidade Federal do Rio Grande do Sul (UFRGS).

[1] Vu, A. et al., Adv Energy Mater, v. 2, 1056-1085 (2012).
[2] Zhou et al. J Alloys Compounds, v. 597, 1–7, (2014).
[3] Bi, Z. et al., J Power Sources, v. 222, 461-466, (2013).

Size and shape tunable iron oxide with core-shell nanoparticles for magnetic hyperthermia applications

Navadeep Shrivastava[1], Sarveena[2], Diego Muraca[3], Pedro Mendoza Zélis[4], M. Singh[2], and S. K. Sharma[1*]
[1]Departamento de Física, CCET, Universidade Federal do Maranhão, 65085-580 São Luis, Brazil
[2]Department of Physics, H. P. University, Shimla, 171005, HP India
[3]Instituto de Física Gleb Wataghin - Universidade Estadual de Campinas (UNICAMP) 13083-970 São Paulo, Brazil
[4]Departamento de Física, Instituto de Física La Plata CONICET 49 y 115 (1900) La Plata, Argentina
*surender76@gmail.com

The present work describes the size and shape controlled synthesis and ageing effect of iron oxide nanoparticles obtained through thermal decomposition of Fe-precursors in a high boiling point organic solvent. A mixed phase iron oxide nanoparticles with narrow particle size distribution has been observed when the sample annealed in vacuum instead of Argon atmosphere. Further, it has been observed that a controlled oxidation in the presence of Au nanoseeds not only facilitate the self-organization of iron oxide nanoparticles, but also to switch these nanocomposites into core-shell structures. Controlled reaction time and oxidation temperature facilitate a systematic improvement in the core and shell shape. Spherical and spherical triangle shaped core-shell structures have been synthesized at an optimum oxidation temperature of 125°C and 150°C for 30 minutes. However, with the further increase in the oxidizing temperature as well as ageing time fully grown core-shell structures were achieved. Due to its superparamagnetism and biocompatibility as well as multipurpose biomedical potential these are best suited to pharmaceutical and industrial application. The prepared nanoparticles were checked for their utility in hyperthermia applications by measuring their specific absorption rate (SAR) value. The observed SAR values were largely dependent upon the shape anisotropy of the particles. These core shell nanoparticles have been thoroughly characterized using x-ray diffraction (XRD), high-resolution transmission electron microscopy (HR-TEM), Mössbauer spectroscopy and superconducting quantum interference device (SQUID) magnetometer.

The financial support from the FAPEMA is greatly acknowledged.

[1] S. K. Sharma et. al., Unusual magnetic damping effect in a silver–cobalt ferrite hetero nano-system 5, 17117 (2015)

Study of size effects in the magnetic properties of the hollow spheres of Ferrites

Olgi Alcalá[1], Yannick Guari[2], Joulia Larionova[2], Pedro Silva[1]
[1] Laboratorio de Física de la Materia Condensada, Centro de Física, IVIC, Caracas, Venezuela.
[2] Institut Charles Gerhardt - UMR5253, Université Montpellier II, Montpellier, Francia.
oalcala@ivic.gob.ve

In the last years a great interest in magnetic nanoparticles has been showed by different researcher groups around the world due to their interesting optical, electrical and magnetic properties which are different from their bulk counterparts. The hollow spheres are, in this scale, very important due to its high surface area, its low density and its utility as transport medium in the drug delivery. In this work, we study the effect of change the diameter of the spheres of cobalt ferrites to improve its magnetic properties and take advantage of its characteristics as mean of transport, for applications in biomedicine and drug controlled delivery [1].

We synthesized cobalt ferrite hollow spheres with different diameter and wall thickness to observe its magnetic behavior. We obtained cobalt ferrite hollow spheres using the solvothermal method at different time of reaction with the aim of study the time effects on the diameter of the spheres [2]. The figure 1(a and c) shows the images obtained with Transmission Electron Microscopy (TEM) of the cobalt ferrite hollow spheres with its respective histograms, where observed average diameters of 287 and 238nm, respectively. The figure 1(b) show the image obtained with Scanning Electronic Microscopy (SEM) and the size histograms of the cobalt ferrite hollow, an average diameter of 265nm is observed. The table 1 shows a summary with the average diameters and wall thickness for hollow spheres of cobalt ferrites synthesized at different reaction times. The average diameter decreases near linearly with increasing the time of reaction, while the average wall thickness increases near linearly with increasing the time of reaction. The study of the dependence of the magnetic properties as function of the different diameter for hollow spheres of cobalt ferrites will be using of the hysteresis curves obtained with a Vibrating Sample Magnetometer at room temperature and the analysis of spectra obtained with Ferromagnetic Resonance [3].

We thank to FONACIT by fund the project ECOS-Nord N° V13PS01 and the Université Montpellier II by its service of microscopy.

[1] Liu F. et al., Chem. Commun., 51, 2357-2360 (2015).
[2] Peng Hu et al., J. Phys. Chem. C, 113, 900-906 (2009).
[5] Ye Q. L. et al, Materials, 3, 1244-1268 (2009).

Table 1. Average diameters and wall thickness for hollow spheres of cobalt ferrites synthesized to different time of reaction

t_R (h)	12	24	36
$D_{promedio}$(nm)	287	265	238
$WT_{promedio}$(nm)	60	66	75

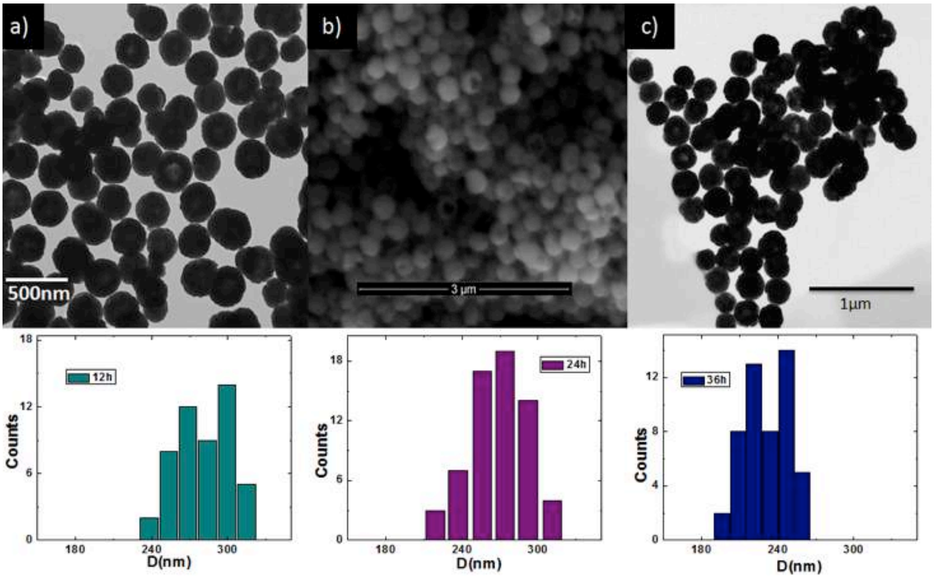


Figura 2. TEM of Cobalt ferrite hollow spheres synthesized to (a)12h, (b) 24h and (c) 36h, with its repective histograms.

Morphological and rheological study on blends of recycled polypropylene/ground tire rubber devulcanized by microwave

Pamela Sierra Garcia[1], Sandra Andrea Cruz[2], Carlos Henrique Scuracchio[3]
[1] Center of Engineering, Modeling and Applied Social Science - Universidade Federal do ABC, Santo André, São Paulo, Brazil
[2] Department of Chemistry - Universidade Federal de São Carlos, São Carlos, São Paulo, Brazil
[3] Department of Materials Engineering - Universidade Federal de São Carlos, São Carlos, São Paulo, Brazil
pamela.s.garcia@gmail.com

This work describes the effect of adding devulcanized tire rubber by microwave into recycled polypropylene (PPr) in order to make the PPr more ductile. For this purpose, the microwave devulcanization method was applied to the scrap ground tire rubber (GTR) to obtain a material able to flow and to be remolded [1]. The GTR samples were submitted to different microwave exposure periods and after that, they were embedded in the matrix formed by PPr. Firstly, the analysis of the rubber showed that long exposure times to microwave made the rubber more fluid due to the breaking of its sulfur cross-links [2], as seen in Figure 1. Mechanical and morphological properties were examined as a function of devulcanized GTR content (15% wt.) into the PPr (85% wt.). The results showed that the long exposure periods interfered positively in the adherence of the rubber with the PPr. Also, the blends composed of the most devulcanized GTR had a finer dispersion (Figure 2) and exhibited high toughness. Although these blends exhibited better results, it is necessary to understand what chemical and physical changes took place at the interface between the rubber and the PPr. So, some analysis will be performed in the LNLS, where the *infrared nanospectroscopy* will be used with the *atomic-force microscopy*. The transmission electron microscopy (TEM) will be an efficient tool to study the interfaces, mainly because this technique provides sufficiently high resolution images. Thus, it will possible to visualize the increase of interfacial width, if the polymer blend presents a good interface adhesion. In order to comprehend the mechanical properties, mainly the toughening mechanisms, it is necessary to use the TEM technique. The TEM micrographs can reveal the internal cavitation of rubber particles and thermoplastic toughening mechanisms, such as multiple crazing, shear-yielding and micro and nanovoids, being that all those mechanisms can only be seen at nanoscale [3-5].

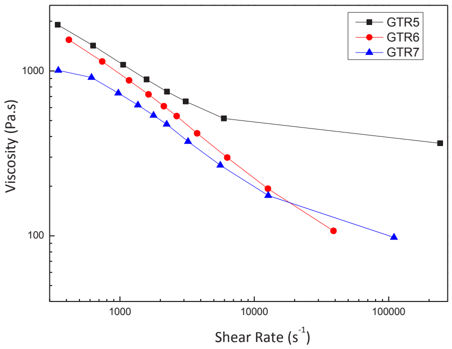


Figure 1. Viscosity versus shear rate for devulcanized samples

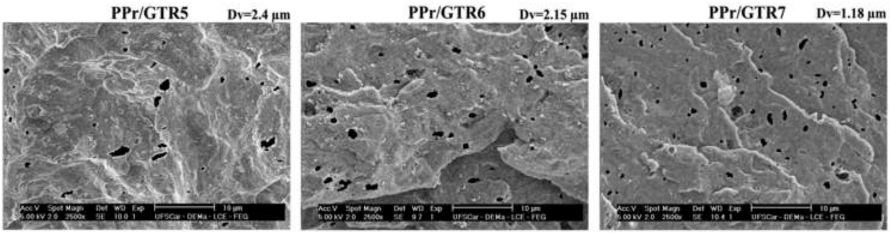

PPr/GTR5 Dv=2.4 µm
PPr/GTR6 Dv=2.15 µm
PPr/GTR7 Dv=1.18 µm

Figure 2. Morphology of blends of PPr/devulcanized GTR and volume average diameter (Dv) of each rubber particle of the different blends studied, where GTR5 represents exposure to microwaves for 5 min; GTR6 for 6 min and GTR7 for 7 min.

The authors are grateful to the Universidade Federal do ABC (UFABC) and Braskem S.A. for financial support and Brazilian Nanotechnology National Laboratory (LNNano) and Brazilian Synchrotron Light Laboratory (LNLS) for assistance in this project.

[1] Karger-Kocsis et al., Journal of Material Science, 48, 1 – 38 (2013).
[2] Garcia et al., Express Polymer Letters, 9, 1015 – 1026 (2015).
[3] Horiuchi et al., Macromolecular Rapid Communications, 28, 915 – 921 (2007).
[4] Song et al., Polymer Journal, *44, 939 – 945 (2012).*
[5] Liu et al., Macromolecules, 43, 6058 – 6066 (2010).

Electrocatalytic activity and stability of platinum nanoparticles supported on carbon/molybdenum oxides for the oxygen reduction reaction

Pedro F. B. D. Martins[1], Edson A. Ticianelli[1]
[1] Department of Physical-chemistry, Instituto de Química de São Carlos, Avenida Trabalhador São-carlense, 400, São Carlos, São Paulo, Brazil
pedrofbdmartins@gmail.com

The degradation of Pt based electrocatalysts used in proton exchange membrane fuel cell (PEMFC) cathodes is one of the main issues that restrict wide PEMFC application as energy converter. This work aims to contribute to the improvement of the stability of platinum nanoparticles (Pt NPs) by modification of the support at which they are anchored. Thus, syntheses of catalyst supports based on MoO_x and carbon were carried out, followed by impregnation with Pt NPs. TEM micrographs for all catalysts before and after the 12,000 cycles of the stability tests are shown in Figure 1. For the as-prepared catalysts, a good distribution homogeneity of the Pt NPs on the supports is clearly seen. Results for the Pt/C and Pt/MoO_3-C catalysts after 12,000 cycles evidence the presence of platinum particles with larger sizes, reflecting the expected NPs agglomeration. For Pt/MoO_2*-C the platinum particles also increased, but in minor extent compared to the others. Also, it is seen that all dispersed catalysts present less Pt particles after ageing, although nothing can be said about the Pt element content, due to the growth of the particles. The histograms in Figure 2 show that initially Pt/MoO_3-C and Pt/MoO_2*-C present homogeneous particle size distributions in a small size range, despite the presence of some agglomerates. After 12,000 cycles, an increase in the particle size range is observed for all electrocatalysts, highlighting a raise in the proportion of bigger particles. The Pt/MoO_3-C catalyst showed the highest specific activity toward the oxygen reduction reaction (ORR), and this must be due to metal/support synergistic effects. Regarding the electrochemical stability of the materials, it is observed that, in principle, none of the Mo oxides really decreases the extent of Pt degradation. However, comparing the specific activities towards the ORR before and after electrochemical ageing, it is concluded that Pt/MoO_2*-C is a more stable material compared to Pt/C and Pt/MoO_3-C.

The authors would like to thank the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), the Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP, project number 2013/16930-7), Brazil.

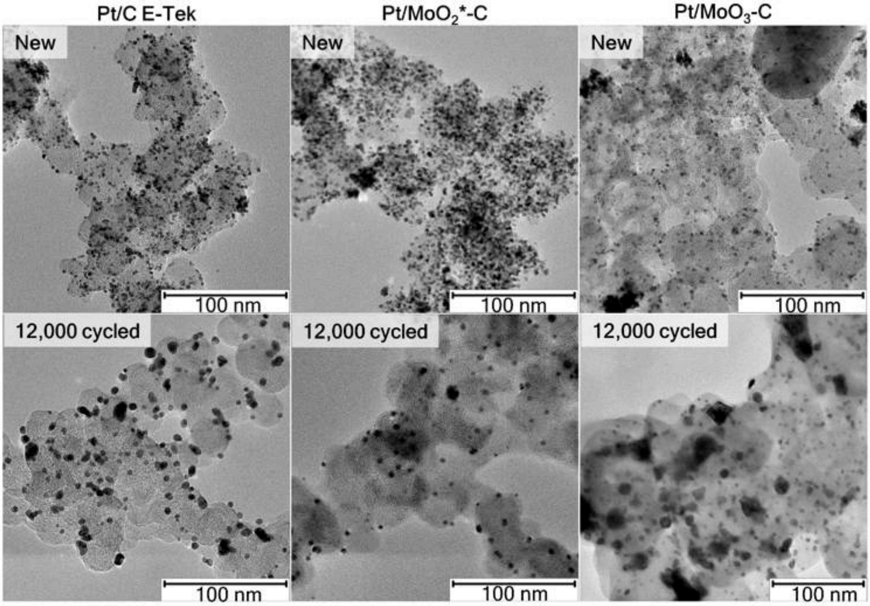


Figure 1. TEM micrographs of each electrocatalyst new and after 12,000 cycles between 0.6 – 1.0 V in 0.5 M H_2SO_4 at ambient temperature in air atmosphere aged.

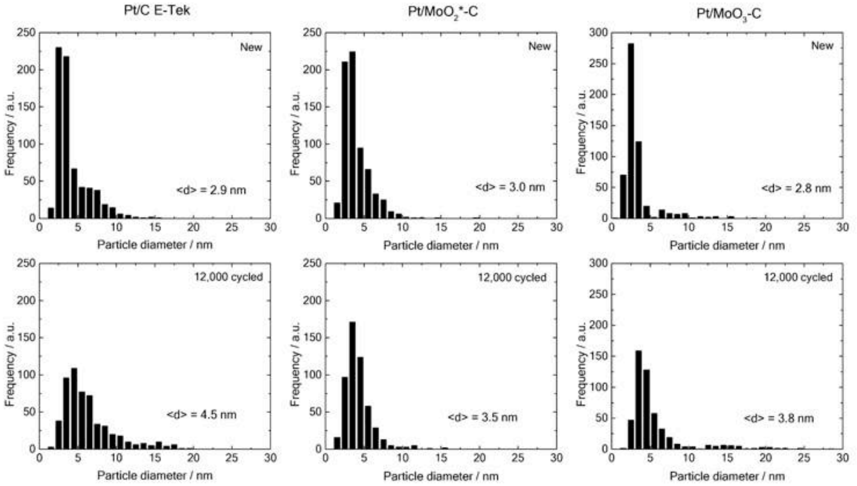


Figure 2. Histograms obtained by TEM micrographs of each electrocatalyst new and after 12,000 cycles between 0.6 – 1.0 V in 0.5 M H_2SO_4 at ambient temperature in air atmosphere aged.

Non-fullerene acceptor based bulk heterojunction solar cells: Morphology analysis using transmission electron microscopy (TEM)

Sivakumar Gangala,[a] Ana Flavia Nogueira*[a]
[a] Institute of Chemistry, University of Campinas, UNICAMP, Campinas, Sao Paulo, Brazil
Corresponding Author: anaflavia@iqm.unicamp.br

Due to their low-cost fabrication by solution processing, lightweight, and compatibility with flexible substrates, bulk hetero-junction polymer solar cells have emerged as potential economical alternatives to silicon-based solar cells. To obtain efficient bulk hetero-junction polymer solar cells, the exciton diffusion lengths in the Donor/Acceptor should be closely related to the scale of phase separation. The morphology can be controlled by many processing parameters during the production and does influence the final cell efficiency.[1] Transmission electron microscopy (TEM) is one of the important tools to have very good idea about the morphology of the organic thin films. To obtain maximum device performance, formation of domain structure with acceptor and donor materials is most important. TEM study can provide us in depth knowledge of the nano structured morphology of the active material in solar cells, which enable to fabricate device with optimize device structures. TEM was used to investigate the phase separation morphology; the digital TEM images will be analyzed by carrying out a spatial Fourier transform of the image intensity to obtain the power spectral density (PSD). PSD has been widely used on digital atomic force microscopy (AFM) images to achieve surface roughness information.[2,3] In this project, we will use spatial Fourier transform and PSD as a method for quantitative analysis of TEM images of the polymer of the BHJ materials used in the fabrication of bulk hetero-junction polymer solar cells.

GSK and AFN thank FAPESP for financial support.

1. D. Veldman et al., JACS, 130, 7721-7735(2008)
2. P. Viville et al., J. Phys. Chem. B, 105, 7499-7507 (2001)
3. S. J. Fang et al., J. Appl. Phys., 82, 5891-5898 (1997)

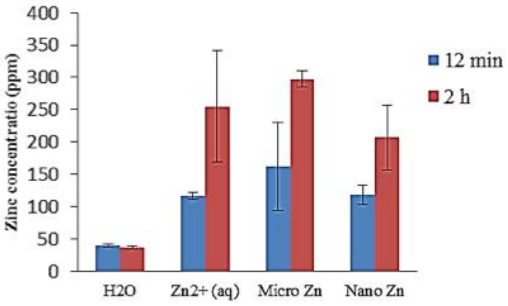
Analysis of the interaction of ZnO nanoparticles with *Phaseolus vulgaris*

Savassa, Susilaine M.[1], Pereira de Carvalho, Hudson W. [1]
[1]Centro de Energia Nuclear na Agricultura – CENA - USP, Piracicaba, São Paulo, Brasil
susisavassa@gmail.com

In recent years has been observed the increasing development of commercial products containing nanomaterials[1,2]. Nevertheless the eco-toxicological implications, assimilation and reactivity of nanomaterials in living organisms are poorly understood[3]. In this context, this project aims at studying the transport, accumulation and chemical transformations undergone by nanomaterials, especially ZnO, absorbed by plants (Phaseolus vulgaris, ie., beans). The absorbed nanomaterials will be quantified and the parameters that govern the absorption, such as particle size, concentration and exposure time of root systems will be evaluated. The plant organs will be mapped by micro X-ray fluorescence, revealing in which specialized tissues nanomaterials are stocked. Morphological analyzes, using techniques like electronic scanning microscopy (SEM) and transmission (TEM), will be performed to observe the plant structures at the nanoscopic level uncovering how ZnO nanoparticles affect the cell morphology. The chemical environment of nanomaterials absorbed will be determined by X-ray absorption spectroscopy. Our recent results show that Zn can be accumulated in seeds, for that we have employed bench top EDXRF. Seeds` germination assays were carried out using the following treatments: Zn^{2+} aqueous solution, 300 nm ZnO and 5 nm ZnO aqueous dispersions. Pristine seeds present Zn content around 40 mg kg^{-1}, whereas seeds treated for 12 minutes showed Zn content ranging from 120 to 160 mg kg^{-1} and those treated for 2 hours presented Zn concentration varying from 225 to 300 mg kg^{-1}. Specifically for the seeds treated with 5 nm ZnO for 2 hours the Zn content was 225 mg kg^{-1}(Fig.1). Although this was the lowest value found, this treatment presented no germination at all(Fig.2). Thus our preliminary results indicate that the 5 nm ZnO particles prevent the seed`s germination. The causes of this effect are under investigation and is one of the main branches of the present PhD project.

To post-graduate program CENA -USP, CAPES for the scholarship , the FAPESP for research support (15 / 05942-0)

[1] Khan F. H., Oriental Journal of Chemistry, 29,1399-1408,(2013).
[2] http://vtu.ac.in/nano-technology/
[3] Klaine, S. J., et al., Environmental Toxicology and Chemistry ,27, 1825-1851, (2008).



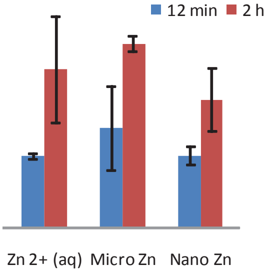


Fig.1: Zinc concentration in seeds. | Fig.2: Effect of Zn on the germination of seeds.

Gold nanoparticle based sensor for early breast cancer detection

Vera Katic[1], Juliano Alves Bonacin[2]

State University of Campinas, UNICAMP, Campinas, State, So Paulo vera.katic@iqm.unicamp.br

Cancer is a disease that alters health status of cells and ultimately leads to malignant tumors. Late detection of disease increases the number of deaths. Therefore, early detection of cancer can save lives [1]. Our objective is to create highly accurate portable device for early breast cancer detection. The portable device (sensor) would be based on the interaction between gold nanoparticles and biomarkers [2]. Biomarker refers to a measurable indication of biological state or condition. Thus, cancer biomarkers are an indication of cancer and via its detection the existence of specific cancer can be verified. One of the most studied breast biomarkers is CA 15-3, located in the blood. Therefore our focus is to create sensitive sensor for CA 15-3 detection. Initially, shape and size controllable gold nanoparticles will be obtained utilizing photoinduced methods. The following steps will include detailed characterization of aforementioned systems via spectroscopy and electron microscopy. Nanoparticles will be characterized with transmission electron microscopy (TEM) in order to investigate morphological, crystallographic and elemental composition. The final step will be focused on the development of electrochemical and plasmonic sensors.

Thanks to LNNano - Laboratório Nacional de Nanotecnologia CNPEM - Centro Nacional de Pesquisa em Energia e Materiais Campinas - SP – Brasil and CNPq grant number (161819/2014-1)

[1] T. N. Seyfried et al. Carcinogenesis, 35, 515-527, 2014
[2] Li et al. Biosensor and Bioelectronics, 43, 25-29, 2013

Mechanical and microstructural characterization of steels Ultra – High- Strength Thermally and Thermochemically Treated by plasma.

Y. O. Iwaki[1], A. S. M. Cardoso[2], D.Y. K. Ranzini[3]
[1] Centro Tecnológico da Marinha em São Paulo - CTMSP, Iperó, SP, Brazil
[2, 3] Centro Tecnológico da Marinha em São Paulo - CTMSP, São Paulo, SP, Brazil yurika.iwaki@ctmsp.mar.mil.br

The high strength steel with low alloy and ultra-high strength steel are materials with great industrial application, in which its technology enables strategic innovation. The understanding of the medium carbon steel composition modification SAE 4340 [1] enabled the purchase of the 300M Stainless steel, although in the development application of rocket and energy areas, the Maraging 300 steels were also correlated. To assess and compare the mechanical properties of these steels under different treatments, together with its microstructural correlation, would enable an understanding of the improvements or fragilization, which are decisive in the resistance of such materials. As received the Maraging steel 300M and 300 exhibited high mechanical strength values catastrophic failure in the plastic regime, as well as high threshold in fatigue life compared to steel 4340 [2]. As for the thermochemical nitritation treatment and the properties studied, there was, in steels 4340, significant increase in tensile strength, but decrease in fatigue life. Nevertheless Maraging steels 300M and 300 declined in strength in tensile tests and fatigue life, however exhibited higher hardness values and corrosion resistance. The 300M and Maraging steel showed unfavorable results in fatigue and stretching. Scholars have noted that thermochemical treatments such as nitritation at certain temperatures (acting as tempering / aging in the inner region of the material), can weaken steel with high grades of silicon and titanium [3].

Centro Tecnológico da Marinha em São Paulo and Marinha do Brasil.

[1] MESQUITA, R. A. et al., Tecnologia em Metalurgia e Materiais, v.4, n.4, p. 7-15, (2008).
[2] CARDOSO, A. S. M. et. al, Advanced Materials Research, Vol. 891-892, p. 1507-1512 (2014).
[3] GARRISON JR, W.M., Materials Science and Technology, v. 3, n. 4, p. 256-259 (1987).

FERNANDES, A. B.; FREITAS, B. C.; RODRIGUES, A. C. B.; BASTOS, E. L. USAGE OF TRANSMITION ELECTRON MICROSCOPY (TEM) TO CHARACTERIZE OF NOBLE METAL NANOPARTICLES USING BETALAINS AS REDUCING AND CAPPING AGENTS. Institute of Chemistry – University of São Paulo, São Paulo,
2015.

Metal nanoparticles can have a variety of technological applications due to their optical, electrical, magnetic chemical properties. There is, nowadays, a great worry about the choose of the reducing agent for nanoparticle production, since the ones currently employed are not environment-friendly.[1] Plant extracts, rich in reducing components such as glycosylated compounds, can have great importance in this process. Betalains are plant pigments that replace anthocyanins in some plants of the order Caryophyllales, divided in yellow betaxanthins and red betacyanins, with antioxidant properties.[2] Beet juice extract, a source of betalains, has been used in the formation of Ag, Au, Pt and Pd nanoparticles.[3] Our group has already made successful attempts to produce single betalains nanoparticles and, in this work, we intend to use Transmission Electron Microscopy (TEM) to characterize the nanomaterials obtained, as well as to establish protocols for betalains nanoparticles production.

The betalains used for nanoparticle formation will be either extracted from beet juice or semi-synthetized from betalamic acid. The synthesis of nanoparticles will be performed by microwave irradiation in an aqueous solution containing betalain and the metal ion. The analysis of morphology and size of nanostructures, related to their reaction conditions, will be obtained by Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). Preliminary results of attempts to produce gold nanoparticles with betanin (Bn), betalocoumarin-120 (BtC) and indicaxanthin (BtP) were analized by SEM. The results showed formation of silver nanospheres with size variation of about 15 nm.

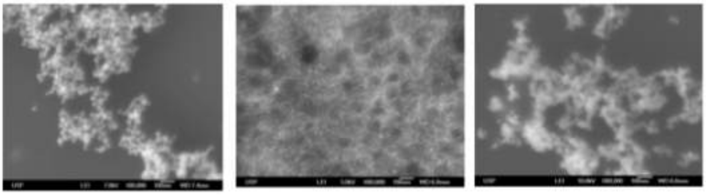


Fig 1. SEM images of AuNPs formed with Bn, BtC and BtP.

The preliminary conclusion is that the formation of betalains nanoparticles is possible. The future perspectives are to define the ideal condition for the synthesis to establish a defined protocol, as well as to use other betalains equivalents as reducing and capping agents. Those next steps rely on TEM's data to better characterize size and morphology of different nanoparticles, as this technique has been applied by other authors to characterize beet juice/betalains nanomaterials.

1. Sheny, D. S.; Mathew, J.; Philip, D., Phytosynthesis of Au, Ag and Au-Ag bimetallic nanoparticles using aqueous extract and dried leaf of Anacardium occidentale. *Spectrochim Acta A Mol Biomol Spectrosc* **2011,** *79* (1), 254-62.
2. Gandía-Herrero, F.; García-Carmona, F., Biosynthesis of betalains: yellow and violet plant pigments. *Trends Plant Sci.* **2013,** *18* (6), 334-343.
3. Kou, J.; Varma, R. S., Beet juice utilization: Expeditious green synthesis of noble metal nanoparticles (Ag, Au, Pt, and Pd) using microwaves. *RSC Advances* **2012,** *2* (27), 10283-10290.

Daiane Y Tezuka

Cysteine proteases are enzymes involved in a series of protein degradation processes, expressed in a myriad of cells. According to many studies in the literature, the inhibition of these proteins can lead to anticancer and antiparasitic activities both in vitro and in vivo among other effects. Inhibitors of cathepsins (mainly L and B) trigger the anticancer activity, while cruzain (Trypanosoma cruzi) and CPB (Leishmania spp.) inhibitors are the ones that lead to the antiparasitic outcome. Here we aim to use a series of bioassays to understand in more details the relationship in between the inhibition of these macromolecular targets and the final biological result of this process, which is the cell death. To do so, in vitro cell-based assays will be performed using metastatic prostate cancer cells (PC-3 and DU145) and the T. cruzi, L. amazonensis and L. chagasi parasites. Many methods will be applied to (i) screen the molecules using colorimetric assays (MTT); (ii) understand the cell cycle perturbations and cell death process; (iii) observe the morphological alterations of parasites and cancer cells, the location and activity of cysteine proteases by means of epifluorescence microscopy, scan electron microscopy (SEM) and transmission electron microscopy (TEM). These studies altogether will help to determine the importance of these macromolecular targets to each cell type, besides providing an in-depth scientific foundation regarding the bioactivity of new chemicals that are being designed and synthesized at the Medicinal Chemistry Group (NEQUIMED).

"To characterize by transmission electron microscopy (TEM) of material deformed cryogenically in high-energy milling process cryogenic and cryogenic rolling."

The cryogenic deformation of metals has found great prominence in the literature due to the large increase in strength and deformation capacity observed for various metals when deformed in these conditions. Studies indicate that this behavior is related to the stacking fault energy (SFE) since the SFE is connected to the dissociation of dislocations and dynamic recrystallization of the metal. Thus, the characterization by transmission electron microscopy for metals of different stacking fault energy will be of utmost importance (Au - low SFE, Cu - average SFE and Al - high SFE). Particularly in this project, the study by cryogenic TEM of formed samples will be extremely important to characterize their defects structure. In this project, intend to characterize the defects structures generated on cryogenic deformation by Transmission Electron Microscopy on cryogenic temperatures using metals samples formed on cryogenic conditions. In all the process, the samples may be keep on cryogenic temperatures, which makes most difficulties to perform. . It is noteworthy that successfull development in fully cryogenic sample preparation for TEM by two routes investigated was done: via ion milling (cutting, punching and ion milling fully cryogenic) and via ultracriomicrotomy with sample maintenance at cryogenic temperature (<-150 ° C) throughout the process. For this process were designed and built several devices for the manipulation of samples in all stages of preparation, and the development of specific methodology to use in addition to the change of conventional methodologies.

Characterization of Icosahedral Quasicrystal in Ti-Fe-Si System

Y. Guo[1*], I. Bataev[2], A.M. Jorge Jr.[1, 3], A.R. Yavari[3]
[1] Department of Materials Engineering, Federal University of São Carlos, SP, Brazil
[2] Novosibirsk State Technical University, K. Marks 20, Novosibirsk, Russian Federation
[3] SIMAP-CNRS, Institut Polytechnique de Grenoble, BP 75, St Martin d'Hères, 38402, France
* Corresponding Author: yaofeng.guo@ufscar.br

Transmission electron microscopy (TEM) was used to confirm the presence of icosahedral quasicrystalline phase in the as--prepared $Ti_{67.5}Fe_{25}Si_{7.5}$ ribbons cast at rotation speed of 1500 rpm through melt spinning (hereafter named as TFS-1500). The TEM observation was done at Novosibirsk State Technical University, Russia, with FEI Tecnai G2 at 200kV. The diffraction pattern of the as--cast ribbons is ring pattern is shown in Fig.1. The dark field image is then obtained from the region marked by red circle. It is found that the size of I-Phase and $Ti_{0.8}Fe_{0.2}$ crystalline precipitates are around 20 nm. Due to the small size of precipitates, the peaks in XRD patterns are much broadened. Neither I-Phase nor simple crystalline phases produce sharp Bragg intensities. Therefore, convergent beam electron diffraction (CBED) technique is then used to obtain the diffraction pattern.

The CBED pattern of as-cast TFS-1500 is shown in Fig. 2. It is found that there exist two phases (Icosahedral quasicrystal and $Ti_{0.8}Fe_{0.2}$) in the region where the CBED patterns were taken. The small solid circles indicate the diffraction pattern of $Ti_{0.8}Fe_{0.2}$ at [111] zone axis. Fig. 2 also shows the three fold symmetry pattern corresponding to icosahedral quasicrystalline phase (I-Phase). The orientation relationship between $Ti_{0.8}Fe_{0.2}$ and I Phase is shown here as [111] $Ti_{0.8}Fe_{0.2}$ // three fold symmetry axis (I-Phase). The schematic presentation shows the indexation of the I-Phase using Elser's indexing method and the size of solid circles indicates the intensity of diffraction spots based on Elser's theoretical calculation.

The five fold symmetry pattern of I-Phase in as-cast TFS-1500 ribbons is shown in Fig.3. $Ti_{0.8}Fe_{0.2}$ and I Phase also has the orientation relationship of [001] $Ti_{0.8}Fe_{0.2}$ // two fold symmetric axis (I-Phase) and as [111] $Ti_{0.8}Fe_{0.2}$ // three fold symmetry axis (I-Phase). The corresponding diffraction pattern is not shown here.

It can be found that the I-Phase in as-cast TFS-1500 ribbons is of primitive lattice in six dimensional hyperspace. The lattice constant of this primitive unit cell in six dimensional space is then calculated according to the peak positions obtained in both XRD and CBED patterns. The quasilattice constant is aq=0.4956 nm. This value is between those of Ti-TM-Si-O (TM=transition metal), Ti-Zr-Fe (0.46 - 0.48 nm) and Ti-Zr-Ni, Ti-Zr-Co (0.51 nm).

Acknowledgments

The BioTiNet ITN (No supported this work. 264635) FP7 Marie Curie project.

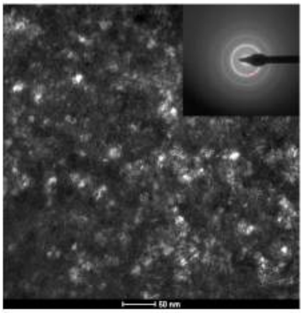


Fig.1 Dark field image shows precipitation of icosahedral quasicrystals and $Ti_{0.8}Fe_{0.2}$ *crystalline phase. Zone axis is [111]* $Ti_{0.8}Fe_{0.2}$*. The inset shows the ring pattern from which the dark field image was obtained.*

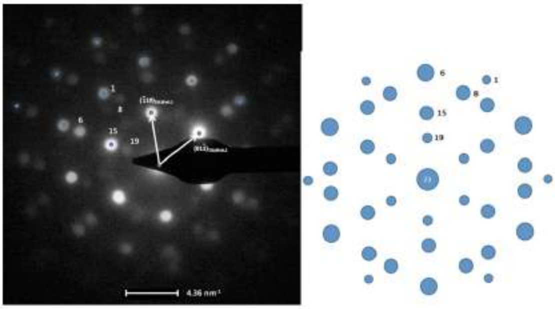


Fig. 2 CBED patterns pattern of as-cast TFS-1500, zone axis [111] $Ti_{0.8}Fe_{0.2}$ *and schematic presentation of three fold symmetry pattern of icosahedral quasicrystal. The circle size in schematic presentation indicates the intensity of diffracted spots according to theoretical calculation. The orientation relationship between Ti0.8Fe0.2 and icosahedral quasicrystal is [111]* $Ti_{0.8}Fe_{0.2}$ *// three fold symmetry axis (I-Phase).*

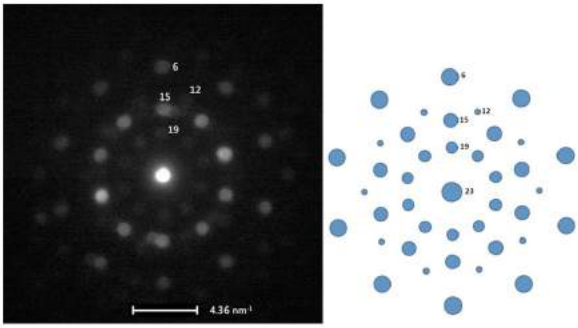


Fig.3 CBED patterns of as-cast TFS-1500 five fold symmetry pattern of I-Phase.

Influence of heat treatment in the purification of carbon nanotubes – removal of encapsulated iron-based phases and enhance graphitization

B. R. C. de Menezes[1], F. V. Ferreira[1], W. Francisco[1], F. S. Brito[1], E. A. N. Simonetti[1], L. S. Cividanes[1], G. P. Thim[1]

[1] *Technological Institute of Aeronautics, São José dos Campos, SP, Brazil*

Carbon nanotubes (CNT) have been the focus of research in nanoscience and technology since its discovery by Sumio Iijima in 1991. Their exceptional mechanical properties, such as elastic modulus greater than 1 TPa and strength of 10 to 100 times greater than the steel, allied to its low density, are expanding their use as reinforcement of composite materials. However, the process of manufacturing CNTs by CVD holds impurities inside de tubes, as iron particles used as catalysts. Moreover, it can generates unwanted carbon structures on the walls of CNTs, such as amorphous carbon. Then, it is necessary to remove theses undesirable defects to be possible to verify the real influence of the nanotubes in polymer matrices. Heat treatments at high temperatures (~1800ºC) under inert argon atmosphere or under vacuum allows the improvment of the CNTs structure, removing the pre-existing defects. This work aimed to verify the influence of heat treatment under vacuum in the purification of carbon nanotubes. The CNTs used in this project was obtained by CVD process. The purification heat treatment was conducted under vacuum at 1800ºC for 3 hours. TGA, Raman, XRD were performed for characterization of the material before and after treatment. The results showed that the treatment was efficient in the removal of iron particles and amorphous carbon, improving the material structure. For a complete characterization will be necessary to analyze the nanostructure of the CNTs, which is possible only by transmission electron microscopy (TEM). It allows to check: the structure of the multi-walled carbon nanotubes – MWCNT (visualization of the presence of concentric tubes, which may account for the amount of walls and estimate its diameter), the presence of residual amorphous carbon (derived from the deposition of hydrocarbons on the outer walls of the CNTs), the presence of remaining metal particles/impurities of different sizes within the tubes and set their composition using EDS. After the complete CNTs characterization it will be possible to initiate the production of nanocomposites.

Acknowledgments: *FAPESP, CNPq, CAPES.*

ORDERED NANOSTRUCTURED LAYERS BY PLASMA PROCESSES

A. Godoy-Jr[1], V. Laurindo-Jr[1], A.L.J.Pereira[1], A.S. da Silva Sobrinho[1], M. Massi[1,2], D.M.G. Leite[1*]
[1]*Technological Institute of Aeronautics, Department of Physics, São José dos Campos, SP, Brazil*
[2]*Federal University of São Paulo, São José dos Campos, SP, Brazil*

Introduction

Ordered nanostructures as carbon-based nanorods or nanotubes arrays have attracted the attention of the scientific community due to their unique properties that allow the production of super-high capacitance layers, low resistance and high specific superficial area counter-electrode for solar cells, among other applications. In this work, we apply an innovative plasma processes to produce carbon-based nanostructured films from pure graphite layers. The objective is to obtain nanostructured arrays with high superficial area aiming the application in dye sensitized solar cell (DSSC).

Experimental

Pure carbon layers (from 500 to 600 nanometers thick) are previously deposited onto glass substrate by magnetron sputtering technique using a pure graphite targets in argon atmosphere. These samples are then subjected to plasma treatment in order to produce the nanostructures. Different additional gases are explored at different working pressures and RF powers. The samples are analyzed by spectroscopic ellipsometry, profilometry and scanning electron microscopy - SEM.

Pleliminary results

Preliminary results show that through the process mentioned above, there is growth of microestrutuas carcono as shown in Figure 3, which is an image acquired by scanning electron microscope - SEM. Figure 4 shows an EDX analysis and tables 1 and 2 expose the corrosion and deposition parameters.

Carbon corrosion parameters	
Flow	SF6: 5 sccm
Pressure	0,1 Torr
Time	5 min.
Power (RF)	100 Watts
Temperature	RT

Figura 2: Carbon corrosion Table

Carbon deposition parameters	
Flow (ar)	15 sccm
Pressure	16 mTorr
Time	60 min.
Power (RF)	138 Watts
Voltage	138 Volts
Temperature	RT
Thickness	500 nm – 700 nm

Figura 2: Carbon deposition Table

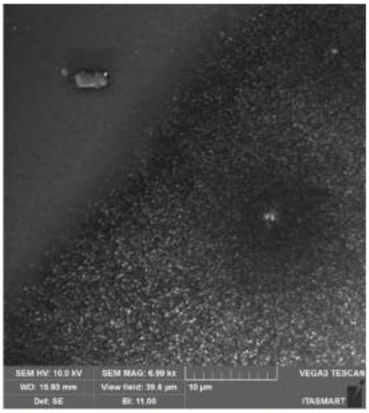
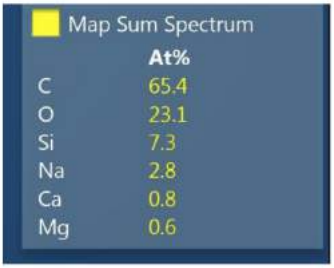


Figura 3: SEM top view from carbon film showing the interface between the corroded and non-corroded areas



🟨 Map Sum Spectrum

	At%
C	65.4
O	23.1
Si	7.3
Na	2.8
Ca	0.8
Mg	0.6

Figura 4: composition by EDX in detail

ANTONIA ALANA LIMA PACHECO
LABORATORY OF PHOTONIC MATERIALS AND DEVICES
STATE UNIVERSITY OF CAMPINAS - UNICAMP

Abstract

The advance of nanoscience enabled the developing of new technologies that can be applied in construction materials, like concrete and cement pastes. Nanosilica and nanoquartz are nanotechnological materials which by being in nano-size, acquire new functions and properties. The addition of these materials in high performance concrete can improve the mechanical and physical properties and may be a better substitute of silica fume, already used in construction market. However, the understanding of the phenomena that occurs with these additions are not complete and need to be analyzed in micro and nano scale. One of the compounds formed in cement hydration is calcium silicate hydrate, responsable for the strength of concrete but a not well defined compound, with variable stoichometry and morphology. The differences between this composite with the addition of nanosilica may provide the necessary information to a better knowledge of the performance of concrete with addition of nanomaterials and correlates the microstructure behavior.

STUDY ON THE SUPRAMOLECULAR INTERACTIONS IN SILVER NANOPARTICLES AND ITS ANTIMICROBIAL ACTIVITY

Student: *Caio Henrique Nasi de Barros*
Supervisor: *Ljubica Tasic*

Institute of Chemistry, State University of Campinas (UNICAMP)

Abstract

Silver nanoparticles (AgNP) have been studied more intensively over the last decades due to its potential antimicrobial activity. The nanoparticles of elemental silver are more effective and less toxic than the silver in its ionic form, as it used to be utilized when this element was first recognized for its potential applications. In this project, we intend to explore the biogenic synthesis of silver nanoparticles using orange peel extract (*Citrus sinensis*) as well as the "green chemistry" synthesis using hesperidin, a flavonoid glycoside abundantly found the orange peel. The biogenic AgNP will be studied in regards to the stabilization produced by the macromolecules present in the extract. Both methods will be optimized with the aim of applying the antimicrobial properties of the AgNP on the microorganism *Xanthomonas axonopodis* pv. *Citri*, that causes citric canker in the orange cultivation in the Sao Paulo State, Brazil. This agricultural disease has brought significant damages in the orange industry and thus methods of containing this pest are extremely relevant and necessary. Therefore, TEM analysis will be carried out in order to characterize the AgNP produced, determining size and aggregation of the particles. Negative staining will be used to make the capping of macromolecules (mainly proteins) visible under the microscope, determining accurately the size of the nanoparticles and of the capping layer that stabilizes them.

Synthesis of $YBa_2Cu_3O_{7-x}$ superconductor nanowires

During the last thirty years, the discoveries of cuprate superconductors had giant impact on scientific community, principally due to $YBa_2Cu_3O_{7-\delta}$, whose temperature of superconducting transition occurs in $T_C = 92K$, above the liquefaction temperature of nitrogen, enabling technological applications.

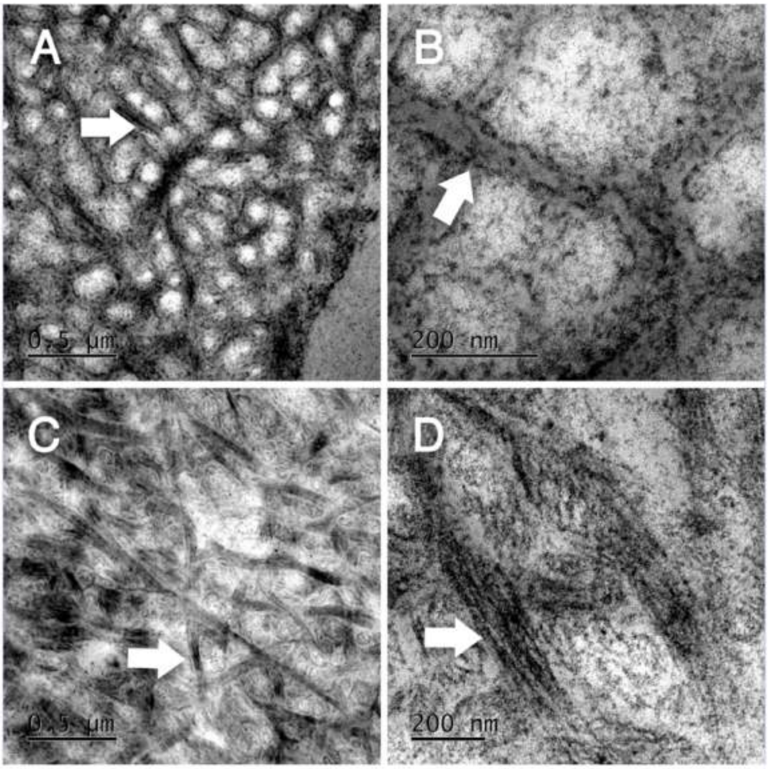
Combined with the possibilities of reduced dimensions until the nanometric scale, this work has as main objective to synthesize $YBa_2Cu_3O_{7-\delta}$ superconductor nanowires to study the effect of size in electronic transport properties during the transition to superconductor state. The nanowires was obtained by sol-gel chemical route using yttrium, barium and copper acetates as precursors and solubilized in a mixture of methanol, acetic and propionic acids and subsequently deposited in nanometric molds of polycarbonate membrane. In order to analyze the influence of the synthesis conditions, the filled membranes were sintered at distinct temperatures in the range from 800°C to 900°C in oxygen flux. The polycrystalline nanowires formed have a diameter less than 80 nm. The characterization methods applied were Scanning Electron Microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDS) and X-Ray Diffraction (XRD) in order to obtain the morphology, stoichiometry and structure of nanowires. Furthermore, magnetization and resistivity *vs.* temperature measurements were obtained using a Physical Property Measurement System (PPMS). Considering that the structures obtained in this work are of nanometer order, it becomes extremely necessary to use instruments with atomic resolution, such as Transmission Electron Microscopy (TEM), to characterize the materials sintered. Therefore, the use of TEM techniques makes possible to obtain images of the morphology of the nanowires, determining the crystallographic orientations and the diffraction patterns obtained from a small amount material as occurs in this work.

Dentin bonding and remineralization of an experimental self-etch adhesive mediated by biomimetic analogs and water reactive calcium phosphates

Gabriel Abuna

To assess the remineralization potential and dentin bonding of a two-step self-etch dental adhesive doped with water reactive calcium phosphates and biomimetic analogs.

Methods: An experimental primer was mixed with biomimetic analogs (polyacrylic acid – PAA and sodium trimetaphosphate – STMP) and an experimental adhesive doped with a mixture of calcium phosphates (beta tri-calcium phosphate and monocalcium phosphate monohydrate). Dentin remineralization of EDTA-demineralized dentin slabs was tracked using FTIR. The groups were: Control – control primer and control adhesive; Primer+Phosphates - control primer and phosphates-doped adhesive; PAA+Phosphates - PAA-containing primer and phosphates-doped adhesive; STMP+Phosphates - STMP-containing primer and phosphates-doped bond; Analogs+Phosphates - both biomimetic analogs in the primer and phosphates-doped adhesive. TEM ultrastructurally evaluated the biomimetic remineralization. For microtensile bond strength (µTBS) test, extracted human molars were bonded according to the aforementioned groups and cut into sticks after 24h or 6 months of simulated pulpal pressure. Interfacial silver nanoleakage was analyzed using SEM. Statistical analysis was performed using two-way ANOVA and Tukey's test ($p<0.05$). FTIR analysis disclosed the presence of apatite. TEM analysis showed deposition of apatite in intrafibrillar organization of needle-like structures. µTBS of the control significantly decreased after aging and the use of PAA or STMP alone reduced the initial µTBS. The use of phosphates with and without analogs promoted stable µTBS ($p>0.05$). Nanoleakage decreased proportionally to the mineralization in phosphates-containing groups whereas it increased for the control. The proposed remineralizing system nucleates apatite reaching the intrafibrillar zones of dentin collagen thereby providing stability to dentin bond. Biomineralization, biomimetic remineralization, sodium trimetaphosphate, dentin, intrafibrilar remineralization, collagen. Results of TEM. The groups with phosphates-doped adhesive without analogs (Figs. 3A and 5B) and that with both analogs in the primer and the phosphates-doped adhesive (Figs. 3C and 3D) were compared. In absence of biomimetic analogs, it was evident the presence of mineralization (arrows). However, the minerals were located mostly in the extra-fibrilar spaces with no direct or indirect evidence of interaction or organization inside the collagen fibrils. On the other hand, Figures 3C and 3D showed the presence of crystals organized and incorporated into the collagen fibrils.



TEM analysis. A – group without analogs after 6 months of PPS (500 nm). B - without analogs after 6 months at higher magnification (200 nm) crystals remineralized extrafibrilar (arrows). C - With both analogs after 6 months (500 nm). D – group with both analogs after 6 months at higher magnification (200 nm) intrafibrilar mineralization, with hierarchical organization.