# activity report 2009



associated laboratory centre for research in ceramics and composite materials

CICECO



cover and back-cover Time-behavior appearance of fibroblast cells cultured on the nanocrystalline diamond coating Amaral M, Gomes PS, Lopes MA, Santos JD, Silva RF, Fernandes MH

**cover** | A–C: Confocal Laser Scanning Microscopy of actin filaments and nucleus staining; **back-cover** | D–F: SEM views Time-behavior appearance (d-number of days)

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associated laboratory centre for research in ceramics and composite materials

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#### 02 | about CICECO



centre for research in ceramics & composite materials



university of aveiro theoria poiesis praxis





Ceramics and Glass Engineering Department built: 1992 - Arq. Alcino Soutinho



Physycs Department built: 1994 - Arq. Alfredo Matos Ferreira



Complexo dos Laboratórios Tecnológicos (CICECO Main office) built: 2009 - Arq, José Rebelo de Andrade



Chemistry Department built: 1993 - Arq. Alcino Soutinho



Laboratório Central de Análises built: 1993 - Arq. Fernando Gomes da Silva



#### about

The **centre for research in ceramics and composite materials** (**CICECO**), is an interdisciplinary laboratory in the University of Aveiro (Portugal) with researchers from Chemistry, Ceramics and Glass Engineering and Physics departments.

CICECO was created in 2000, as a result of the fusion of two research units of the University of Aveiro:

Centro de Química Inorgânica e de Materiais and Unidade de Investigação em Materiais Cerâmicos.

In March 2002, CICECO was awarded the status of Associated Laboratory by the Portuguese Ministry of Science and Technolgy.

CICECO is regularly evaluated by international panels and has been rated 'Excellent'.

This document reports the rmain activities developed in 2009 as well as the actions aimed for 2010.

#### general aims

To develop novel nano- and micro-structured materials, and innovative methods of synthesis and processing, leading to the foundation of basic scientific knowledge, which allows the study of structure-property (electrical, magnetic, optical...) relationships and the design of devices for communications technologies. Much attention will be devoted to organic-inorganic hybrids, multifunctional materials and multiferroics;

To develop new materials and functional coatings for industrial applications and materials with improved structural properties;

Design recycling/reuse alternatives for wastes and by-products in ceramic or cement-like materials;

Develop, in the frame of the biorefinery concept, the scientific and technological knowledge of the chemical and biological processes of production and transformation, at the laboratory, pilot and industrial scale, of polymeric materials and lignocellulosics, adding value to forestry materials and industrial wastes, while minimising the environmental impacts;

To develop biomedical and biomimetic materials and methods.

#### mission vision

To develop the scientific and technological knowledge base required for the innovative production and transformation of ceramic and composite materials. To become a leading inter-disciplinary European research laboratory in the field of materials;

To contribute to the development of a scientific culture at a national level;

To stimulate innovation within the industrial sector.

## **Research Areas**

Our research is organised in **3 lines** and **8 interdisciplinary groups** from the Departments of Chemistry, Ceramics and Glass Engineering and Physics, considering: - the surrounding industrial environment (ceramics, chemical and forest-based companies); - our skills and expertise; - our motivation to develop new and stimulating scientific and technological fields.

research lines	advanced micro- and nanostructured materials for communications technologies
research groups	<ul> <li>g1   inorganic functional nanomaterials and organicinorganic hybrids</li> <li>g2   electroceramics</li> <li>g3   magnetostructural and multiferroic modulation of strongly correlated electron materials</li> </ul>
research lines	advanced materials for industrial applications
research groups	g4   reactive ceramic components for process control g5   ceramic composites and functional coatings for structural applications g6   wastes recycling and green products
research lines	biorefineries and biomaterials
research groups	g7   macromolecular materials and biorefineries g8   biomedical and biomimetic materials



## **Management Structure**

The Management structure encompasses the Scientific Council (SC), Directors, Directing Board (DB), International Advisory Board, Research Lines and Research Groups, integrating also the Centre for Imaging and Structure of Materials (CISM), Centre for Design and Technology of Materials (CDTM) and the new Centre for the Study of Science, Education and Technology (CIETE).

#### **Scientific Council**

Is the most important body of CICECO, gathering all members with a PhD degree. Meets 1-2 times/year and approves the year's scientific and financial report, the following year scientific and financial plans, and discusses general issues. It has the power to recommend the Rector the discharge of the Directors. Its President is elected for 3 years.

#### **Directing Board**

The General Director is Prof. João Rocha and the Vice-Directors are Profs. Joaquim Vieira and Luís Dias Carlos. The Directing Board is appointed by the Directors (meets once a month) and includes 12 other researchers (2 are full-time researchers).

#### **Research Lines and Research Groups**

Research is organised in 3 lines and 8 interdisciplinary groups from Departments of Chemistry, Ceramics and Glass Engineering and Physics, chosen considering:

- surrounding industrial environment (ceramics, chemical and forest-based companies); - our skills and expertise;

- motivation to develop new and stimulating scientific and technological fields. The research lines and groups Coordinator's are appointed by the Directors.

#### **Centre for Imaging and Structure of Materials**

**CISM**, headed by the Directors, gathers all the medium and large-scale equipment and has been a very effective way of managing a large number of facilities. All CICECO members have free access to the equipment available. Service to external users is also provided.

#### **Centre for Design and Technology of Materials**

**CDTM** is a knowledge transfer centre and interface with industry financed by CICECO at a basal level (2 researchers, 2 administrative staff).

#### Centre for the Study of Science, Education and Technology

**CIETE** focuses on the understanding and development of systems, processes and contexts that favour and sustain the creation and use of knowledge in universities, research centres, schools and companies.

### research team

**CICECO** is the largest Portuguese institute in the field of materials. On 31st December 2009 CICECO hosted 409 people, an increase of 16.8% relatively to the previous year.

Almost 33% of the Research Team hold a PhD degree.

Under the Government Programme for hiring researchers for the National Scientific and Technological System, CICECO hired 4 researchers in 2008 and 9 researchers in 2009.

	'02	'03	'04	'05	'06	'07	'08	'09
professors and lectures	47	47	50	52	53	50	48	49
full-time researchers	5	9	12	16	20	23	29	35
post-doctoral associates		22	29	47	46	47	51	47
collaborators	16	13	12	10	23	46	14	64
PhD students	54	60	61	51	67	69	81	87
MSc students and other students		44	54	63	49	39	116	118
laboratory technicians	4	8	5	5	5	4	4	3
administrative personnel	1	3	5	6	7	7	7	6
total	176	206	228	250	270	285	350	409

	'02	03	'04	'05	'06	07	'08	'09	total
PhD theses	14	13	11	14	19	20	10	23	124
MSc theses	10	8	7	17	16	41	75	73	247
SCI papers (IF >=5)	1	3	4	5	7	17	23	23	83
SCI papers (IF≺5)	204	225	283	310	374	273	396	321	2386
books	-	-	1	1	1	-	3	3	9
book chapters	4	14	12	10	5	17	36	13	111
national patents	7	3	1	6	6	6	4	10	41
international patents	2	-	-	0	1	4	1	10	18

## scientific output

CICECO is one of the most productive research institutes in the country in all scientific areas, with an average publication of 4.5 - 5 SCI papers per year per academic staff or full-time researcher in 2009.

#### 08 | about CICECO

Platform for physical measurements at low temperatures with a magnetic field up to 10 Tesla







ALL AND A







High-temperature graphite furnace









High temperature mechanical testing system



### Facilities Centre for Imaging and Structure of Materials



Technicians: Maria do Rosário Soares rosarios@ua.pt

Marta Ferro marta.ferro@ua.pt

Maria Celeste Azevedo cazevedo@ua.pt

CICECO is one of the best equipped materials science centres in the country. in the recent FCT equipment programme we have been awarded over 4.4 M€

The Centre for Imaging and Structural Studies manages, in an integrated way, medium and large-scale equipment, granting free access to all members. Some 250 k€/year from FCT budget are allocated to maintain and upgrade equipment

Main instruments have service contracts and dedicated technicians:

- academic users from Aveiro and other institutions in Portugal and Europe have privileged access conditions;

- industrial players pay a larger fee (exception for those engaged in CICECO-industry consortia) Electron microscopes and Nuclear Magnetic Resonance spectrometers are part of national networks (coordinated by CICECO) and the access conditions to Portuguese academic users are very favourable.

Our single-crystal X-ray diffraction facility was granted through a joint proposal with Associated Laboratory, REQUIMTE, which secures up to 25% of the users time

In 2009 we have made upgrading investments in the electron microscopes, solid-state NMR spectrometer, infrared and UV-vis spectrometers.

CICECO's has also a computer cluster, which is housed and embedded in the Aveiro computer centre.



Transmission Electron Microscopy (High resolution)



Chromatography (Gas and HPLC)



Solid Nuclear Magnetic Resonance (NMR)

### **Technology Transfer** Centre for Design and Technology of Materials

general aims

mission

To contribute to the development of R&D activities through people and knowledge valorisation.

To develop and foster market knowledge valorisation practices, acting in three main areas:

Innovation management, promoting actively the development of R&DT projects in partnership with companies:

Promotion and support of entrepreneurship activities;

Promotion of IP protection and commercialisation.

The promotion of the collaboration between CICECO and companies was a main concern of the 2009 activities, and we provide the following examples:

CDTM staff visited 26 Portuguese companies aiming at promoting CICECO research capabilities, and surveying R&DT needs which could lead to new projects;

CDTM has participated in the 1st working session "University-Industry relationship", which was held at the University of Aveiro, within the framework of "Encontros para a Competitividade" promoted by IAPMEI. CICECO contributed to this event by hosting the visit of 28 companies, mostly from the Central region of Portugal and from different business sectors;

CICECO opened up a call for the development of applied research projects, and four projects in partnership with companies were selected. These projects intend to both foster cooperation among our research groups and develop, in a short time, novel products which address specific market needs, completing the entire knowledge transfer path from science to market.



centro de design e tecnologia de materiais

Coordination: Joaquim Vieira jvieira@ua.pt

**Executive Director:** Ana Daniel anadaniel@ua.pt

**Project Manager:** Maria Paula Seabra pseabra@ua.pt

Paula Sousa Pais sousa.pais@ua.pt

Vera Fernandes verafernandes@ua.pt





**Spin-off Companies** 'FoodMetric SA' was terminated;

Tetracarbon, still in formation, was put on hold until the market situation improves.

In the case of Ceramics, the technology platform may take the form of a competitiveness cluster networked with a similar cluster in Limoges, France. In the French system, 'Pole de compétitivité' is a combination in a given geographical area of companies, training centres and public sector or private research facilities, all committed to a partnership approach in order to create synergy around innovative projects. A CICECO delegation went to Limoges and this competitiveness cluster is close to be created. Some 30 Portuguese Ceramics companies are interested in this initiative, which has progressed during 2008.



#### **Technology Platforms**

These are CICECO-companies clubs where companies have exclusive prior access to research output, against a 7.5 k€ annual fee. They also have special access to equipment and services, consulting, literature search, etc. The first one, created in 2006, is IDPoR-Research and Development in Polymers from Resources Renewable (http://idpor.ciceco.ua.pt), and it aims at developing scientific and technological knowledge driven by the needs of 6 national companies. 6 Ph.D. theses are in progress. IDPoR is involved in the Network for Competence in Polymers with other companies and U Porto, and financed for 2 years by AdI with 1 M€, to promote new investments and business opportunities.c) Competitiveness Cluster



As an output of this effort, 26 specific R&DT projects/services contracts with companies were in progress in 2009, 14 of which began this year. Their main objective was the development of new materials and/or processes, as well as the resolution of specific industrial problems and/or other specific services. This represented a total net income of 252.837, 65€.

SEVENTH FRAMEWORK

Despite the international economic crisis and the problems faced by Portuguese companies since 2008, CICECO efforts to foster the interaction with industry have been rewarded, since there is an increase in 2009 of the earned income (graphic 1).

The QREN programme, promoted by the Portuguese Government to foster companies' innovation, was also an opportunity for researchers, actively promoted by CDTM. In 2009, CDTM promoted 5 applications to QREN Co-promotion projects and several applications to R&D Cheques, 4 of which were approved (BIIPP; ECOPOLYOL, INOVALIGANTES e NATAL) and one is waiting for a financial redress (BIOSWEET). In the same line, CDTM supported a CICECO application to the FAI (Fundo de Apoio à Inovação), a ministerial initiative that finances projects in energy efficiency and renewable energy.

The consortium IDPoR (Research and Development in Polymers from Renewable Resources) aims at the development of scientific and technological knowledge driven by the needs and competitive challenges of a group of six national major companies. In 2009, IDPoR submitted two patents at national or international level, and promoted advanced training programs at master and doctoral level, as well as other training courses and seminars. Moreover, several initiatives were taken with the objective of creating a new cooperation platform between University and Industry in the field of Ceramics, similarly to IDPoR. In this case, in September CICECO's researchers visited the European Centre of Ceramics, located in Limoges, France. In this meeting several areas of cooperation were identified, and further initiatives were proposed in order to establish a new consortium.

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In the area of Entrepreneurship, the goal was to support researchers and technology valorization project promoters in the early stages of idea development, "proof-of-concept" implementation stage and business strategy development. After several meetings with CICECO researchers, one business plan was produced. This business plan aims at developing a spin-off company which will operate in the area of corrosion, and will target established companies of inks and coating materials.

of inks and coating materials. Concerning the protection of intellectual property and the valorization R&D results, CDTM promoted internal actions to highlight the benefits of IP protection. The increasing awareness regarding the importance of potential international markets drove CICECO/University of Aveiro to look for protection outside national boundaries, as is well expressed in graphic 2.

The external promotion of CICECO was carried out through the organization of several workshops and participation in certain events:

- Fair "4<sup>ª</sup> Jornadas de Inovação", promoted by AdI from 18 - 19 de June 2009, FIL – Lisboa; - Workshop "Is innovation the solution for the Portuguese Ceramic Sector?", 21st of July 2009, Municipality of Aveiro;

- 8th Inorganic Chemistry Conference, 16th to 17th of October 2009, Curia; - Woorkshop "Nano 09", 10th to 11th of December 2009, International Iberian Nanotechnology Laboratory, Braga.

The interaction with local government is also a strategic objective of CICECO. Urban Network for Innovation in Ceramics (UNIC) project, promoted in the frame of the URBACT programme, aims at exchanging experiences between European cities, as a mean to promote innovation in Ceramic sector. The Municipality of Aveiro and the National Association of Ceramic Producers – APICER are also partners of this project. In 2009, a Local Action Plan was developed in order to fuel local economy by building upon industrial ceramic heritage and traditional competitive factors.

Several events were organised with the goal of raising the awareness of CICECO's researchers to the relevance of technology transfer and to other financing opportunities: - FP7 working session on Nanosciences, Nanotechnologies, Materials & New Production Technologies (NMP) thematic, 22th of May 2009, Anf. do Departamento de Engenharia Cerâmica e do Vidro;

- VI jornadas CICECO, 5th and 6th of March, Auditório da Reitoria;

Workshop "One Day Seminar on Valuation of Research Results and Technology Transfer",
 30th of May 2009, Anf. do Departamento de Engenharia Cerâmica e do Vidro;
 Joint course on 3D Design Introduction and FactSage Thermodynamic Calculation 23nd of May, Anf. do Departamento de Engenharia Cerâmica e do Vidro;

- One-to-one meetings;

- Monthly Newsletter.

CDTM developed several initiatives designed to promote internationalization of CICECO research and members, as well as to find additional financing. CDTM advertised and supported all opportunities for networking grants and scholarships, namely the Treaty of Windsor Programme,

## **Creation and Use of Knowledge** Centre for the Study of Science, Education and Technology

#### mission:

CIETE is a CICECO structure devoted to contributing to the understanding and development of systems, processes and contexts that favour and sustain the creation and use of knowledge in universities, research centres, schools and enterprises. Coordination: Júlio Pedrosa julio.pedrosa@ua.pt

#### main goals:

To contribute to the development and understanding of modes of creating and using knowledge;

To investigate models, processes and contexts of governance, management and evaluation of Science and Education Institutions;

To contribute to the development of novel approaches to the use and understanding of Science in schools, public services and companies.

#### programmes:

a) Developing platforms for the cooperation of Universities and Research Centres with society This is a programme aimed at designing, testing and evaluating platforms to promote knowledge share, transfer and development in research centres and organisations outside universities; this programme was associated with the establishment of IDPOR, in 2006. At present the focus is on the creation of a platform for the cooperation between University researchers, schools and municipalities.

b) Developing the understanding and value of education and science in schools and local communities:

School/Science at home: this is part of the project 'A Escola em Casa', aiming at developing and testing instruments and materials to promote and support conversations between children and their parents at home, that is being financed by the Gulbenkian Foundation since 2004.
'Caminhar Juntos para Gostar de Aprender e Aprender com a Escola' is a three years project financed through a protocol signed by: Universidade de Aveiro; Agrupamento de Escolas Gândara Mar, Tocha; Direcção Regional de Educação do Centro, Câmara Municipal de Cantanhede e Junta de Freguesia da Tocha. The Project is financed by the latter two partners and started in September 2009.

- Interdisdiplinarity in research and teaching: this programme is just starting, with the aim of understanding the foundations and identifying the relevant conditions to promote interdisciplinarity in higher education.

c) Governance of Science and Education Institutions: at present, this programme is the basis for two doctoral theses, one focusing on knowledge management in research centres and the other on the design and implementation of policies for the development of higher education.

## research projects selected examples

The number of Projects in progress in 2009 was 119, similar to the last six years. The main sources of funding are FCT, National Science Foundation (80%), and the European Funding Agencies and Programmes, European Commission, FEDER, (16%). Section 5 lists all projects funded.

#### **Projects with local Governments**

URBACT: project supported by UNIC and aims at promoting sustainable economical development of local ceramic industries. Partners - Municipalities of Aveiro, Limoges, Pécs, Delft and Selb;

POVT Sustainable Water Management in Public Buildings: with Aveiro Municipality;

Sustainability Park of Aveiro, with Aveiro Municipality; Parcerias para a Regeneração Urbana (QREN) (2009-2011).

#### National Network Action

Institute of Molecular Materials, Processes, and Products (M2P2): consortium CICECO-Associated Laboratories REQUIMTE and LSRE-LCM;

CICECO heads the national facilities networks on electron microscopy http://www.ua.pt/rnme/default.aspx)

ede nacional

oscopia

Nanomedicine Research Networks: we participate in several such Portuguese-Spanish networks, e.g. NANO/NMed-SD/0140/2007

and nuclear magnetic resonance (http://ptnmr.dq.ua.pt/);

"Integrated Platform for Medical Diagnostics"- QREN cluster "Plataforma para a Construção Sustentável"













GRAMA OPERACIONAL TEMÁTICO

2007-2013

#### International Network Action

EU Network of Excellence (2005-08): 'Functionalised Advanced Materials and Engineering of Hybrids and Ceramics-FAME' (6th framework programme, ca. 200 researchers and 50 Ph.D. students in 7 countries, http://www.famenoe.org/), which has now evolved to European Multifunctional Materials Institute-EMMI;

Network with Brazil: 'Molecular and Interfaces Nanotechnology Research Network'.

#### **European Projects (selection)**

NMP3-CT-2006-032616 – MULTICERAL Multifunctional Ceramics Layers with High Electromagnetoelastic couplin in complex geometries

NMP2-CT-2004-515960 ULCOS ULTRA LOW CO2 STEELMAKING

STRP 033410 MATSILC MATSILC-NOVEL MATERIALS FOR SILICATE BASED FUEL CELL

NMR3-LA-2008-214261 Multi-level protection of materials for vehicles by 'Smart' nanocontainers (MUST)

WACHEUP - New Concepts For Upgrading Pulp Mill Waste Streams to Values - Added Chemicals

RFSR-CT-2008-00028

Prediction of the kinetics of self-repaired of forming induced defects on thin functional primers for advances automotive applications (KINSREP)

CP-IP 228589-2

AFORE – Forest Biorefinery: Added Value Chemicals and Polymers by new integrated separation, fractionation and upgrading technologies

SUNPAP - Scale-up of Nanoparticles in Modern Papermarking



## <u>WaCheU</u>p

MatSILC





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## trainning activity









**Erasmus Mundus** 



Norwegian University of Science and Technology



## outreach, society and science









CICECO received 23 undergraduate students with BII (Bolsa de Integração na Investigação) grants from FCT, which joined our groups and had a fresh start to research;

University of Aveiro Ph.D. and M.Sc. Courses: highlight - 24 Ph.D. and 73 M.Sc. theses terminated in 2009. We lecture a number of M.Sc. degrees of the Departments of Chemistry, Physics and Ceramics and Glass Engineering. CICECO is now involved in Ph.D. courses with other research units in Aveiro in Chemistry, Chemical Engineering, Nanosciences and Nanotechnologies and Materials Science and Engineering. It is also involved in MAP-Fis, a Physics doctoral programme with Universities of Minho, Aveiro and Porto.

Bilateral Ph.D. Programmes: 6 theses in progress with U Montpellier, U Bordeaux, U Zaragoza, U Santa Catarina (Brazil), Norwegian University of Science and Technology. Informal schemes of student's exchange with other foreign laboratories are also in operation. ERASMUS MUNDUS M.Sc. Programmes: 'EMMS-Joint European Masters Programme in Materials Science' with the universities of Aalborg and Hamburg, which is now in its fifth edition (http://emms.web.ua.pt/); and a FAME-promoted programme (http://www.fame-master.com/) in its year 2.

Workshops: on January, a 2 days general workshop was organised in the format of a conference, with oral communications and poster presentations; seminars are organised every ca. 2 weeks and aimed at all our members. Supervisors-students group meetings take place on a regular basis.

Specialised courses for graduate students - EELS in the TEM: Studying the geometric and electronic structures of materials at the nanometer scale (1 day); Polymers from Renewable Resources (Posgraduate course), São Paulo University, Brazil, Mai 14-29, 2009, also University of the Basque Country, San Sebastian, Spain, December 10-18, 2009; 2nd ESF/UB.

Formal creation of Centre for the Study of Science, Education and Technology

Activities with families: School/Science at home

Activities with schools: Over 40 activities with 30 schools, including visits to Chemistry laboratories, conferences in schools, demonstrations, School Science Fairs, and Science Cafes. Active participation in up to 15 activities, including demonstrations (Chemistry Show), School Science Fairs, and Science Cafes. Fairs, and Science Cafes.

Large audience activities: Summer (secondary) school (25 h lab work); Chemistry Olympiads (25 Basic and 35 Secondary Schools); Ca. 10 radio (Antena 1, TSF) and 1 TV (RTP) programmes; Ca. 5 newspaper articles

## research line advanced micro- and nanostructured materials for communications technology

research groups g1 | Inorganic Functional Nanomaterials and Organic-Inorganic Hybrids g2 | Electroceramics line coordinator Luis Dias Carlos lcarlos@ua.pt

g3 | Magnetostructural and Multiferroic Modulation of Correlated Electron

## research line advanced materials for industrial applications

research groups g4 | reactive ceramic components for process control

line coordinator Jorge Ribeiro Frade jfrade@ua.pt

g5 | ceramic composites and functional coatings for structural applications

g6 | wastes recycling and green products



research groups g7 | macromolecular materials and biorefineries g8 | biomedical and biomimetic materials

line coordinator João Coutinho jcoutinho@ua.pt

research line 1 | general aims i) To design, prepare, process and characterise novel inorganic and organic-inorganic hybrid, functional and multifunctional materials and nanostructures, of different dimensionality (0-3D), for communications technologies (optical and magnetic properties) and heterogeneous catalysis.

ii) To improve understanding of electroceramics, and develop new low-cost materials and devices for dielectric, piezoelectric, ferroelectric and multiferroic applications. To understand nanosize effects and properties in bulk, films and nanocomposites.

iii) To study magnetic properties, and their interplay with structural and electronic correlations, of magnetic oxides, superconductors, bulk and thin-film metal alloys and nanoparticles.

iv) To develop solid-state NMR and apply at the highest level: photoluminescence, vibrational and X-ray absorption spectroscopies, XRD, electron and scanning probe microscopies, magnetisation, magnetoresistance and magnetothermal analyses, impedance spectroscopy, ferroelectric and piezoelectric analyses, hiperfine local probing using radioactive isotopes; quantum mechanics and molecular dynamics modelling.

#### research line 2 | general aims

i) High T energy conversion, based on improving materials performance by mastering correlations between properties/applicability and composition, structure and microstructural features;

ii) Conversion or processing of fuels, with emphasis on conversion of natural gas to syngas; iii) Improved performance of hard materials and coatings (wear, friction, toughness), including industrial products, and new concepts based on nanostructured materials;

iv) Highly performing nanostructured materials for functional applications (e.g.biomedical); v) Corrosion protection based on active protection, self-healing, multi protection, and methods for their applications or non destructive monitoring;

vi) Development of novel electrochemical devices;

vii) New products and added-value materials based on recycled wastes and by-products, used as raw materials, or to eliminate toxic wastes;

viii) Lower CO<sub>2</sub> footprint in materials processing; ix) Heat management/storage.

#### research line 3 | general aims

i) Implementation of the forest-based biorefinery, focused on characterization of agro-forest biomass components and extraction of valuable components, using benign extraction systems and assessment of potential technologies for industrial implementation;

ii) Development of new polysaccharide based materials and composites, including functional materials bearing inorganic nanophases;

iii) Development of novel polymeric materials based on biomass derived monomers; iv) Conversion of biomass components into valuable chemicals for: efficient catalytic conversion for production of platform chemicals from polysaccharides and biotechnological processes for conversion of biomass components into fine chemicals and biofuels;

v) Production of novel biomaterials for medical uses;

vi) Study biological recognition and membrane transport mechanisms;

vii) Production of new drugs and drug molecular transporters along with toxicity assessment; viii) Application of metabonomics for evaluation of metabolic profiles and fluxes in biological processes: disease, exposure to drugs/biomaterials.



**group coordinator** Tito Trindade tito@ua.pt

#### scientific highlights

i) Miniaturized prototype for pH sensing in the pH range 5-7.5, constructed from a photoluminescent Eu<sup>3+</sup> metal-organic framework containing two different Eu<sup>3+</sup> sites;

ii) First extended system where framework embedded Eu<sup>3+</sup>-O-Eu<sup>3+</sup> dimers behave like a molecule, exhibiting a unique emission signature and one of the longest <sup>5</sup>D<sub>0</sub> lifetimes so far observed for Eu<sup>3+</sup> in solids;

iii) A ligand-assisted rational design was used to process the Ln<sup>3+</sup>-containing organic-inorganic hybrids displaying the highest emission quantum yield (0.60±0.06) reported so far;

iv) The role of oxygen moieties at graphene surface on gold nucleation and growth has been investigated and the derived platforms were investigated as SERS substrates;

v) Heteroepitaxial growth of MFI zeolites over titanosilicate molecular sieves;

vi) The influence of step sites in the molecular mechanism of the water gas shift reaction catalyzed by copper was investigated;

vii) The key role of the surface membrane in why gastropod nacre grows in towers was explained.



SEM and TEM compilation of MW-CNT's with vanadium oxide, hafnium oxide and titania

#### research team | 21



















collaborators

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**Microporous Materials.** The exceptional photoluminescence of microporous AV-24, K<sub>7</sub>[Ln<sub>3</sub>Si<sub>12</sub>O<sub>32</sub>]•xH<sub>2</sub>O, the first silicates possessing Ln<sup>3+-</sup>O-Ln<sup>3+</sup> dimers (inter-Ln distance ca. 3.9 Å), i.e., two edge-sharing {LnO<sub>6</sub>} octahedral embedded in a crystalline matrix, were reported. It is totally unprecedented that in AV-24 Eu<sup>3+-</sup>O-Eu<sup>3+</sup> dimers behave like discrete entities, i.e., molecules: they (i) have a unique emission signature, with pseudopoint group symmetry (Ci), different from the symmetry (C1) of each individual constituent Eu<sup>3+</sup> ion, and (ii) exhibit the unusually long <sup>5</sup>D<sub>0</sub> lifetime of 10.29 ms (12 K). In accord with the experimental evidence, a molecular orbital model shows that the Eu<sup>3+-</sup>O-Eu<sup>3+</sup> dimers are energetically more stable than the individual metal ions.

Stirred tank experiments with microporous titanosilicates ETS-4 and ETS-10 were carried out to study the equilibrium and the kinetics of the removal of  $Hg^{2+}$  and  $Cd^{2+}$  (former material) and  $Cd^{2+}$  (latter material) from aqueous solution. While ETS-4 has a considerable affinity for  $Cd^{2+}$  ions, ETS-4 has a high affinity for both metal cations, even when their initial concentrations are low. The uptake rates for  $Hg^{2+}$  and  $Cd^{2+}$  were well described by both Nernst-Planck and pseudo-second order models. Results confirmed that the kinetics of the removal of  $Cd^{2+}$  is faster than that of  $Hg^{2+}$ . However, at equilibrium, ETS-4 has a higher capacity to remove  $Hg^{2+}$  than  $Cd^{2+}$ .

*Hybrid Materials.* A series of innovative di-urea cross-linked poly(oxyethylene) (POE)/siloxane hybrids (di-ureasils) modified by distinct lanthanide  $(Ln^{3+})$ -based complexes have been prepared with enhanced photoluminescence features. In particular, the  $[Eu(btfa)_3(MeOH)_2]_2$ bpeta<sub>2</sub> complex  $(Ln^{3+}=Eu^{3+}, Gd^{3+}, btfa is the 4,4,4-trifluoro-I-phenyI-1,3-butanedionate ion, MeOH is methanol and bpeta is 1,2-bis(4-pyridyI)ethane) has been incorporated into the di-ureasil hybrid. The synergy between the absorption ability of the btfa and bpeta cromophores and the hybrid's emitting centres creates additional and efficient bpeta-to-hybrid and bpeta-to-btfa transfer channels that optimize the metal sensitization process contributing for the large measured emission quantum yield. The incorporation of Na<sub>3</sub>[Eu(dipic)<sub>S</sub>]•xH<sub>2</sub>O (dipic<sup>2-</sup> is the dipicolinate ion) complex into the di-ureasils accounts for an increase of both the quantum efficiency and quantum yield values, with respect to those of the isolated complex. Di-ureasils incorporating Tb(acac)<sub>3</sub>•3H<sub>2</sub>O (acac is acetylacetonate) were also synthesized via conventional hydrolysis sol-gel reaction in the presence and absence of an acid catalyst. An increase in the Tb<sup>3+</sup> excited state lifetime values, relatively to that of the isolated Tb(acac)<sub>3</sub>•3H<sub>2</sub>O complex, was observed, suggesting the replacement of the Tb<sup>3+</sup> coordinated water molecules by the oxygen atom of the carbonyl group of the di-ureasil host.$ 

The unusual role played by the di-urethane cross-linked POE/siloxane hybrid matrix (di-urethanesil) in the immobilization of the  $\beta$ -diketonate aquocomplex Eu(btfac)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub> (btfac is the 4,4,4-trifluoro-1-phenyl-2,4-butanedionate ion) demonstrate that the di-urethanesil host acts as an inert (although optically active) support, enabling Eu<sup>3+</sup> sensitization by the btfac ligands and the the hybrid host excited states. It was also provided evidence that the incorporation of the Eu(btfac)<sub>3</sub>phen (phen is 1,10-phenantroline) complex into the same hybrid matrix is disadvantageous from the quantum efficiency standpoint, because of the severe steric hindrance that emerges between the POE chains of the host structure and the bulky phen molecules, leading to the expulsion of these ligands from the Eu<sup>3+</sup> first coordination sphere and to their replacement by two water molecules.

A series of novel, colourless, and transparent sol-gel derived hybrid materials Ln-DBM-Si covalently grafted with Ln(DBM-OH)<sub>3</sub>•2H<sub>2</sub>O (where DBM-OH=o-hydroxydibenzoylmethane, Ln=Nd, Er, Yb, and Sm) were prepared through the primary  $\beta$ -diketone ligand DBM-OH. The results revealed that the lanthanide complexes were grafted in situ into the corresponding hybrids Ln-DBM-Si.

Ternary europium complex Eu(tta)<sub>3</sub>phen (tta=2-thenoyltrifluoroacetonate) was covalently bonded with the mesoporous material SBA-15 and SBA-15-type of periodic mesoporous organosilica (PMO) material via impregnation of Eu(tta)<sub>3</sub>•2H<sub>2</sub>O into phen-S15 and phen-PMO, respectively, through a ligand exchange reaction. The photophysical properties of the hybrids, such as the photoluminescence (PL) spectra, PL intensities, symmetry properties, luminescence decay times, and Judd-Ofelt parameters, were investigated. In addition, a novel BA-PMO (BA=benzoic acid) material was also synthesized through one-step co-condensation of 1,2-bis(triethoxysilyl)ethane (BTESE) and BA-functionalized organosilane using cetyltrimethylammonium bromide (CTAB) as a structure-directing agent under basic conditions. BA-PMO was attempted as a supporter to link the Tb<sup>3+</sup> ions via impregnation of TbCl<sub>3</sub> into BA-PMO through a ligand exchange reaction. The result showed that the mesostructure of the sample remained intact. Under the UV radiation, the sample exhibited the characteristic strong emission of Tb<sup>3+</sup>.

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The emergent complex behaviour in self-assembled alkylene/siloxane organic-inorganic hybrid nanostructures will be modelled through the emitted relaxation energy of the nanohybrid upon repeated heating/cooling cycles. The individual dynamics of the amide crosslinkages connecting the organic and inorganic components will be related to the hierarchical dependence on the system's collective dynamical features. On the other hand, new organic-inorganic hybrids lacking activating centres will be developed seeking for the development of new phosphors featuring (i) high quantum yield, (ii) high brightness, (iii) stability in time and under irradiation, and (iv) ability to be excited with cheap light sources (LEDs).

Organic-inorganic hybrid materials were prepared by combining lanthanide(III) substituted Wells–Dawson anions as inorganic building blocks and 3-hydroxypicolinate (picOH) as the organic ligand. Photoluminescence measurements on the prepared hybrid materials show that in all cases the lanthanide emission was sensitized by both the picOH ligand and the polyoxometalate moiety.

A miniaturized prototype for pH sensing in the pH range 5-7.5 was constructed from a photoluminescent Eu<sup>3+</sup> metal-organic framework that contains two different Eu<sup>3+</sup> sites and self-assembles through hydrogen bonding and  $\pi$ - $\pi$  interactions. This material has a very high quantum yield and an excellent balance between absorption, energy transfer, and emission rate.

The use of the polyphosphonic acid ligand (carboxymethyl)iminodi(methylphosphonic acid (H<sub>5</sub>cmp) with lanthanide centres allowed the preparation, via the hydrothermal method, of two systems of functional micro-crystalline powders:  $[Ln(H_2cmp)]\cdot xH_2O$  [x < 1;  $Ln^{3+} = Nd^{3+}$  and  $Eu^{3+}$ ] and  $[RE(H_2cmp)(H_2O)]$  [ $RE^{3+} = Y^{3+}$ ,  $La^{3+}$ ,  $Pr^{3+}$ ,  $Nd^{3+}$ ,  $Sm^{3+}$ ,  $Eu^{3+}$ ,  $Gd^{3+}$ ,  $Tb^{3+}$ ,  $Dy^{3+}$ ,  $Ho^{3+}$  and  $Er^{3+}$ ]. Their structure was elucidated from high-resolution powder X-ray diffraction (collected at the ESRF in Grenoble, France) with solid-state NMR, TGA, electron microscopy, vibrational spectroscopy and elemental composition studies. [ $RE(H_2cmp)(H_2O)$ ] materials were found to efficiently heterogeneously catalyse the cyclodehydration of xylose to furfural. Catalysts could be easily separated from the reaction medium and re-utilised without loss of activity.

Modular mixed-metal  $M_4[M_{12}V_{24}O_{24}(OH)_8(H_2hedp)_8(Hhedp)_{16}(H_2O)_{64+n}]$ •88+ $y(H_2O)$  (M<sup>3+</sup> = Y<sup>3+</sup>, Ce<sup>3+</sup>, Sm<sup>3+</sup>, Eu<sup>3+</sup>, Tb<sup>3+</sup>, Gd<sup>3+</sup>, Er<sup>3+</sup>; H<sub>5</sub>hedp = etidronic acid) were prepared either as large single-crystals (hydrothermal method) or microcrystalline powders from reactions at ambient temperature. Structures have large channels and it was found that the co-existence of V<sup>4+</sup> and Eu<sup>3+</sup> allows the tuning of the photoluminescence emission from white to purplish-blue.

It has been shown that according to the synthetic approach adopted (hydrothermal and solvothermal), 2,5-pyridinedicarboxylic acid (H<sub>2</sub>pydc) forms different metallic clusters (buildings units) with lanthanides which ultimately lead to topologically distinct MOF compounds:  $(CH_3)_2NH_2[Ln(pydc)_2] \cdot \frac{1}{2}H_2O$  [Ln<sup>3+</sup>= Eu<sup>3+</sup>or Er<sup>3+</sup>], [Er<sub>4</sub>(OH)<sub>4</sub>(pydc)<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub>] • H<sub>2</sub>O and [Pr<sup>III</sup><sub>2</sub>Pr<sup>IV</sup>1.25O(OH)<sub>3</sub>(pydc)<sub>3</sub>].

Detailed investigations have been performed on the experimental and predicted (using the Sparkle/AM1 model) photophysical luminescent properties of the  $[Ln_2(MELL)(H_2O)_6]$  MOF material (where  $Ln^{3+} = Eu^{3+}$ ,  $Tb^{3+}$  and  $Gd^{3+}$ ;  $H_6MELL =$  mellitic acid). It was inferred that the theoretical models reproduce well the observed features, and this opens a new opportunity for the rational in silico design of novel and highly efficient MOFs. The porous features of the CuBTC MOF were also investigated by comparing the experimental isotherms with grand canonical Monte Carlo simulations, showing that the adsorption of propane occurs preferentially in small octahedral pockets while propylene interacts strongly with the unsaturated metal sites.

A new family of cyano-bridged coordination polymers  $Ln(H_2O)_5[M(CN)_8]$  (Ln=Eu, Tb, Sm, Gd; M = Mo, W) were obtained. The Eu- and Tb-containing coordination polymers are room-temperature optically active emitters displaying the characteristic intra-4f transitions, revealing long-range magnetic ordering at low temperatures. The coexistence of luminescence with ferromagnetic ordering for  $Tb(H_2O)_5[M(CN)_8]$  (M=Mo, W) suggests that these compounds may be considered as bifunctional magneto-luminescent coordination polymers exhibiting diverse physical responses when subjected to external stimuli.

**Mesoporous Materials.** Stable mesoporous membranes with a cubic structure, based on MCM-48, were prepared on alumina supports by hydrothermal synthesis, starting from sols with CTABr and TPAOH templates. The inclusion of a zeolite (MFI-type) precursor during membrane synthesis led to partial zeolite incorporation into the porous structure, giving rise to a hydrothermally stable membrane. Membranes were tested in the gas phase separation of binary organic (cyclohexane, benzene and n-hexane)/O<sub>2</sub> mixtures.

Tetrakis(naphthoyltrifluoroacetonato)Ln(III) complexes (Ln = Eu, Gd) containing tetrabutylammonium, imidazolium and pyridinium cations were prepared and characterised by single crystal XRD and photoluminescence spectroscopy. An immobilised analogue of the 1-butyl-3-methylimidazolium salt was prepared by supporting  $[Eu(NTA)_4]^-$  on an ordered mesoporous silica derivatised with 1-propyl-3-methylimidazolium groups. The emission quantum yield measured for the supported material was the highest so far reported for lanthanide-containing ordered mesoporous silicas.

A mesoporous silica-supported molybdenum oxide catalyst was prepared by liquid phase deposition of MoO<sub>2</sub>Cl<sub>2</sub>(dimethylformamide)<sub>2</sub> onto MCM-41. FTIR spectroscopy, solid state MAS NMR and Mo K-edge EXAFS studies showed that the Mo atoms were mainly present as isolated, monomeric dioxomolybdenum(VI) species, bipodally anchored via Mo-O-Si linkages. The catalyst exhibited high activity, stability and recyclability in the liquid-phase oxidation of unfunctionalised olefins using *tert*-butylhydroperoxide as the oxidant. Under optimised conditions, the corresponding epoxides could be obtained as the only reaction products.

**Layered Materials.** Carboxylate intercalated (terephthalate, TA and oxalate) layered double hydroxides (LDHs) were aged under a microwave–hydrothermal treatment. The influence of the nature of the interlayer anion during the ageing process was studied. The microwave–hydrothermal method may be extended to synthesize LDHs with anions other than carbonate, such as TA.

A novel layered zinc phosphate,  $[N_2C_6H_{12}]_2[Zn_7H_3(HPO_{4-x})_5(PO_4)_3]$ •H<sub>2</sub>O, with unique 10 memberedring ellipsoidal channels running perpendicularly to ladder-shaped tetrahedral layers, was synthesized ionothermally via in situ generation of 1,4-diazabicyclo[2.2.2] octane.

A supported catalyst prepared by the immobilisation of  $CuCl_2$  in a layered double hydroxide containing 2,2'-bipyridine-5,5'-dicarboxylate (BDC) anions was tested in the oxidation of various substrates at room temperature, using aqueous  $H_2O_2$  or *tert*-butylhydroperoxide as oxidant. The main products were benzaldehyde from styrene, acetophenone from ethylbenzene, and a mixture of cyclohexanol and cyclohexanone from cyclohexane. Titration experiments showed that LDH-BDC/Cu was significantly more efficient than the model homogeneous catalyst [Cu(bipy)Cl<sub>2</sub>] in terms of the "productive" consumption of the oxidant.

Hydrotalcite-like Mg-Al-NO<sub>3</sub>-layered double hydroxide (LDH) was successfully prepared in a mortar by manually grinding the hydrated magnesium and aluminum nitrate salts with sodium hydroxide. The LDH prepared in the mortar does not require heating/refluxing treatment, CO-free atmosphere and solvent as in the conventional preparation methods and allows obtaining LDHs in a short reaction time.

**Nanostructured Materials.** The motion of *individual* Sr adatoms within the limits of periodic Si surface reconstructions was investigated and could determine, for the first time, the average speed of a Sr atom wandering around in a Si surface. Experimental results have shown that the fast movement of the atom at the Si surface produces sharp signal fluctuations in scanning tunneling microscopy (STM) images resulting into noise like patches. It was demonstrated the possibility to estimate the average speed of an atom moving on the surface by simulating the STM image streaks within such noise like patches. This was accomplished through Monte Carlo simulations of independently moving Sr atom and scanning tip. Thus, by colleting STM images at various scanning speeds and matching simulated image features to the experimental observations, allows the average speed of Sr adatom to be deduced: 300nm/s.

Device structures based on GaN and related alloys, including thin films, single (SQW) and multiple quantum wells (MQWs), diamond and electroceramic structures were studied by high-resolution X-ray diffraction in order to gain an insight regarding the effects of strain and composition on various material physical properties relevant in terms of device performance and functionality. Moreover, the nitride light emitting MQWs was used as a platform to integrate other material systems, namely metallic nanocrystals, achieving plasmonicaly-active nanostructures tailored with nanometre scale control. Surface properties of such materials have also been investigated.

Hydrogel nanospheres having superparamagnetic properties were prepared via reverse microemulsions containing iron oxides and combined with thermally induced gelation of the biopolymer (e.g. carrageenan). The research focused on the synthesis of size-controlled composite nanospheres, chemical surface functionalisation and antibody conjugation for biological recognition purposes. The thermal properties were investigated and revealed the potential of these systems for thermally controlled release of loaded drugs.

Nanocomposite materials of fine divided inorganic materials, such as Ag (or ionic silver) and TiO<sub>2</sub>, dispersed in cellulose fibres have been prepared and their properties have been evaluated, which include antimicrobial activity and surface hydrophobicity. Chemical surface strategies of both the fibres and nano-fillers have been investigated.

Submicron particles of amorphous  $SiO_2$  have been used to grow  $Ag_2S$  nanophases at their surfaces. These nanocomposites were investigated as anti-fungal agents in different experimental conditions, including as nanofillers in cellulosic fibres. The anti-fungal activity in these composite systems is suggested to result from a synergistic effect due to Ag2S anti-fungal centres and the SiO<sub>2</sub> surfaces in promoting the adsorption of the fungus.

A process of Ti $O_2$  photosensitization by coupling it with a narrow band gap semiconductor has been investigated. Distinct Ti $O_2/Ag_2S$  nanocomposites were prepared by a single-source decomposition method. After sensitization, the Ti $O_2$  materials were evaluated as photocatalysts on the degradation of aqueous phenol solutions. The experimental results show that nanocomposites photocatalytic activity is related with the existence of  $Ag_2S$  over the Ti $O_2$  surface.

Photoluminescent nanoparticles comprising a core of lanthanide complexes and shells of amorphous silica have been prepared, using reverse micelles as nanoreactors and envisaging biotagging applications. 3 Hydroxypicolinate complexes of Eu(III), Tb(III), and the corresponding heteronuclear complexes have been investigated as the photoactive cores. The size of the silica particles is within the nanometer scale, which, together with the ability for surface biofunctionalization, opens up perspectives for their use in bioapplications. Optical studies of the as-prepared nanoparticles reveal that the luminescence properties of the 3-hydroxypicolinate complexes in the matrices are markedly different from their original features.

The synthesis of quantum dots (QDs)/polymer nanocomposites by reversible addition-fragmentation chain transfer (RAFT) polymerization in miniemulsions using a grafting from approach has been investigated. First, the surfaces of CdS and CdSe QDs were functionalized using a chain transfer agent, a trisalkylphosphine oxide incorporating 4-cyano-4-(thiobenzoylsulfanyl)pentanoic acid moieties. Using a free radical initiator (AIBN) to activate the RAFT process, a polystyrene (PS) block was grafted from the surface of the QDs. Quantum confinement effects were identified for the nanocomposite obtained, so attesting to the integrity of the QDs after the polymerization. Free PS chains were also present in the final nanocomposite, indicating that the RAFT polymerization from the surface of the QDs was accompanied by conventional free radical polymerization. After isolating the nanocomposite particles, a second poly(n-butyl acrylate) block was tentatively grown from the initial PS block. The results indicated a successful polymerization of the second polymer and show the potential of the current strategy to prepare block copolymers from the surface of the RAFT-modified QDs

The work on ordered hybrid and doped nanostructures was continued especially by targeting new nanostructured inorganic materials (e.g. Mn, Cr doped nanoparticles). As an example, the functionalization/coating of complex nanostructures (e.g. nanotubes, nanowires, opals) with various metal oxides for application in various timely fields such as energy storage, (photo)-catalysis and gas sensing was studied. Advanced structural characterization techniques were applied for a deep understanding of the structure-properties relation especially in gas sensing devices.

Nanostructured materials synthesized by non-aqueous sol-gel routes, as well as thin metal oxide films that have been deposited by atomic layer deposition onto the surface of a variety of supports, have been characterized by electron microscopic techniques. A combination of high resolution imaging and spectroscopic techniques, such as energy dispersive X-ray spectroscopy (EDXS) and electron energy loss spectrometry (EELS), was used to study the materials in terms of structure, growth mechanism, chemical composition and purity.

The hierarchical assembly of organic and inorganic layers in nacre was studied. Observation of the inorganic part, which is made up from calcium carbonate platelets, revealed that the platelets consist of densely packed nanocrystals. Although some of these nano building blocks are oriented in a random way, each platelet diffracts like a single crystal. The assembly and hierarchical ordering of the constituting nanoscopic building blocks as well as the role of organic molecules in the process of crystallisation is not fully understood yet and will be the subject of future work in this biomineralization research topic.

**Non-Aqueous Chemistry Applied to Atomic Layer Deposition.** Non-aqueous sol-gel approaches applied to the atomic layer deposition technique was further investigated and new materials were deposited on different substrates targeting application in the field of energy and environment. The development of multiferroic materials was continued using the approaches developed in the last few years by embedding a film made of ordered magnetic nanoparticles in a piezoelectric matrix.

**Polyoxometalates.** Synthesis, structural studies, reactivity and applications of polyoxometalates have developed in the following lines: (1) Hybrid compounds with polyoxometalates and organic moieties: the study of compounds with  $[PW_{11}O_{39}M(H_2O)]_n$ - (M = Fe, Mn, Co) and 1-butyl-3-methylimidazolinium was continued. Compounds with the same anions and trihexyltetradecylphosphonium were prepared and characterized. (2) Polyoxometalates supported on silica nanoparticles: the materials prepared were tested as heterogeneous catalysts for the epoxidation of monoterpenes with hydrogen peroxide. (3) Polyoxotungstates in the homogeneous catalytic oxidation of organic compounds. (4) Preparation of chemically modified electrodes by the layer–by-layer method with polyoxotungstates. Electrodes modified with iron-silicotungstates have been also prepared by electrodeposition.

**Catalytic Materials.** A series of molybdenum(VI) complexes were prepared and characterised, namely the thiocyanate complexes (PPh<sub>4</sub>)<sub>2</sub>[MoO<sub>2</sub>(NCS)<sub>4</sub>], MoO<sub>2</sub>(NCS)<sub>2</sub>(di-tBu-bipy) and Mo<sub>2</sub>O<sub>5</sub>(NCS)<sub>2</sub>(di-tBu-bipy)<sub>2</sub> (di-tBu-bipy) = 4,4'-di-tert-butyl-2,2'-bipyridine), the complex MoO<sub>2</sub>(L) bearing a tetradentate oxazoline ligand with four stereocenters, and the adducts MoO2Cl2(L)2 (L = N,N-dialkylamide). The treatment of MoO<sub>2</sub>Cl<sub>2</sub>(DMF)<sub>2</sub> with an excess amount of tert-butylhydroperoxide (TBHP) gave the dimer Mo<sub>2</sub>O<sub>4</sub>(µ<sub>2</sub>-O)Cl<sub>2</sub>(DMF)<sub>4</sub>, which was characterised by single-crystal XRD. The complexes were studied as catalysts or catalyst precursors for the oxidation of olefins, the oxidation of benzyl alcohol, the dehydrogenation of alcohols, and the sulfoxidation of sulfides, using either DMSO or TBHP as the oxidant. In related work, an amino acid-functionalised cyclopentadienyl molybdenum tricarbonyl complex was prepared, characterised by XRD, and examined as a catalyst precursor in the epoxidation of *trans*- $\beta$ -methylstyrene.

Bis(oxazolines) chiral ligands and its functionalised derivatives were synthesised. The former were encapsulated in Cu(II) permutated zeolite type materials and tested as heterogeneous catalysts for the cyclopropanation of styrene showing activity, chemo and regioselectivity. A biomimetic tetradentate ligand and 1<sup>st</sup> series transition metal coordination compounds were also synthesised for application as catalysts in the sustainable selective oxidation of alkanes.

**Development of Spectroscopic and Microscopic Techniques for Materials Characterization.** The performance of various high-resolution 1D windowed H-1 CRAMPS pulse schemes (wDUMBO, wPMLG3 and wSAM3) using state-of-the-art electronics is investigated on small biological molecules. H-1 CRAMPS spectra are reported for the first time. Two-dimensional H-1 homonuclear correlation NMR spectra of biological and inorganic solids have been recorded at high magnetic fields (up to 18.8 T) and MAS rates up to 67 kHz, using BABA and RNnv symmetry-based homonuclear recoupling and CRAMPS decoupling. These methods afford exceptional spectral resolution and are well suited to probe H-1-H-1 proximities in powdered solids. 1H resonance assignment was confirmed with the help of DFT calculations of NMR parameters.

We have developed a new high-resolution two-dimensional (2D) heteronuclear correlation experiment between half-integer quadrupolar and H-1 nuclei, combining Satellite Transition Magic-Angle Spinning (STMAS) and wPMLG3 CRAMPS methods. The experiments use split-t(1) versions of DQ/DQF-STMAS adapted to 3/2 and 5/2 spins to obtain a Na-23 and Al-27 isotropic dimension, respectively.

Molecularly imprinted polymers (MIPs) of poly(ethylene glycol dimethacrylate) and poly(Nisopropylacrylamide-co-ethylene glycol dimethacrylate) were synthesized for the first time in supercritical carbon dioxide (scCO<sub>2</sub>), using Boc-I-tryptophan as template. Supercritical fluid technology provides a clean and one-step synthetic route for the preparation of affinity polymeric materials with sensing capability for specific molecules. The polymeric materials were characterized by <sup>13</sup>C solid-state NMR.

New SERS (Surface-Enhanced Raman Scattering) substrates have been investigated. Graphene/gold nanocomposites were studied as potential substrates for SERS in particular for single gold nanoparticle SERS studies. A good SERS signal was obtained for rhodamine 6G adsorbed at a graphene/gold nanocomposite. Complete vibrational studies including SERS studies were performed for the compounds 2-(Methoxycarbonylmethylsulfanyl)-3,5-dinitrobenzenecarboxylic acid and 2phenoxymethylbenzothiazole.

Cyclodextrins and Inclusion Compounds. It has been shown by SANS that methylated and unsubstituted cyclodextrins interact in a qualitative different way with sodium decanoate micelles in water. In particular, permethyl- $\alpha$ CD, dimethyl- $\beta$ CD and permethyl- $\beta$ CD display linear increases of the specific surface area, with slopes following the degree of methylation of the cyclodextrins, whereas  $\alpha$ CD and  $\beta$ CD present close S/V values which are approximately independent of the cyclodextrin concentration, at least for the considered concentration range (from 5 mM up to 45 mM). The linear slopes of S/V observed for the methylated cyclodextrins are consonant with equilibrium between the adsorbed cyclodextrin and the cyclodextrin in bulk water. In addition, when a cyclodextrin is added to the 200 mM perdeuterated sodium decanoate NaDec( $d_{19}$ ) solution in D<sub>2</sub>O ([CD]o=30 mM), methylated cyclodextrins show correlation peaks in the I(Q) distributions, whereas  $\alpha$ CD and  $\beta$ CD do not originate any correlation maximum. On the whole, the experimental results point to the adsorption of methylated cyclodextrins on the surface of the formed decanoate micelles. In turn, unsubstituted cyclodextrins are not adsorbed by the decanoate micelles and so are involved in guest-host equilibrium with the decanoate ion in solution. It is suggested that methylated cyclodextrins should be more easily adsorbed on the electric double layer of the decanoate micelle-water interface than the unsubstituted cyclodextrins, as the former sample a more favorable environment, where the dielectric permittivity is lower than in bulk water, and so is closer to those of the methylated cyclodextrins.

The preferential inclusion geometries, as well as their determining intermolecular interactions, in the inclusion compounds of organic molecules in alpha, beta and gamma-Cyclodextrins have been studied by vibrational spectroscopy, combined with TG data, *ab initio* calculations and information from CSD database. For phenol derivatives, the inclusion compounds of meta-substituted guests in aCD present unusual 1:2 and 2:3 stoichiometries. The Raman spectra of these inclusion compounds reveal the split of several modes, spread over the entire spectral range, indicating the presence of guest molecules inside and outside the CD cavity. In the case of cinnamic acid derivatives, the inclusion of host/guest hydrogen-bonding contacts appear to be the main factors determining the inclusion geometries.

**Computer Aided Characterization of Materials' Structure and Properties.** Particular attention has been given to the description of materials by combining computational modelling with spectroscopic techniques. The development and optimization of new methodologies for the study of molecular crystals at *ab initio* level and their further extension to functional materials and hybrids are two main goals pursued. Contacts with groups with expertise in the computational approach to problems such as SERS effect and rare-earth luminescence quantum yield widened our modelling skills – and improved the links between the computational bench and the conventional laboratory bench.

Calculations based on DFT functional theory (DFT) were applied to the study of intermolecular contacts in crystalline samples of pharmaceutically active compounds, such as nitrofurantoine and transcinnamic acid. Through the combined use of vibrational spectroscopy and DFT results, it was possible to identify the most relevant effects of intermolecular contacts in the pseudo-polymorphic anidrate/hydrate forms of nitrofurantoine and the conformational preferences of trans-cinnamic acid pure and included in cyclodextrins. An example of the use of computational tools in the interpretation of SERS spectra was provided with the study of 5-Fluorouracil adsorbed on silver nanostructures. Comparison of observed and calculated SERS intensities shows that the Charge Transfer mechanism is dominant relative to the Electromagnetic Enhancement mechanism and that the 5-Fluorouracil molecule lies almost perpendicular to the metallic surface.

Classical and first principles parallel calculations were performed in Flamingo@CICECO cluster aiming at the calculation of NMR chemical shifts in solids, determination of gas-phase thermochemical properties, calculation of thermodynamic and kinetic profiles of heterogeneously catalyzed reactions, and interpretation of molecular reactions occurring in the condensed phase. The most expensive calculations involved the optimization of the structures of different types of systems (reactants and products of reactions either in the gas or condensed phases), searches of transition state structures, and calculation of vibrational frequencies or NMR shifts. Several of these calculations were done in close collaboration with experimental work. For instance, the combination of density functional theory (DFT) and periodic approaches was found to be quite promising in aiding the interpretation of experimental NMR data for complex solid systems. Furthermore, *NpT* classical molecular dynamics (MD) simulations have been carried out for aqueous solutions of amino acids (Ala, Gly, Ile, Val, ...) in the presence of salts (NaCl, KCl, NaNO<sub>3</sub>,...) aiding the interpretation of the molecular-level mechanisms by which ions affect the solubility behaviour of amino acids (salting-in to negligible to salting-out effects) measured experimentally in CICECO.



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### scientific highlights

i) Fabrication of BaxSr<sub>1-x</sub>TiO<sub>3</sub> thin films at 120 °C on flexible polymeric Kapton films.

ii) Synthesis of the novel porous BaTiO3 ferroelectric films and particulates.

ii) Identification of high effective piezoelectric coefficient values in self-assembled diphenylalanine peptide nanotubes.

iv) Polarization switching kinetics of ferroelectric polymer nanomesas fabricated by selforganization from Langmuir–Blodgett.

v) Modelling of the effect of the annealing rate on the crystallization of SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub>.



SEM micrographs of TiTe<sub>3</sub>O<sub>8</sub>

#### 30 | research team

## research team

at 31<sup>st</sup> december '09











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## activity report 2009

**High Frequency Dielectric Materials.** TiTe<sub>3</sub>O<sub>8</sub> thick films were fabricated by electrophoretic deposition on platinized Si substrates using TiTe<sub>3</sub>O<sub>8</sub> powders synthesized by a conventional solid-state reaction. The permittivity of TiTe<sub>3</sub>O<sub>8</sub> films is 54, with loss tan d of 0.009, measured at 100 kHz. The temperature coefficients of permittivity of TiTe<sub>3</sub>O<sub>8</sub> films and ceramics between 35 and 200 °C are +78 and -100 ppm/°C, respectively. It was proved that TiTe<sub>3</sub>O<sub>8</sub> ceramics and films can be well sintered below 800 °C and, consequently, have the potential to be used for low-temperature co-fired ceramics.

The modification of the structural and dielectric properties of sol gel derived MgTiO<sub>3</sub> films by doping with Ni and Zn was exploited. The change of the dielectric response and unit cell parameters of doped MgTiO<sub>3</sub> was correlated with Ni and Zn occupancy. The temperature stability of MgTiO<sub>3</sub> thin films was improved with doping, while the dielectric losses were aggravated with both Zn and Ni doping which is correlated with the localised d electrons of the dopant cations. The dielectric permittivity decreased with Ni doping while it increased with Zn, which is attributed to the lower ionic polarizability of Ni<sup>2+</sup> (1.23 ?3) as in comparison with Mg<sup>2+</sup> (1.32 A3) while Zn<sup>2+</sup> has a higher ionic polarizability (2.04 ?3).

A systematic approach was used to successfully fabricate composite thick films by EPD. Firstly, BLT and BNT powders were prepared by solid-state reaction synthesis and the phase purity of the powders was confirmed by XRD. The size and morphology of the powders were assessed by particle size analysis and scanning electron microscopy. BNT and BLT suspensions were prepared in different suspension media such as water, ethanol and acetone. The pH of the suspension was varied by dilute nitric acid and triethanolamine. Concomitantly the stability of the suspensions were used for the deposition of particles in acidic and basic conditions, and the processing parameters such as thickness, deposit weight, current as a function of time and voltage were studied.

*Ferroelectric Ceramics and Ferroelectric Fibres, Single Crystals and Films.* Lead Zirconate Titanate (PZT, 53/47) fibres were prepared by sol-gel method using organic acids - acrylic and methacrylic acid - to modify the precursors. The macroscopic properties, molecular structure, crystallization behaviour and microstructure of the fibers were investigated as a function of the content and type of acid. Organic acids produce long gel and ceramic fibres, due to the beneficial effect of the long polymeric chains that are generated in the precursor gel. However the longest strongest, densest and with the highest homogeneity fibres were obtained when acrylic acid is used. The linear shape of the molecular structure of acrylic acid, together with a lower content of organic species to be released, is favourable to the preparation of round and crack free PZT fibres, when acrylic acid is used.

 $Ba_xSr_{1-x}TiO_3$  (x = 1, 0.9, 0.7, 05, 0.3, 0.1, and 0) polycrystalline thin films were fabricated at low temperature (120 °C) and for a short time (1 h) by a hydrothermal process on commercial flexible polymeric Kapton films. Microstructural analysis showed that dense  $BaTiO_3$  thin films comparable to those derived from long time hydrothermal processes were achieved with the present synthesis conditions. With increasing strontium content,  $Ba_xSr_{1-x}TiO_3$  film thickness decreased and grain size increased. For x = 0, i.e.,  $SrTiO_3$ , the films displayed a monolayer of coarse grains. The variation of the film morphology with the composition suggests a faster nucleation and reaction kinetics for  $BaTiO_3$  than  $SrTiO_3$ . Electrical characterization showed high capacitance densities and acceptable dielectric loss for the films after post-annealing in oxygen. Existence of polar domains in the hydrothermally synthesized  $BaTiO_3$  thin films was proved by piezo- response force microscopy (PFM). All the used processes were compatible with commercial Kapton films, showing the technological value of this work for the deposition of large area capacitors onto flexible printed circuits, such as for embedded capacitors integrated into Printed Circuit Boards (PCB).

The effect of rapid thermal annealing and conventional furnace annealing on the crystallization of  $SrB_2Ta_2O_9$  was modelled using an Arrhenius-type equation. Based on the obtained results and on the analysis of literature data two concurrent reaction mechanisms were suggested to occur: (i) direct transformation of the reagents into the perovskite phase and (ii) transformation of an intermediate into the perovskite phase. These findings allowed to support that no different reaction mechanisms occur if different heating rates are employed during heat treatment as previously suspected. Moreover the validity of the Arrhenius equation to predict the behaviour of the crystallization process by either of the two heating methods mentioned above was confirmed too.

#### 32 | activity report 2009

Studies on the preparation and properties of Aurivillius oxides (AO) with n=5 were initiated.  $Sr_{2}$ ,  $Ca_xBi_4Ti_5O_{18}$  (x=0, 0.05) [SCBTx] compositions have been synthesized by conventional solid state reaction. The adequate heat treating conditions for obtaining dense and single phase SCBTx (x=0, 0.05) ceramics were identified. The uniaxial pressing used for green powder consolidation allowed the ceramics to develop a modest but sufficient texture for enabling anisotropic microstructure and electrical properties to be obtained. The dielectric and ferroelectric properties of the obtained ceramics showed to be strongly dependent on the applied field direction being the values measured with the electric field parallel to (a,b) plane almost twice higher than those measured along c axis. Ca addition increases the Curie temperature from 280C to 310C. Although undopped ceramics denote better dielectric and ferroelectric properties than their Ca (5%) doped counterpart the present study demonstrates that it is possible to benefit from the increase of SCBT0.05 Curie temperature with a minimum loss of dielectric and/or ferroelectric property if a measurement direction that maximizes the ceramic properties is selected.

Lead zirconium titanate (PZT) sol–gel solutions were prepared based on distilled lead acetate precursor solutions. A detailed analysis of the distillation effect on the lead precursor and the final PZT solution were carried out by Infrared and Raman techniques. It was found that the increase in the number of distillation steps experienced by the lead precursor solutions removes the constitutional water and increases the lead acetate–2-methoxyethanol interconnectivity; thus improving stability and avoiding the aging effect of the resulting PZT solutions. Dense microstructure was found in all analyzed films and an incipient columnar grain growth was revealed in PZT films prepared based on lead precursor solution with more than three distillation steps. The dependence of the dielectric, ferroelectric and piezoelectric properties on the number of distillation steps was revealed and a correlation between the distillation process, film microstructure properties and electrical performance was established.

Zinc oxide (ZnO) thin films were grown on uncoated and zinc-coated Corning glass substrates by pulsed laser deposition (PLD). Piezoresponse imaging and local hysteresis loops acquisition were performed to characterize the piezoelectric and possible ferroelectric properties of the films. The outof-plane (effective longtitudinal, d??) and in-plane (effective shear, d||) coefficients were estimated from local piezoresponse based on the comparison with LiNbO<sub>3</sub> single crystals. Measurements of all three components of piezoresponse (one longitudinal and two shear signals) allowed constructing piezoelectric maps for polycrystalline ZnO and to relate the variation of piezoelectric properties to the crystallographic and grain structure of the films. Shifted piezoresponse hysteresis loop under high voltages hints to the possible pseudoferroelectricity as discussed recently by Tagantsev (Appl. Phys. Lett. 93, 202905, 2008).

Inclusions of lead oxide in ex-situ grown PZT thin films are known to give rise to a phenomenon of self-polarization. It is shown that dependence of self-polarization on thickness in the films deposited on glass ceramic/Pt substrate differs from those deposited on Si/SiO<sub>2</sub>/Pt substrate. Different behaviour is discussed in terms of mechanical constraints or tensile stresses acting upon the films by the substrate. Two types of mesoscopic scale dielectric constant nonuniformity over the entire surface of the film samples were studied. One of them deals with a local broken texture of grains in self-polarized films and another one is observed in the films annealed in the temperature range of phase transformation from perovskite polycrystalline disordered phase to perovskite <110>-textured phase. The role of lead oxide inclusions in the films is discussed.

PZT films were prepared "ex-situ" on Pt/Ti/SiO<sub>2</sub>/Si and Pt/Ti/pyroseram substrates by RF magnetron sputtering from ceramic targets additionally containing excess lead oxide. An unusual "beak" shape of pyroelectric and piezoelectric hysteresis loops measured by "remanent hysteresis" method was studied upon the application of strong electric fields, temperature, and surface morphology of PZT films. The nature of observed anomalies was explained.

PZT thin films were deposited directly onto copper-coated polymer foils. (111)-textured PZT was fabricated on these flexible substrates by means of a RF-modulated plasma jet system comprising a hollow cathode for reactive sputtering. Film composition and microstructure as well as piezoelectric and dielectric film properties were investigated. The deposited films are shown to be suitable as embedded capacitors as well as flexible piezoelectric sensors, actuators and power generators.
The characterization of sol-gel derived morphotropic phase boundary (MPB)  $0.37BiScO_3-0.63PbTiO_3$  (BSPT) thin films, deposited on IrO<sub>2</sub>/TiO<sub>2</sub>/SiO<sub>2</sub>/Si and Pt/TiO<sub>2</sub>/SiO<sub>2</sub>/Si substrates, was performed to identify the influence of the IrO<sub>2</sub> electrodes on the film's microstructure and electrical properties. Though the ferroelectric behaviour of both films is similar, with remanent polarization values of 26 micronC/cm2 and 23 micronC/cm2, respectively, for IrO2 and Pt bottom electroded films, the leakage current density (JL) at room temperature markedly decreases from > 10x6 A/cm2 for BSPT on Pt to the order of # 10x8A/cm<sup>2</sup> for BSPT on IrO<sub>2</sub>, under the maximum voltage of 4 V (80 kV/cm1). The formation of an interface layer between the film and the electrode, as observed by Rutherford Backscattering Spectroscopy, is proposed to have a space charge sink effect and, as a consequence, to account for the improvement of the leakage current behaviour of the IrO<sub>2</sub> electroded films.

**Incipient Ferroelectrics.** The effect of nonstoichiometry on the densification of  $SrTiO_3$  ceramics with Sr/Ti ratios from 0.997 to 1.02 was systematically addressed. The kinetics of densification was studied by dilatometric analysis. X-ray diffraction, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used for crystallographic and microstructure characterization. Ti excess enhanced matter transport during sintering whereas Sr excess decreased it. The shrinkage rate and average grain size increased with the decrease of Sr/Ti ratio. Close values of the activation energy for the initial densification and the near constant onset temperature for densification indicates that identical transport mechanisms control the densification of all the compositions. Small excesses of TiO<sub>2</sub> and SrO were mostly incorporated into the perovskite lattice inducing alterations in the defect chemistry of the material and the mass transport during sintering is controlled by Sr vacancies. Very small stoichiometric variations have a strong influence on the sintering kinetics and resulting microstructure of ST ceramics.

In this work it was proved that multiglass materials with simultaneous occurrence of two different glassy states applies to  $Sr_{0.98}Mn_{0.02}TiO_3$  ceramics, where A-site substituted  $Mn^{2+}$  ions are at the origin of both a polar and a spin cluster glass. Spin freezing is initiated below the dipolar glass temperature, Tge ~ 38 K, which is seemingly indicated by a divergence of the nonlinear susceptibility,  $\chi^3$ . Below Tgm ~ 34 K both glass phases are independently verified by memory and rejuvenation effects. Biquadratic interaction of the  $Mn^{2+}$  spins with ferroelectric correlations of their off-centre pseudospins in the incipient ferroelectric host crystal  $SrTiO_3$  explains the high spin glass temperature and comparably strong third-order magnetoelectric coupling between the polar and the magnetic degrees of freedom. Preliminary results on the related compound  $K_{0.97}Mn_{0.03}TaO_3$  favourably comply with the magnetoelectric multiglass concept. "Multiglass" materials extend the frame of conventional multiferroicity, which is devoted to crystalline materials with coexisting uniform long-range electric and magnetic ordering.

High quality potassium tantalate (KTaO<sub>3</sub>, KT) single crystals are grown by a high temperature self-flux solution modified method in which potassium carbonate ( $K_2CO_3$ ) and boron oxide ( $B_2O_3$ ) are used as a complex flux. Additions of small amounts of boron oxide, used because of its low melting temperature (450°C) and tendency to decrease the weight losses, increased the metastable region, requiring lower temperature (= 1300°C) for the growth of large KT crystals thereby suppressing the K volatilization tendency. By changing the flux composition and flux to solute proportion optimum growth conditions are established. The as-grown potassium tantalate crystals exhibit a dielectric permittivity of 6600 and dielectric losses of 0.004 at 13 K and 100 kHz. These results suggest a new promising approach for growing large size and high quality single crystals within KT based system.

**Nanoscale Properties of Ferroelectrics and Related Materials.** Piezoreponse Force Microscopy is a very important instrument that appears to be indispensable for studying novel nanoscale phenomena, especially in multifunctional materials. In the article published in MRS Bulletin (Sept. 2009), we review recent progress in this field that demonstrates great potential of PFM for the investigation of static and dynamic properties of ferroelectric domains, nanofabrication and lithography, local functional control, and structural imaging in a variety of inorganic and organic materials, including piezoelectrics, multiferroics, semiconductors, polymers, biomolecules, and biological systems. Future pathways for PFM application in high-density data storage, nanofabrication, and spectroscopy were discussed.

Piezoresponse force microscopy has emerged as a powerful and versatile tool for probing nanoscale phenomena in ferroelectric materials on the nanometer and micrometer scales. In the Feature Article published in the Journal of American Ceramic Society we summarized the fundamentals and recent advances in PFM, and describe the nanoscale electromechanical properties of several important ferroelectric ceramic materials widely used in memory and microelectromechanical systems applications. Probing static and dynamic polarization behaviour of individual grains in PZT films and ceramics is discussed. Switching spectroscopy PFM was introduced as a useful tool for studying defects and interfaces in ceramic materials. The results on local switching and domain pinning behavior, as well as nanoscale fatigue and imprint mapping were presented. Probing domain structures and polarization dynamics in polycrystalline relaxors (PMN-PT, PLZT, doped BaTiO<sub>3</sub>) were briefly outlined. Finally, applications of PFM to dimensionally confined ferroelectrics were demonstrated. The potential of PFM for studying local electromechanical phenomena in polycrystalline ferroelectrics where defects and other inhomogeneities are essential for the interpretation of their macroscopic properties was illustrated.

The spontaneous transition between the ferroelectric and relaxor states was investigated in  $0.86PbMg_{1/3}Nb_{2//3}O_3$ -0.14PbTiO<sub>3</sub> ceramics using piezoresponse force microscopy. Macroscopically, the transition from the ferroelectric to relaxor phases manifests itself by an anomaly in the temperature dependences of the dielectric permittivity and by a sharp decline of the remanent polarization. Alternatively, PFM reveals a decay of the ferroelectric micron-size domains at the macroscopic Curie temperature,  $T_c$ . Simultaneously, smaller domains of submicron sizes are observed at temperatures appreciably above  $T_c$ , being concentrated near grain boundaries. It is argued that the particular mechanical and electrical conditions at the grain boundaries promote nucleation of the ferroelectric phase.

Polarization switching in ergodic relaxor and ferroelectric phases in the PbMg<sub>1/3</sub>Nb<sub>2/3</sub>O<sub>3</sub>-PbTiO<sub>3</sub> (PMN-PT) system is studied using Piezoresponse Force Microscopy, single point electromechanical relaxation measurements, and voltage spectroscopy mapping. The dependence of relaxation behaviour on voltage pulse amplitude and time was found to follow a universal logarithmic behaviour with a nearly constant slope. This behaviour is indicative of the progressive population of slow relaxation states, as opposed to a linear relaxation in the presence of a broad relaxation time distribution. The role of relaxation behaviour, ferroelectric non-linearity, and the spatial inhomogeneity of the tip field on hysteresis loop behaviour is analyzed in detail. The hysteresis loops for ergodic PMN-10%PT are shown to be kinetically limited, while in PMN with larger PT content, true ferroelectric hysteresis loops with low nucleation biases are observed.

The influence of the neutralization process after hydrothermal synthesis on the structure and morphology of titanate nanotubes was investigated by X-ray diffraction, high-resolution transmission electron microscopy and Raman spectroscopy. Well formed nanotubes were obtained during the hydrothermal treatment of anatase in highly alkaline conditions. Synthesis at 150 °C led to the formation of layered titanate structure with the general formula Na<sub>2-x</sub>H<sub>x</sub>Ti<sub>2</sub>O<sub>5</sub> 1.8 H<sub>2</sub>O, where x depends on pH.

The synthesis of nanoporous barium titanate prepared under the assistance of Pluronic PE 10300 block copolymer was studied. Nanopores reside inside the BaTiO<sub>3</sub> crystallites that exhibit a specific BET surface area around 70 m<sup>2</sup>/g and nanopore volume fraction of 44.7%. X-ray diffraction of nanoporous BaTiO<sub>3</sub> indicates an average cubic structure while Raman spectra suggest local structural distortions of the lattice. With Landauer- Bruggeman effective medium approximation (LB-EMA), the dielectric constant (at 1 MHz) of nanoporous BaTiO<sub>3</sub> and solid BaTiO<sub>3</sub> (excluding all porosity) was estimated as 112 and 706, respectively, implying an effective way to manipulate the dielectric constant of materials by introducing nanopores. Morphology modification of ferroelectric materials at the nanoscale is an important aspect for further development of ferroelectrics.

*Multifunctional Ceramic Films and Composites.* [(BiFeO<sub>3</sub>)y(BiMg<sub>0.5</sub>Ti<sub>0.5</sub>O<sub>3</sub>)1-y]x[PbTiO<sub>3</sub>]1-x(BF–BMT–PT) ceramic powders were prepared by high temperature solid-state reaction method. X-ray diffraction analysis of the powders suggests the formation of a single-phase material with tetragonal structure. SEM images exhibit the uniform distribution of grains. Polarization vs electric field (P–E) hysteresis studies show maximum remanent polarization (?14  $\mu$ C/cm<sup>2</sup>) for composition x = 0.65. Dielectric studies of the compounds as a function of temperature show that the compounds undergo a diffuse phase transition with a transition temperature increasing with decreasing x. The diffusivity parameter of the phase transition for these compounds yielded values between 1.6 and 1.8 indicating significant variation of degree of disordering in the system.

**Polarization-Induced Self-Assembly of Organic and Biomolecules.** Ferroelectric polarization can be used to assemble various organic and inorganic species and to create nanostructures with controlled properties. In this work, we used P(VDF-TrFE) ultrathin films deposited by Langmuir-Blodgett technique as templates for the assembly of various phospholipids that are the essential components of cell membranes. It was observed that 1,2-Di-O-hexadecyl-*sn*-glycero-3-phosphocoline phospholipids (DHPC) form self-assembled structures (molecular domains) on bare P(VDF-TrFE) surface. These were revealed by the formation of homogenous and stable round blobs with diameters in the range 0.5-3 µm. Further, ferroelectric polymer films were polarized by the application of various voltages via conducting tip using Piezoresponse Force Microscopy (PFM) set up and PFM images were obtained showing controlled polarization distribution. After this, phospholipid molecules were deposited from the solution. Conventional Atomic Force Microscopy (AFM) experiments were then performed to assess the selectivity of the deposition process. It was observed that the deposition process is very sensitive to the concentration of the solution and type of phospholipids used. The selective deposition was observed only at the domain boundaries and selectivity reached a maximum value of 20-40%. In this way, the controlled assembly of organic molecules on the polymer surfaces could be achieved. In addition, the tip could be functionalized by the phospholipids and switchable lines of the polar molecules on the P(VDF-TrFE) surface could be obtained.

The polarization switching kinetics of ferroelectric polymer nanomesas was investigated using piezoresponse force microscopy. The nanomesas were made by self-organization from Langmuir–Blodgett films of a 70% vinylidene fluoride and 30% trifluoroethylene copolymer. The polarization switching time exhibits an exponential dependence on reciprocal voltage that is consistent with nucleation-type switching dynamics.

It was shown that anomalously strong shear piezoelectric activity in self-assembled diphenylalanine peptide nanotubes (PNTs), indicating electric polarization directed along the tube axis. Comparison with wellknown piezoelectric LiNbO<sub>3</sub> and lateral signal calibration yields sufficiently high effective piezoelectric coefficient values of at least 60 pm/V (shear response for tubes of \_200 nm in diameter). PNTs demonstrate linear deformation without irreversible degradation in a broad range of driving voltages. The results open up a wide avenue for developing new generations of "green" piezoelectric materials and piezonanodevices based on bioactive tubular nanostructures potentially compatible with human tissue.



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### scientific highlights

i) Observation of bias-induced phase transition to ferroelectric state in charge-ordered and magnetic manganites;

ii) Development of a nanometric luminescent ferrofluid;

iii) Development of a method to correctly calculate the magnetic entropy change in first-order phase transitions;

iv) Development of a method to produce ultrathin metallic oxygen barrier diffusion applied to Si-based components and microelectronics devices



Cover of the MRS bulletin of September 2009

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at 31<sup>st</sup> december '09

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# activity report 2009 Strongly Correlated Electron Systems: Theory and Experiment a) Multifunctional/multiscale phenomena in mixed valence colossal magnetoresistive and multiferroic oxides

The role of magneto-structural-electronic coupling is studied in a multiscale approach, from atomic ordering and nanoscopic phase separation phenomena to macroscopic phase transition effects. Techniques range from nuclear probe hyperfine measurements, scanning piezoresponse and magnetic force microscopies, neutron and X-ray diffraction to macroscopic electric and magnetic (SQUID and VSM) measurements.

Studies on multiferroic hexagonal manganites: REMnO<sub>3</sub> (RE=Er, Lu, Eu ferroelectric). Competition of orders and doping effects on non-stoichiometric LuMn<sub>1-x</sub>O<sub>3</sub> and (Eu-Y)MnO<sub>3</sub> multiferroics. Study of the role of microstructure on magnetic properties of LFZ-grown manganite oriented ceramics and single crystals (La-CaMnO<sub>3</sub>). Studies on multiferroic ferrites: Bi<sub>1-x</sub>Gd<sub>x</sub>FeO<sub>3</sub>, where Gadolinium substitution induces a polar- to- polar R3c-Pn2<sub>1</sub>a structural phase transition at x~0.1 and suppresses spontaneous polarization at 0.2<x<0.3, resulting in a ferroelectric-paraelectric Pn2<sub>1</sub>a-Pnma phase transition. Investigation of diamagnetically substituted Bi<sub>1-x</sub>A<sub>x</sub>FeO<sub>3-x/2</sub> (A= Ca, Sr, Pb, Ba; x= 0.2, 0.3) polycrystalline samples with rhombohedrally distorted perovskite structure. The heterovalent A<sup>2+</sup> substitution forms oxygen vacancies in the host lattice. The spiral spin structure of BiFeO3 is suppressed by large radius A-site substitution giving rise to the appearance of weak ferromagnetism. Solid solutions of Bi<sub>1-x-y</sub>Gd<sub>x</sub>BayFe<sub>1-y</sub>Ti<sub>y</sub>O<sub>3</sub> were also prepared to obtain magnetoelectric coupling at room temperature. Investigations of multiferroic coupling in two-phase composite ceramic materials, consisting of dielectric and magnetic components such as BaTiO<sub>3</sub> and LaBa manganites were started. [(BiFeO<sub>3</sub>)<sub>y</sub>(BiMg<sub>0.5</sub>Ti<sub>0.5</sub>O<sub>3</sub>)1-y]x[PbTiO<sub>3</sub>]1-x(BF–BMT–PT) single-phase material with tetragonal structure were prepared. Maximum remanent polarization (~~14 µC/cm<sup>2</sup>) is found for composition

 $[(BiFeO_3)_y(BiMg_{0.5}Ti_{0.5}O_3)1-y]x[PbTiO_3]1-x(BF-BMT-PT) single-phase material with tetragonal structure were prepared. Maximum remanent polarization (~~14 µC/cm<sup>2</sup>) is found for composition x=0.65. A diffuse phase transition with a transition temperature increasing with decreasing x and significant variation of degree of disordering in the system is observed. Studies on polycrystalline samples Bi<sub>4-x</sub>Gd<sub>x</sub>Ti<sub>3</sub>O<sub>12</sub> (x=1, 1.5, 2) showed that increasing the gadolinium content suppresses the spontaneous polarization in Bi<sub>4-x</sub>Gd<sub>x</sub>Ti<sub>3</sub>O<sub>12</sub>, resulting in a polar to non-polar phase transition near x=1.5. All samples are paramagnetic, proving that Gd ions do not lead to multiferroic behaviour into the ferroelectric Aurivillius-type compound.$ 

b) Ferroelectricity driven by magnetic order or charge/orbital order and bias-induced phase transitions Scanning probe microscopy was used to create and to detect local charged state in manganite  $(Pr_{0.06}Ca_{0.40}MnO_3 \text{ and } La_{0.89}Sr_{0.11}MnO_3)$  single crystals at room temperature. In the latter, the lifetime of these non equilibrium states exceeds 100 hours. These bias induced states display also a ferroelectriclike hysteresis with piezoelectric contrast reversed by the applied field. Complementary studies on fast scanning technique were carried at Oak Ridge National Laboratory within joint project. BEPS grid measurements are not yet totally conclusive to attribute to ferroelectric properties within the produced by the lithographic tests. The application of sufficiently high magnetic field and low temperatures had to be postponed due to technical difficulties.

### c) Studies on multiferroic thin films and heterostructures

Multiferroic structures of systems of magnetic shape-memory /ferroelectrics were studied in the MULTICERAL collaboration project. (Ni-Mn)Ga thin films were prepared by co-deposition of Ni<sub>50</sub>Mn<sub>50</sub> and Ni<sub>50</sub>Ga<sub>50</sub> targets on several substrates: sapphire(0001), Si, MgO, and SrTiO<sub>3</sub> (100) and also ferroelectric active PMN-PT single crystals, in low temperature conditions (<400°C). XRD analysis shows co-existence of amorphous and crystalline phases on NMG. Magnetic measurements reveal room temperature ferromagnetism, with TC ?332.5K, saturation magnetization ~200 emu/cc (half of bulk martensite) and low coercivity (~100 Oe). Magnetic contrast and surface roughness was analyzed using MFM. No in-plane anisotropy is detected by FMR. Studies on NMG films deposited onto LaNiO<sub>3</sub>/Pb(Ti,Zr)O<sub>3</sub> (LNO/PZT) ferroelectric buffer layers were also undertaken. Extended four poles high resolution XRD analysis allowed to discriminate the intended Ni-Mn-Ga tetragonal martensitic phase induced by the (100) LNO/PZT oriented buffer. The low temperature process appears to be very promising, allowing separate control of the functional layers' properties, while trying to achieve high electromagnetoelastic coupling.

## d) Theoretical and experimental study of magnetic systems and phase transitions with multiple order parameters

Magnetic modelling of physical properties in the vicinity of phase transitions is undertaken, using Landau theory and mean field approaches to provide a systematic understanding of coupled magnetic, structural and electric order parameters, including systems with chemical or structural disorder.

A novel scaling approach was developed, reaching a quantitative estimate of relevant parameters, applied to: inhomogeneous states in manganites revealing cluster persistence below the Curie temperature and magnetic alloys with large magnetostructural coupling (MnAs, Gd-Si-Ge) with simultaneous structural and magnetic transitions.

#### Magnetocaloric Effect and Application to Magnetic Cooling

The investigation of materials with magneto-structural coupling for applications in magnetic refrigeration, particularly near room temperature, was continued on  $(Mn_{1-x}M_x)As$  (M=Cu,Cr x<0.02) combining calorimetry, XRD (micrometer coherence), magnetic force microscopy (100 nm range), hyperfine and magnetic measurements and allowing to assess the role of phase mixing in magnetic first-order phase transition kinetics.

A quantitative method to solve a long-standing problem on how to estimate entropy changes using experimental nonequilibrium magnetic data in first-order phase transition systems was developed. A correlation between the mixed-phase state and (wrong) high entropy value obtained from Maxwell's equation was established. This modeling of mixed phase state leads to values in agreement with calorimetric experiment and theoretical simulation in MnAs-like systems. We get a corrected value of ~20 Jkg<sup>-1</sup>K<sup>-1</sup> at 5 Tesla compared to 80 Jkg-1K<sup>-1</sup> obtained from simple use of Maxwell equation.

### Hyperfine Interactions and First-Principles Calculation (DFT) of Properties of Materials

Two new international projects in CERN were started (IS487: Study of Local Correlations of Magnetic and Multiferroic Compounds and I81: Radioactive probe studies of coordination mechanisms of heavy metal ions from natural waters to functionalized magnetic nanoparticles). Hyperfine techniques (Perturbed angular correlation spectroscopy), addressing charge/orbital order and electronic phase segregated systems; measurements of electric field gradient and hyperfine magnetic field in oxides and magnetic semiconductors for structural, electronic polarization and magnetic field studies. Samples include multiferroic and ferromagnetic manganites (RMnO<sub>3</sub>), chromites (MCrO<sub>2</sub>) and nickelites (RNiO<sub>3</sub>), as well as MnAs, in broad temperature range (10-1000K). Studies on polaron dynamics and percolative effects in lightly doped ferromagnetic insulator manganites and on the effect of charge/orbital ordering and local electronic structure using ab-initio DFT methods (Wien2K) to study the role of defects, the local lattice distortions on the hyperfine parameters and the electronic charge distribution was started. A study of the lattice location of Hg<sup>2+</sup> ions in the several steps of the cations uptake by magnetite nanoparticles, modified at the surface with amorphous SiO<sub>2</sub> and functionalized by grafting dithiocarbamate groups to the particles surface was also initiated.

### Thin Film and Structures Preparation Studies with RF Sputtering Deposition

Deposition optimization studies of several types of materials on different substrates and different thermodynamic conditions were carried out. The studies include thorough investigation of structural XRD, (including grazing incidence and HRXRD), SEM, TEM and scanning probe microscopies. The substrate-induced lattice distortion effects and anisotropy towards the growth of (multi) functional thin films and heterostructures are analysed for: i) La-Sr and La-Ba manganites with highest Tc, above room temperature; ii) NiMnGa magnetic shape memory alloys; iii) Multifunctional oxides, such as luminescent magnetic vanadates and doped ZnO, TiO<sub>2</sub> and Ta<sub>2</sub>O<sub>5</sub> thin films for optical applications; and iv) Metallic and oxide buffer layers for oxide/oxide multilayered structures and silicon/oxide for electronic applications (high k-oxide materials, as HfO<sub>2</sub>).

#### Advanced Multifunctional Materials

We have explored the growth of different iron-based magnetic nanoparticles and luminescent molecular complexes inside organic-inorganic hybrid matrices and dispersible in water to obtain optically functionalized magnetic ferrofluid nanoparticles. The use of the organic-inorganic matrices allows the control of the phase and the magnetic particles size and agglomeration state, since nucleation occurs at defined points and the particles are wrapped around the polymer chains.

We have developed these materials aiming both biomedical applications (hyperthermia) and to investigate basic problems, such as the origin of the magnetic anisotropy energy barrier in antiferromagnetic nanoparticles.



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### scientific highlights

i) Development of (Ce,Pr)O<sub>2</sub>-based mixed conductors with the highest known levels of mixed conductivity in fluorite materials;

ii) Demonstration of proton and mixed conductivity in a novel material type (Ba<sub>4</sub>Nb<sub>2</sub>O<sub>9</sub>) and their correlations with structural features and stability limits;

iii) Interpretation for limitations of mixed transport properties in Sr<sub>3</sub>La(Fe,Al)<sub>3</sub>O10-d based on consistent spectroscopic studies and computer modelling.



Photo illustrating parts of the group facilities

### research team | 41

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### activity report 2009

*Materials for High Temperature Electrochemical Applications.* Activities included work on zirconia-based and ceria-based electrolytes, apatites based on  $La_{10}Si_6O_{26+x}$ , proton conductors based on  $BaZrO_3$ ,  $Ba_4Nb_2O_9$ ,  $Yb_2Ti_2O_7$ -based pyrochlores, and nanostrured ceria-carbonate composites.

Work on zirconias comprised conventional sintering schedules and also 2-phase materials to attain improved microstructures and/or enhanced mechanical behaviour. A re-examination of ceria-based materials showed multiple positive effects of cobalt oxide additions as a sintering aid and also positive impact on the kinetics of oxygen reduction.

One developed a suitable mechanosynthesis method for single phase BaZrO<sub>3</sub>-based materials and attempted to improve their sinterability by sintering additives.

Work on apatites was based on mechanosynthesis to obtain powders with better sinterability and also to obtain improved microstructure-property relations. Potential applicability included preparation of electrochemical cells, electrocatalytic activity studies of perovskite-related air electrodes and assessment of multilayer cells with protective layers;

Studies of  $Ba_4Nb_2O_9$ -based materials showed mixed protonic, oxygen ionic and electronic conductivity, depending on crystal structure, phase transitions and hydration. One found that properties of Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>-based materials depend on heterogeneities and defect chemistry changes induced by non optimized powder preparation and thermal history.

The ionic conductivity of nanostrured ceria-carbonate composites showed unique trends and one started the design of suitable models to understand their properties.

Research activities during 2009 also included studies of a variety of glass-ceramic materials as potential SOFC seals. Optimization of diopside based glass-ceramics was made by attempting different additions/substitutions (La<sub>2</sub>O<sub>3</sub>, Nd<sub>2</sub>O<sub>3</sub>, Yb<sub>2</sub>O<sub>3</sub>, B<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, BaO, SrO) to achieve desirable characteristics for sealants. Other work on glass-ceramic materials refers to materials with selected crystalline phases (e.g. clinopyroxene) and conflicting kinetics of crystallization and sintering of enstatite-based materials.

*Microstructural Effects.* These studies include continuation of previous studies of microstructural effects on ionic or mixed transport properties, based on ceramics with different grain size distributions and modifications of grain boundary properties by selective grain boundary engineering or resulting from sintering additives (e.g. cobalt oxide added to cerias). By adjusting both bulk and grain boundary properties one attained the highest mixed conducting properties for fluorite-type materials in oxidizing conditions.

More recent activities have been directed to 2-phase or heterogeneous materials. This work demonstrated novel concepts of materials with enhanced transport properties related to internal interfaces (e.g. ceria-carbonate composites). Other 2-phase materials are been designed to enhance their thermomechanical properties while retaining good conductivity.

One re-examined experimental procedures which lead to misleading interpretations of microstructuralproperty effects, with emphasis on in-plane impedance measurements.

### Mixed Conductors and Catalysts for Oxygen Separation or Partial Oxidation of Hydrocarbons.

Developments of mixed-conducting membranes was mainly based on materials with layered and fluorite structures. Attention was also focused on ion diffusion mechanisms in complex lattices and for materials with core-shell microstructures with sub-micrometer grain sizes. One started modeling of mixed-conducting membranes, to evaluate prospective operation conditions and relevance of membrane properties. Main achievements were:

- identification of defect formation, interaction and transport mechanisms in Ruddlesden-Popper type  $Sr_3La(Fe,M)_3O_{10-\delta}$  (M = AI, Ga),  $LaSr_2(Mn,Ni)_2O_{7-\delta}$ ,  $(La,Sr)_4(Ni,M)_3O_{10-\delta}$  (M = Co, Cu), and YBa(Co,Fe)\_4O\_{7+\delta}, and analysis of their electrical and physicochemical properties;

- Modelling of oxygen permeation through asymmetric  $La_2NiO_{4+\delta}$  membranes, allowing analysis of interfacial exchange kinetics based on dependence of oxygen fluxes and conductivity on oxygen chemical potential and nonstoichiometry;

- Modelling of a natural gas-fired oxy-combustion combining a power plant cycle with  $CO_2$  capture, upon replacing the combustion chamber by a mixed conducting membrane-based reactor, making it possible to obtain highly concentrated  $CO_2$  for capture and storage;

- Demonstration of high mixed conductivity in  $Ce_{1-x}Pr_xO_{2-\delta}$  fluorites modified with cobalt oxide-rich grain boundaries by a combination of bulk transport and transport along highly conducting grain boundaries.

*Materials for other Electrochemical Processes.* One demonstrated that electrochemical deposition of Ni-Co-B films yields anodes which combine high electrocatalytic activity and also enhanced wear resistance. The system MgO-FeO<sub>x</sub> has been studied for potential use as consumable electrodes in pyroelectrolysis; this includes experimental studies and computer modelling of their structure and properties.

## 5 research group ceramic composites and functional coatings for structural applications

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### scientific highlights

i) A new generation of hybrid sol-gel coatings doped with ceria nanoparticles or with different organic inhibitors was developed for active corrosion protection of aluminum alloys;

ii) New smart self-healing coatings based on layered double hydroxide (LDH) nanocontainers loaded with organic inhibitors were developed;

iii) Anodic coatings on titanium and aluminium were deposited using high-voltage powerful discharge technique for the first time;

iv) Nanocrystalline diamond (NCD) coatings were demonstrated to provide a suitable surface for cell attachment, spreading and proliferation;

v) Water lubricated NCD/NCD tribosystems confirmed to have very high film delamination loads (85 N) and very low friction coefficient values ( $\mu$ =0.02 to 0.05) combined with a high wear resistance (10-9 mm<sup>3</sup>.N<sup>-1</sup>.m<sup>-1</sup>);

vi) NCD coated bits presented a superior excel behaviour in bone drilling when compared to steel conventional ones;

vii) *In situ* TEM study of the effect of an encapsulated alloy in the mechanical behaviour of filled turbostratic carbon nanotubes, providing the first experimental evidence for potential nanomechanics control of these nanostructures;

viii) Composites prepared from WC powders sputtercoated with stainless steel were shown to possess higher fracture toughness versus hardness values, when compared with identical composites conventionally prepared.



Active protective AI-Ce alloy surface

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Carbon based materials (CVD Diamond Coatings and Carbon Nanotubes). activity report The effect of the core on the stiffness of filled carbon nanotubes (CNTs) was confirmed which represents a major advance in the nanomechanics field and in situ TEM studies. For almost a decade, a number of theoretical papers had previously analysed this issue but their predictions had never been experimentally tested. Group 5 also initiated in 2009 the production and characterization of CNTs by growing dense forests with more than 1mm height on the new homebuilt thermal CVD apparatus.

## 2009

Micro- and nanocrystalline diamond (MCD, NCD) coated surfaces continued to be produced and characterized for tribological purposes. The main achievements are here summarized: - Concerning the production issue, studies on the influence of the substrate temperature on the formation of NCD films prepared by an argon-based hot filament chemical vapor deposition (HFCVD) allowed the estimation of an activation energy for NCD growth (5.7 kcal/mol) lower than the values found for standard diamond deposition (around 11 kcal/mol). This behaviour is attributed to the simultaneous growth of non-diamond phases within the NCD film, especially sp<sup>2</sup> compounds, contrarily to the higher activation energy needed for pure sp3 phase film growth.

- A new procedure was tested with success with respect to the surface pre-treatments' importance to the NCD films growth: a surface activation step before ultrasonication in diamond suspension for seeding, allowed the formation of an amorphous carbon layer that further helped on diamond nucleation and adhesion.

- The NCD coatings were characterized in sliding in the presence of water, or aqueous solutions, a situation that occurs, for example, in mechanical face seals, MEMS, or in preliminary testing bearing surfaces for biotribological applications. The homologous NCD/NCD tribosystem presented a threshold load of 85 N prior to film delamination, and very low friction coefficient values ( $\mu$ <0.05) combined with a high wear resistance (<10<sup>-8</sup> mm<sup>3</sup>N<sup>-1</sup>m<sup>-1</sup>).

- Aiming biotribological applications, a biocompatibility study with fibroblasts showed that both the L929 cells (a mouse permanent cell line) and human gingival ones completely covered the NCD coatings after a few days, and, compared to standard polystyrene culture plates, no deleterious or cytotoxic responses were observed.

- The erosion wear resistance of MCD and NCD varieties was also investigated showing a similar behaviour of coatings produced by HFCVD and microwave plasma (MPCVD) techniques, with a wear rate of 3.7±0.8 x 10<sup>-5</sup>mm<sup>3</sup>N<sup>-1</sup>m<sup>-1</sup>.

- As odontological drill bits, the use of MCD/NCD bilayered coatings allowed drilling with significantly lower forces (fourfold smaller), lower rise in temperature (4 °C less), lower spindle speeds (100 rpm) and higher infeed rates (30 mm/min), when compared to the commercial steel (AISI 420) drill bits. - As cutting tools for dry turning of WC-18 wt% Co bars, CVD diamond coated tools showed better performance than the current PCD (high pressure sinterd polycrystalline diamond) tools, with respect to the cutting forces, tool wear and workpiece surface quality.

- Electrically conductive boron-doped NCD coatings started to be produced. Ultramicroelectrodes (UMEs) involving the sharpening of W filaments were coated with a thin layer of conducting B-NCD. These will be further characterized to be used for electroanalytical chemistry purposes.

Advanced Ceramics and Other Hard Materials. Processing and characterization of advanced ceramics and cermet materials was accomplished on several themes:

- Thermal stability and crystallization kinetics of ternary Se–Te–Sb semiconducting glassy alloys. - Development of ZnTe thin films and their microstructural and optical properties. - Preparation of polycrystalline  $ZrN_{1-x}C_x$  Layers with (111) preferred orientation by carbothermal nitridation of ZrO<sub>2</sub> Ceramics.

- Coloidal processing of SiAIONs and AIN in aqueous media. Colloidal processing, including slip casting and direct consolidation techniques, were also used to consolidate ceramic parts of ZTA composites, magnesium aluminate spinel, combustion-derived Al<sub>2</sub>O<sub>3</sub> powders, mullite aggregates. - A new direct consolidation technique called "Hydrolysis induced aqueous gelcasting" was developed, which synergistically explores the features of "Hydrolysis Assisted Solidification" and "Gelcasting" techniques.

The dispersion of Cu<sub>2</sub>O particles in aqueous suspensions was also studies aiming at establishing the experimental conditions for processing metal-ceramic composites in the Al-Cu-O system.
Composites prepared from WC powders sputter-coated with metals showed very interesting mechanical properties, such as, increased ductility with Ni coatings and higher fracture toughness versus hardness with stainless steels coatings, when compared with composites conventionally prepared. These benefits were attributed to the remaining high uniformity of phase distribution and nanocrystalline binder structure in the composites, coming from the powder coating process. Ni coatings on WC-Co substrates, after heat treatment at 1273 K, showed high adhesion and relevant surface characteristics for applications in high corrosion mediums at high temperatures.

*Protective Coatings for Metallic Materials.* The research activity on new active surface protection technologies can be summarized to the following main topics:

- The new smart self-healing coatings based on nanoreservoirs of corrosion inhibitors were developed during 2009. Mainly Layered Double Hydroxides (LDH) doped with corrosion inhibitors were used as smart nanocontainers.

- New hybrid sol-gel derived nanocomposite thin films doped with corrosion inhibiting compounds were developed for corrosion protection of aluminium and magnesium alloys.

- The new ion-selective micro-electrodes and multi-microelectrode cells to be used in corrosion studies were developed.

- For the first time the aluminum-cerium alloy metallic protective coatings were electrodeposited using ionic liquids as electrolyte.

- Modeling of the corrosion processes on micro-scale started using geochemical approaches supported with novel localized electrochemical measurements.



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### scientific highlights

i) Design of green products and search for new functionalities;

ii) Valorisation of secondary raw materials, some of them toxic, through its use in the preparation of inorganic ceramic pigments;

iii) Development of traditional ceramic products that show new functionalities. These include decontamination of aerial pollutants (NOx, SOx, etc), decolouration of dyes and wastewaters, antimicrobial and self cleaning effects. The deposition of active layers in the surface of ceramic tiles and AI sheets, by expedite and easy controllable techniques (e.g. jet spray, and screen printing) seems to be a viable way to assure those requirements. Porcelain tiles having anti-microbial action, high chemical resistance, and anti-stains characteristics, were also developed in collaboration with a local producer;

iv) Sustainable Built Environment is particularly appealing area for partnership with the Habitat cluster companies and also municipalities, that face tricky questions regarding wastes and its managing in their daily activity. This attempt has been coordinated by the Sustainable Construction Platform (www.centrohabitat.net).



Black pigment: Pigment based on chrome-iron-nickel spinel exclusively formulated with industrial wastes

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Earth's natural resources and the man-made environment are under intense pressures from growing population, urbanization, continuous expansion of the agriculture, transport and energy sectors, as well as climate variability and warming at local, regional and global scales. Europe needs to engage in a new sustainable relationship with the environment while improving competitiveness and strengthening European industry.

## activity report 2009

The EU needs to strengthen its position in world markets for environmental technologies. Such technologies help deliver sustainable growth providing eco-efficient solutions to environmental problems at different scales and protecting our cultural heritage. Environmental requirements act as a stimulus for innovation and can provide business opportunities. European Technology Platforms on sustainable chemistry confirm the need for EU level action and their research agendas are taken into consideration in the activities below. Other Platforms (e.g. on Construction) partially deal with environmental technology issues and are taken into consideration as well.

The activities of group 6 are included in the topics:

**Sustainable Management of Resources.** Conservation and sustainable management of natural and man-made resources: waste management and prevention; soil protection, approaches against land degradation; sustainable management and planning of urban environment.

**Environmental Technologies.** Environmental technologies for prevention, mitigation, adaptation, remediation and restoration of the natural and man-made environment: related to soil, waste treatment, recycling, clean production processes, and protection of cultural heritage and of the built environment.

*Waste Based Inorganic Pigments.* Development of inorganic pigments complying with technological and environmental demands and incorporating alternative (and less expensive) raw materials. This alternative will help the reduction of the consumption of primary (scarce) resources. Several industrial wastes have been investigated for this purpose, in particular metal-rich sludges: Alrich sludge generated in the wastewater treatment unit of an anodizing or surface coating industrial plant; galvanizing sludge from the Cr/Ni plating process; sludge generated in the steel wiredraw process; foundry sand; etc. Distinct pigment structures have been prepared, characterized and applied in colouring galzes and ceramic bodies: chrome-tin red malayaite, Ca(Cr,Sn)SiO<sub>5</sub>; chrome-iron-nickel black spinel, (Fe,Ni)(Fe,Cr)<sub>2</sub>O<sub>4</sub>; and a novel blue pigment based on cobalt/nickel hibonite structure.

*New Eco-Friendly Decontamination Techniques.* Use of advanced oxidative processes to remove resistant organic pollutants through their conversion into inorganic products ( $CO_2$ ,  $H_2O$ , etc), with supported semiconducting layers ( $TiO_2$  and ZnO). Ceramic and aluminium substrates had been tested and deposition conditions are under optimization.

**Reuse of Biomass Fly Ashes.** Work was done on the characterization of the biomass fly ashes sourced from a thermal power plant and from a co-generation power plant located in Portugal, and the study of new cement formulations incorporated with the biomass fly ashes. The study includes a comparative analysis of the phase formation, setting and mechanical behaviour of the new cement–fly ash formulations based on these biomass fly ashes. Techniques such as X-ray diffraction (XRD), X-ray fluorescence spectroscopy (XRF), thermal gravimetric and differential thermal analysis (TG/DTA), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and environmental scanning electron spectroscopy (ESEM) were used to determine the structure and composition of the formulations.

**Sustainable Mortars for Rehabilitation.** Lime based mortars has been studied specially for rehabilitation works. In this work, the fresh state properties of aerial lime pastes and aerial lime based mortars were investigated. The mortar rheological parameters (relative yield stress and plastic viscosity) were obtained using a rheometer suitable for mortars. The correlation of rheological data with slump and relative density measurements was studied. The mortars workability is affected by several parameters, namely, the binder/aggregate and water/binder ratios, the kneading water content, the admixtures type and amount. The admixtures influence (type and amount) on the fresh state properties of aerial lime based mortars are discussed. The used admixtures were the most common ones for several mortars, such as a water-retaining agent, a plasticizer and an air-entraining agent.

The effect of two different water retaining agents was specially studied in single-coat render mortars. Rheological behaviour, slump and density as well as mechanical strength, transport properties through capillary absorption tests and water retaining capacity were measured in fresh and hardened state.

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### scientific highlights

i) The use of the ionic liquid [EMIM][HSO4] instead of H<sub>2</sub>SO<sub>4</sub> was used with success for the conversion of pentoses and hexoses into furfural or 5-hydromethylfurfural;

ii) New polyesters of 2,5-furandicarboxylic acid (derived from renewable resources) with several diols were prepared. In particular, the ethylene glycol homologue, poly(ethylene 2,5-furanedicarboxylate) showed properties comparable to those of the basic polyester industrial counterpart, obtained with the aromatic analogue terephthalic acid, which is a petrochemical commodity;

iii) Novel transparent nanocomposite films were prepared from mixtures of chitosan and bacterial cellulose, following a simple and green method involving the dispersion of the bacterial cellulose nanofibrils in a chitosan solutions, followed by water casting; iv) Cellulose/Ag nanocomposites, were prepared using two distinct cellulose substrates (vegetable and bacterial cellulose). Detailed studies of their antibacterial activity were carried out with several bacterial strains. Silver nanoparticles present in the cellulose fibers in concentrations as low as 5.0×10<sup>-4</sup> wt.% turned these nanocomposites into effective antibacterial materials;

v) lonic liquids with a basic character, suitable for the capture of acid gases such as CO<sub>2</sub> were developed and studied. The mechanism of interaction between CO<sub>2</sub> and the acetate ion was identified;

vi) Correlations for the thermophysical properties of ionic liquids allowing the design of new task specific ionic liquids using computer aided molecular design were proposed;

vii) The mechanism behind the salting-in/out of charged molecules in solution by salt ions was disclosed. The knowledge was used to study and develop new aqueous two-phase systems for the extraction and purification of biomolecules.







Transparent nanocomposite films prepared from mixtures of chitosan with bacterial cellulose



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## research team at 31<sup>st</sup> december '09





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#### Novel Biomass-Derived Materials and Composites

The research on the development of novel functional materials based on polysaccharides, namely vegetable and bacterial cellulose, and chitosan was continued and strengthened.

Vegetable cellulose fibers modified with two perfluorinated reagents (trifluoropropanoyl chloride and pentaflourobenzoyl chloride) were tested in the preparation of new composites with one perfluorinated polymer matrix (poly(vinylidene fluoride-co-hexafluoroproplylene). The obtained materials were characterized in terms of their thermal and mechanical properties, morphology and dimensional stability (water uptake).

The evaluation of the barrier properties of acylated cellulose membranes was also pursued, since it is a crucial parameter in several domains, such as in packaging applications. During this period, we focused mainly on the assessment of the dry and wet permeability of these materials to various gases.

Two novel strategies for the modification of cellulose fibers were also investigated during this year, viz the preparation of new organic --inorganic hybrid materials and of highly hydrophobic and lipophobic cellulose fibers by a straightforward gas-solid reaction. The preparation of the novel cellulose based class-II organic-inorganic hybrid materials involved the heterogeneous chemical modification of cellulose fibers with (3-isocyanatopropyl)triethoxysilane, followed by the acid hydrolysis (and condensation) of the appended siloxane moleties as such, and in the presence of either tetraethoxysilane or 1H,1H,2H,2H-perfluorodecyltriethoxysilane aiming to introduce different functionalities onto the fibers surface. The strategy of modification of cellulose fibers in the vapor state consisted on the reaction with gaseous trichloromethylsilane (TCMS). In both cases The characterization of the obtained materials involved FTIR-ATR and solid-state <sup>29</sup>Si NMR spectroscopy, scanning electron microscopy (SEM), Xray diffration, thermogravimetry and contact angle measurements with different liquids. New cellulose/silica hybrid (CSH) composites were prepared from bleached Eucalyptus globulus kraft pulp or primary treatment sludge cellulose fibers by a sol-gel method which aging was accomplished by hot pressing of pre-formed CSHs. The incorporation of a silica network in cellulosic materials increased significantly their dimensional stability during soaking in water, hydrophobicity, thermal stability and bending strength. The thermal conductivity of these hybrid materials is comparable to commercially available insulation foams. Similar approach was applied to produce hydrolysis lignin/silica hybris (LSH) composites. These were characterized by X-ray photoelectronic spectroscopy, FTIR and <sup>29</sup>Si and <sup>13</sup>C NMR and nitrogen sorption. The high bioremediation performance of the hybrid materials was proved

by chemosorption of inorganic (Cu<sup>2+</sup>) and organic (2,4-dichlorophenoxyacetic acid) soil pollutants. The studies on the coating of *E. globulus* paper sheets with chitosan and one water soluble chitosan derivative and mixtures of chitosan (and its derivative) and bacterial cellulose nanofibers were continued and optimized. The obtained coated materials were extensively characterized in terms of surface, mechanical and barrier properties. Moreover, the printability and aging of the coated papers were also assessed.

The mixtures of chitosan (and one of its water-soluble derivative) with bacterial cellulose were also tested for the preparation of novel transparent nanocomposite films. The method consisted in the simple dispersion of the bacterial cellulose nanofibrils in the chitosan solutions, followed by water casting. The obtained materials were characterized by SEM, AFM, thermogravimetry, X-Ray Diffraction, Light Transmittance, DMA and mechanical essays. This strategy is particularly relevant because of its simplicity, green connotation and also because of the interesting properties of the obtained films.

Another research area was started during this year that consisted on the implementation of the production of bacterial cellulose in our laboratory. A pure *Acetobacter* strain was isolated from a commercial kombucha fermented tea sample and used on the production of bacterial cellulose under different culture conditions.

In this context, bacterial cellulose membranes were investigated as substrates for the controlled release of model drugs. This preliminary study involved kinetic studies (followed by FTIR and UV-Vis) of the migration of lidocaine into wet, dry and lyophilised membranes and its subsequent release. Research on novel nanocomposites based on cellulose and other polysaccharides incorporating

Research on novel nanocomposites based on cellulose and other polysaccharides incorporating nanostructured metals was pursued. New cellulose/Cu and cellulose/Fe(III) nanocomposites, involving plant and bacterial cellulose where prepared and characterized. The same approach was extrapolated to different metal alloys. Metal nanoparticles (Ag, Au) where successfully applied in the development of novel polymer nanocomposite films, using chitosan and chitosan derivatives as matrice. A new research line, dealing with the development of new nanofibrilated cellulose materials (NFC) was initiated. Ag/NFC and TiO<sub>2</sub>/Ag where prepared and its characterization was initiated.

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#### Polymers Derived from Renewable Resources.

The synthesis of monomers bearing furan and maleimide functionalities suitable for the synthesis of polymer materials through the Diels-Alder cyclo-addition (DA) was continued. Particular attention was given to the preparation of AB (Meleimide-Furan) type monomers, in order to prepare intermediate structures that could be stored until polymerization. This involved the protection (through a Diels-Alder reaction) of the maleimide moiety with a volatile furan. Before polymerization, the volatile furan was removed through the retro-Diels-Alder reaction at high temperature, followed by the polymerization process, which took place as the temperature of the reaction medium decreased. The DA/retro-DA cycle was also applied to linear (AA+BB systems) and crosslinked (AA+B<sub>3</sub> system) polymers. These systems were analyzed in terms of the kinetics of the linear polymerization (based on preliminary studies on monofunctional model compounds) followed by UV and <sup>1</sup>H-NMR spectroscopy. This investigation is supported by a FCT project.

New polyesters of FDCA with several diols (1,3-propanediol, 1,-2-propanediol, 1,4benezenedimethanol isosorbide etc) were prepared, following polytransesterification and/or polycondensation approaches. The new materials were characterized in detail, and showed promising characteristics in terms of crystallinity and thermal properties, comparable to those obtained for the polyesters obtained with the synthetic aromatic analog terephthalic acid.

Two different types of structures and hence two different polymerization methods are at the basis of this doctorate study which aims at valorizing lignosulphonate fragments. The first topic concerns the radical and cationic polymerization of methoxy-substituted styrenes. The best results were obtained with cationic systems. The second topic deals with the polycondensation of differently substituted aromatic hydroxyacids, which provided highly stiff semicrystaline polyesters.

The synthesis of new monomers derived from unsaturated fatty acids was started. During this period the synthesis of fatty acids vinyl esters was studied. The best results in terms of yields and selectivity were obtained by Iridium-catalysed transvinylation of fatty acids with vinyl acetate. The vinyl esters were tested with success in radical polymerization/copolymerization with vinyl acetate and these materials tested in oxidative curing.

A new research line was started involving the development of new chemical/biochemical tools to produce fatty acid hydroperoxides or other oxidised derivatives and their transformation into valuable products, namely new monomers for polymers synthesis.

The development of new polyesters derived from suberin components was continued, involving the optimization of the polymerization conditions as well as the extension of these studies to birch outer bark suberin.

# The conversion of biomass components into value added chemicals focusing on the development of: efficient catalytic conversion for the production of platform chemicals from polysaccharides; and biotechnological processes for the conversion of biomass components into fine chemicals and biofuels

One of the areas of interest in G7 is the production of FUR and HMF from sugars and polysaccharides. The current approach uses sulphuric acid as acid catalyst for this conversion. G7 is actively investigating the use of ILs as alternative solvents and catalysts. In considering the potential of acid ILs to replace sulphuric acid in processes for the transformation of saccharides into furfural (FUR) or 5-hydromethylfurfural (HMF), it must be recalled that  $H_2SO_4$  is very hygroscopic and difficult to dry in vacuum, and when heated it emits highly toxic fumes, which include sulfur trioxide, leading to the accumulation of acidic waste. The dehydration of xylose and fructose and, on the other hand, the one-pot hydrolysis and dehydration of di/polysaccharides containing fructose units, in [EMIM][HSO<sub>4</sub>]/co-solvent gives fairly high yields (80-90%) of FUR and HMF, at 100 °C. Furthermore, better results were achieved with [EMIM][HSO4] (IL) than with aqueous H2SO4, under similar conditions. The IL can be recovered and reused without a significant drop in FUR yield in recycling runs. The use of [EMIM][HSO<sub>4</sub>] instead of H<sub>2</sub>SO<sub>4</sub> may allow process intensification with reuse of the acid IL.

Another aspect of interest is the valorization of spent sulphide liquor (SSL) to a second generation bioethanol. SSL contains dissolved sugars (40-45 g/L), mainly xylose, and around 10 g/L of acetic acid. Study on the bioethanol production by *Pichia stipitis* revealed that besides acetic acid *Pichia stipitis* is also inhibited by polyphenolics. *Paecilomyces variotii* can consume some inhibitory compounds and conversion to Single Cell Protein (SCP) is being optimised. Another research trend in the valorization of SSL is its biotransformation into biopolymers as polyhydroxyalkanoates (PHA) employing mixed cultures of microorganisms.

The kinetic study of the castor oil acetylation has been started, in order to be applied for the production of dielectric oils.

On the development of analytical techniques to support these studies the advanced 2D NMR techniques were applied for the first time for the analysis of muconic acid type structures (MATS) in oxidised lignins. This allowed the reliable assignment of MATS signals thus providing a methodology for detection and distinguishing of MATS from structurally similar moieties. <sup>13</sup>C NMR and advanced 2D NMR techniques were combined with specific <sup>13</sup>C-enrichement of lignin model polymers (DHP) to avoid the signal-overlap problems and aiding in definitive signal assignments. This allowed a new database for the lignin signals assignment. The work was initiated for application of advanced mass spectrometry techniques (ESI-MS/MS and ESI-MSn) for the study of minor functionalities in hemicelluloses. The application of new electronic tongue (ET) multisensor system for the real-time monitoring of polyoxometalates (POM) re-oxidation with laccase and molecular oxygen has been accomplished. New methodology to assess the chromophores in bleached pulps employing micro UV-Raman spectroscopy has been developed.

#### Development of new separation processes applied to the biorefinery

G7 is actively investigating the development of new separation processes based on ionic liquids for the extraction of biomolecules or the enhanced separation of biorefinery products using a greener approach. For that purpose ILs have been studied for the formation of aqueous two-phase systems (ATPS). The effect of the inorganic salts on the solubility of ionic liquids in aqueous solutions was investigated and the mechanisms responsible for the salting-in/out of the IIs were identified. An extensive study of the IL cation and anion on the ATPS formation was developed allowing the design of ATPS with defined characteristics. The extraction of biomolecules such as aminoacids, food dyes, proteins and other biomolecules were carried with success. The IL based ATPS present larger partition coefficients and lower viscosities than the conventional polymer based ATPS allowing for a faster mass transfer and easier phase manipulation.

The use of ILs for the purification of biogas and syngas by the removal of the acid gases (CO<sub>2</sub> and H<sub>2</sub>S) has been extensively studied. The CO<sub>2</sub> solubility in a large number of ionic liquids was measured and the mechanism of CO<sub>2</sub> solubility on ionic liquids was disclosed. A general correlation allowing the design of ILs for enhanced CO<sub>2</sub> solubility was developed. The study of the CH<sub>4</sub> solubility was started aiming at understanding the methane solubility in ILs and develop ILs with optimized selectivities for biogas purification.

We have also been developing the CPA-EoS for the description of the phase equilibria relevant for biodiesel purification. The current version of the CPA is now able to describe the VLE and LLE, in binary or higher order systems, containing short chain alcohols, water, glycerol, fatty acids and fatty acid esters. It is shown that this model is far more accurate and possesses predictive capabilities than current models implemented in process simulators such as ASPEN.

The separation of alcohol-water or organic acids-water systems, common in biorefinery processes, using extractive or azeotrópico distillation involving the use of ILs or other solvents is being under research. Concerning Liquid-liquid extractions work on the dynamics of liquid-liquid dispersions in chemical processing is being continued.

Another type of separation processes under study uses membranes. On this subject we are carrying the dynamic characterization of new inorganic membranes. The experimental set-up necessary for the measurement of pure gas permeances is already installed. Assays of pure gas permeation at constant temperature and at programmed temperature have been carried out, and new models for the representation and interpretation of transport mechanism across membranes have been proposed and validated with data from literature.



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#### scientific highlights

i) Spray-dried hydroxyapatite-5-Fluorouracil (Hap/5FU) granules as drug delivery systems;

ii) Confirmation that porosity of glass/PLLA composite scaffolds for bone tissue engineering applications, developed by TIPS, can be tailored by simply controlling the glass filler solubility without the use of toxic surfactants (patent);

iii) In silico research of synthetic receptors for medicinal applications;

iv) The protocol for cell metabonomics was developed to ensure reproducibility in cell/drug studies;

v) Insight into human fetal metabolism under conditions of prenatal disorders/disease: use of NMRmetabonomics for diagnosis, follow-up and prognosis;

vi) Insights into lung cancer metabolism and demonstration of the use of NMR-metabonomics in monitoring and diagnosing cancer;

vii) Study of the interaction mechanisms between DNA quadruplexes and antitumor complexes using computational methods;

viii) Investigation of the diffusion and transport of drugs across membranes using molecular dynamics approaches.



Spray-dried hydroxyapatite-5-Fluorouracil (Hap/5FU) granules as drug delivery systems







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### full time researchers

Biomaterials. Novel glass compositions of the Ti-Ca-P system, of interest in bone regenerative medicine, have been developed and their structure assessed by NMR and Raman spectroscopy. For serial compositions with Ca=constant an interesting phospho-titanate structural model has been found. Degradation rates of these glasses in SBF are closely related with structure and bond strengths of oxides within the glass network. Ti-based glass compositions induce the precipitation of Ca-P layers in SBF and promote cell adhesion and proliferation. Si-Ca-P-Mg glass scaffolds produced by a salt sintering process (~60 % porosity, macropores 150-400  $\mu$ m and micropores < 60  $\mu$ m) indicated their mineralization capability and osteoblastic biocompatibility with cells adhering and proliferating on the scaffolds surface. In addition, Ti-Ca-P, Si-Ca-P-Mg and B-P-Mg glass compositions were used as fillers in PMMA cements. New cement formulations with enhanced in vitro bioactivity and mechanical properties were developed. Osteoblastic cell growth was confirmed on Ti and Si-based glass composites but it was inhibited on the B glass-based composite, probably due to the high degradation of the borate glass. For the glass/PLLA composite scaffolds prepared by TIPS (high interconnectivity and pores >150 µm) an interesting effect of the glass content on the pore size was observed for the first time and patented. In vitro mineralization and biocompatibility have been observed in these composite scaffolds.

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Some other work has focused on the development of cements based on calcium phosphates doped with Mg, Sr and Zn, for clinical applications. The studies included powder synthesis, crystalline phase transformations, including phase quantification and structural refinement of powders and cements determined by X-ray diffraction with Rietveld refinement, BET specific surface areas and particle size analysis. Also, formulation of the cement pastes was carried out, along with the study of the setting process and the characterization of the hardened cements for their physical/mechanical properties and *in vitro* and *in vivo* performances. Cell cultures were used to evaluate citotoxicity, bioactivity and biocompatibility of cements. The biocompatibility *in vivo* and cements resorption were evaluated using a pig model through histological and histomorphometric studies of decalcified sections. Several series of glass compositions were prepared aiming at developing lithium disilicate glass-ceramics in the system SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>–K<sub>2</sub>O–Li<sub>2</sub>O for dental applications. Specimens prepared from powder frits were sintered at temperatures in the range of 800-900°C and characterized for density, microstructure, phase composition, Vickers hardness, flexural strength, and chemical durability. The crystallization of SiO<sub>2</sub>-TiO<sub>2</sub> nanocomposites was investigated varying the type of precursors and pirolysis temperature. According to results the crystalline size depends on titanium content and type of cross-linking agents.

Functionally graded bioglass-apatite composite layers were electrophoretically deposited onto Ti<sub>6</sub>Al<sub>4</sub>V alloy and characterized for their electrochemical and structural properties. The results showed that coating metallic implants with bioactive materials is necessary to decrease the susceptibility to localized corrosion and enhance the biocompatibility required to establish good interfacial bonds between the metal substrate and bone. The results also demonstrated the suitability of the electrophoretic technique for the preparation of graded coating on  $Ti_{6}AI_{4}V$  substrates. Other studies have dealt with the influence of magnesium doping in biphasic (hydroxyapatite (Hap) and ß-tricalcium phosphate) mixtures, or Zn-doped ß -Tricalcium phosphate powders using Rietveld structural refinement and in vitro analysis. Sr-substituted Hap was also studied. Hybrid chitosan-polylactic acid/Hap composites for biomedical applications were also developed and characterized for their rheological, microstructural, and in vitro properties. The study of the preparation and characterization of Hap-5-Fluorouracil (Hap/5FU) granules to be used as chemotherapeutic delivery matrices and bone regeneration templates was also undertaken. Suspensions of Hap nanoparticles in 5FU solution were spray dried being 80 degrees C the optimized condition for obtaining granules composed by Hap and 5FU without secondary phases. The optimization of the 5FU releasing rate is now under study aiming at a potential application of the (Hap/5FU) granules as a drug delivery system.

The in vitro bioactivity of new gelatine/silicocarnotite hybrid materials was studied. According to FTIR results after an immersion of 3 days in 1.5 SBF, A and B-type  $CO_3HA$  can be observed on the surface. The presence of Hap with well defined crystallinity was detected by XRD. SEM/EDS of the precipitated layers showed the presence of  $CO_3HA$  and amorphous calcium phosphate on the surface of the samples. In other studies, the thermal stability of PDMS/TEOS hybrid materials was mainly related to the TEOS content, whereas the inorganic component structural stability depends on the relative PrZr content in the alkoxides mixture.

Artificial Receptors for Pharmaceutical and Environmental Applications. In this line, research has focused on the in silico development of synthetic receptors with pharmaceutical and environmental applications. Computational methods (quantum chemical calculations, molecular mechanics (MM) and molecular dynamics (MD) simulations) were applied extensively on the design of novel receptors and in the understanding of their molecular recognition mechanisms. The majority of the designed molecules were anion receptors. Experimental studies on supramolecular anion associations have been carried out by single crystal X-ray diffraction (XRD).

The binding properties towards aromatic carboxylate anions of three novel poly-azamacrocycles, containing two 1,10-phenanthroline units connected by two polyamine spacers of different length, [32]phen<sub>2</sub>N<sub>4</sub>, [30]phen<sub>2</sub>N<sub>6</sub> and Me<sub>2</sub>[34]phen<sub>2</sub>N<sub>6</sub>, were investigated in water solution by means of experimental an theoretical methods. The binding arrangements between protonated receptors and selected carboxylate aromatic anions were established by MD. The binding free energies, estimated by MM-PBSA calculations, agree with the experimental data. In other studies, two related cryptands were used as receptors for the binding of inorganic anions with different charge and shape. The first receptor is a protonated hexamine cage composed of two 1,3,5-tris(aminoethyl)2,4,6-triethylbenzene fragments and two *m*-xylyl spacers (Hőxly<sup>6+</sup>) while in the second one, the spacers between the 2,4,6triethylbenzene caps are two m-pyridine moieties (H6pyr)<sup>6+</sup>. The supramolecular associations between  $(H6pyr)^{6+}$  and  $NO_3^-$ ,  $H_2PO_4^-$  or  $SO_4^{2-}$  anions were investigated by XRD. The X-ray structure of  $[(H_6xyl)(SO_4)(H_2O)_6]^{4+}$  showed the sulfate anion encapsulated into the receptor cage, between the two 2,4,6-triethylbenzene caps, and hydrogen bonded to N-H sites. MD simulations allowed to understand the selectivity of the protonated receptor for sulphate and the role of methanol and water on anion molecular recognition. The structural preferences and the binding ability of a macrobicycle to recognize KCI in CHCI<sub>3</sub> were investigated by MD. A novel triply interlocked capsule based on tris-urea motifs containing a trapped sulfate anion was established by MM and MD. MD simulations elucidated the association between a [2]rotaxane and NO3<sup>-</sup>/halide anions. Alchemic mutations of CI- to Br- and Brto I- were performed in explicit DMSO, in the presence and absence of rotaxane leading to relative binding free energies consistent with experimental data. Other work includes XRD of hybrid networks based on the assembly of cobalt complexes with organic anions.

**Analytical Tools on Biological Systems.** Much of the work in this line has focused on NMR-based metabonomic approaches to meet a variety of ends and biomolecule structural characterization by NMR spetroscopy.

Work has been produced concerning the NMR metabolic profiling of human cells. The influence of sampling and storage procedures on the integrity and metabolic composition of different cell types (e.g. lung, osteosarcoma) has been systematically evaluated, and optimized protocols have been established for subsequent studies involving cells exposure to chemotherapy drugs. A study of the exposure of osteosarcoma (OS) cells to cisplatin has been carried out, varying drug dose and exposure time. The metabolic profile of OS cells, measured by HR-MAS NMR, has shown evidences of drug-induced changes in several metabolic pathways. Preliminary studies carried out with 13C-enriched nutrients aim at pinpointing specific metabolic changes in treated cells. Some other work has dealt with the optimization of the experimental procedure for metabolite extraction for NMR based metabolic profiling of mistranslating yeast cells and growth curves for control and mistranslating yeast samples were obtained. Separation, by multivariate methods, between control samples and mistranslating yeast samples was obtained. Metabolites that gave rise to this separation were identified. Interesting results have been obtained in the characterization of lung tissue and biofluids of cancer patients. In particular, the NMR analysis of tissues and biofluids (blood plasma and urine) and the multivariate modelling of the spectral data highlighted metabolite patterns correlated to malignancy, providing insights into lung cancer metabolism and showing the potential diagnostic value of this methodology. NMR characterization of biofluids was carried out to attempt the identification of early markers of pregnancy pathologies. Amniotic fluid (AF) showed clear evidence of disturbances in the energy metabolism and kidney development, for foetal malformation cases. This was complemented with FTIR and MS analysis, the former having shown that the IR profile of AF is significantly changed for fetal malformations, thus opening interesting possibilities for FTIR use for rapid biofluid analysis and disease diagnostics. Urine analysis has shown remarkable early indicators of conditions diagnosed or occurring later in pregnancy such as gestational diabetes and pre-term delivery. The possibility of early prediction of these conditions has triggered an extension of sample collection to a new hospital centre in the north of Portugal.

Metabonomics has also been applied to food quality control namely to the brewing and wine industries. This has been applied to the study of forced beer ageing to identify quality indicators and correlate chemical changes with product sensorial properties, a similar approach being underway in the wine industry.

In other studies, molecular modelling of the mHBP-PPIX and mHBP-hemin systems was continued and a number of key residues involved in the HBP-hemin interaction were identified. Functional studies of mHBP were continued using novel siRNA based methodologies in collaboration with CEA (Grenoble, France). Eight HBP mutants were also prepared and initial NMR and FQ studies were carried out. In addition, a preliminary x-ray structure of hSOUL was determined and new clones for hSOUL were obtained to improve spectral quality for subsequent high-resolution structure determination.

Bio-Inorganic Systems and Toxicity Studies. Several chromium compounds considered to be involved in biologically relevant functions, have been tested due to a current important controversy about their essentiality. Mice, previously administered with controlled levels of different metal complexes, were used as pre-clinical models, in order to evaluate the role of those compounds, following their routes in the body, aiming to better understand their paths in vivo. Their adverse effects were investigated using slices of target organs (kidney, liver and testis), prepared for histological, histochemical and ultrastructural methods. Complementary approaches, such as flow-cytometry that allows, in real time, a multi-parametric assay of cells, have been also used to get more complete insights into the underlying mechanisms of toxicity. Altogether, these methodologies are good contributions for the evaluation of the toxicological effects of some heavy metals in public health. Other metal-based mixtures were also assayed *in vivo* in small rodents in order to evaluate adverse effects on relevant organs such as kidneys. In particular, extension of these studies will be made to chromium(III) complexes with picolinate ligands, widely used as a nutritional supplement (although mainly in USA), and a controversial issue because it is now suspicious of provoking damages in vivo. The compound has been synthesized and it is intended to be tested (in vivo) and studied by ultra-structural techniques, in order to try to clear the controversy. Within in vivo testing studies, a wide range of molecular and cell markers were used to evaluate the effects of some compounds on fertility parameters in both human and animal male. These include genomic *imprinting* in spermatogenesis, mitochondrial bioenergetics, acrosome reaction, and DNA integrity.

New Ru(II) complexes bearing new organic molecules serving as models for natural products (eg. lapachol) have continued to be synthesized and characterized mainly by separation chromatographic techniques and <sup>1</sup>H and <sup>13</sup>C NMR. Ru(II) complexes have also been used to obtain inclusion complexes with cyclodextrins (CDs). CDs are drug solubilisers exhibiting, in particular cases, drug activity enhancement function. [Ru(9aneS<sub>3</sub>)(1,10-phenanthroline)CI]CI (9aneS<sub>3</sub> = trithiacyclononane) was included in native  $\beta$ -CD and heptakis-2,3,6-tri-O-methyl- $\beta$ -CD (TRIMEB) its minimal inhibitory concentration (MIC) against selected strains of gram-negative and gram-positive bacteria, albeit moderate, was lowered from 2- to 8-fold upon encapsulation in these hosts. A novel ruthenium complex, [Ru(9aneS<sub>3</sub>)(glycine)CI]CI, was also developed, aiming at cytotoxic action against osteosarcoma by targeting the osteoblastic glutamate receptors, in which glycine acts as a co-agonist. Cytotoxicity on the osteosarcoma MG-63 line of the free and CD-encapsulated complex, however, was mild and time-delayed (appearing only after 72h of incubation), so a further optimization of the drug structure is needed.

Regarding the development of new biomaterials for guided therapeutical uses, chemically derivatized magnetite/carrageenan and magnetite/gold/carrageenan nanoparticles have been functionalised with antibody binding and the study of the controlled release of magnetic particles is currently underway.

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A dry active bio signal electrode with an hyrbid organic-inorganic A dry active bio signal electrode with an hyrbid organic-inorganic interface material interface material da Silva Cunha JP, Carlos LD, Dieteren Ribeiro D da Silva Cunha JP, Carlos LD, Dieteren Ribeiro D IB2009/55758 PPN104882 15-12-2009 11-12-2010 Nanotubos luminescentes de aluminatos de berílio, magnésio, Materiais híbridos nanomagnete-porfirina, processo para a sua síntese e respectiva aplicação em desinfeçção de águas Almeida MA, Cavaleiro JAS, Rocha J, Carvalho CMB, Costa LAS, Alves ESCF, Cunha MA, Tomé JPC, Faustino MAF, Neves MGPMS, cálcio, estrôncio ou bário dopados com cério (III) e co-dopados com outros iões lantanideos M(1-x-y)N2O4:Cex,Lny Zurba NK Tomé AC, Lin Z, Rainho JP PT 103828 PCT/PT2009/00070 10-12-2009 23-03-2009 Termómetro Molecular Luminiscente Carlos LD, Amaral VS, Lima PP, Brites CDS, Palácio F, Millán A, Silva NJO P200930367 Processo de encapsulamento de aluminatos luminescentes de berílio, magnésio, cálcio, estrôncio ou bário dopados com cério (III) encapsulados com TiO2 e as suas respectivas utilizações Žurba NK, Ferreira JMF PPN104801 26-06-2009 Tunable Low Loss (High Q) Dielectric Composite Thick Films and 11-04-2009 Method of Making the Same Vilarinho PM, Fu Z, Wu AY, Kingon AI, PCT/IB2009/055753 Nanotubos luminescentes de aluminatos de berílio, magnésio, cálcio, estrôncio ou bário dopados com cério (III) e co-dopados com outros iões lantanideos M(1-x-y)N2O4:Cex,Lny 15-12-2009 Zurba NK PPN104486 Method for the preparation at low temperatures of ferroelectric thin films, the ferroelectric thin films thus obtained and their applications 03-04-2009 Vilarinho PM, Wu AY, Calzade ML, Rioboo RJ, Ignos Bretos I PCT/IB2009/055699 Filmes espessos compósitos de dieléctricos de perdas dieléctricas baixas e sintonizáveis e método de fabrico dos mesmos Vilarinho PM, Fu Z, Wu AY, Kingon Al 11-12-2009 Ultrathin metalic oxygen barrier diffusion applied to Si-based PPN104881 components and microelectronics devices Rauwel EY, Lourenço AAC PCT IB2009/055667 11-12-2009 Method for the preparation at low temperatures of ferroelectric thin films, by diphasic precursors and photochemical solution 10-12-2009 deposition and their applications Vilarinho PM, Wu AY, Calzade ML, Rioboo RJ, Ignos Bretos I Silicon nitride sealing rings with diamond coating Silva RF, Fernandes AJS, Amaral M, Almeida FA, Oliveira FJ, Costa FM, Carrapichano, JM WO/2009/083778 PT 104751 18-09-2009 09-07-2009 Ultrathin metalic oxygen barrier diffusion applied to Si-based Mortars containing phase change material microcapsules, their components and microelectronics devices preparation process and use Lucas S, Ferreira VM, Barroso de Aguiar JL, Labrincha JA Rauwel EY, Lourenco AAC PPN 104865 PCT/PT2009/000072 09-12-2009 10-12-2009 Argamassas contendo microcásulas de materiais de mudança de fase, processo para a sua preparação e sua utilização Lucas S, Ferreira VM, Barroso de Águiar JL, Labrincha JA PT 104866 Cerâmicos produzidos a partir de escórias de incineração de resíduos sólidos urbanos Fernandes MHF, Monteiro RCC, Davim EJCR, Figueiredo CFML, Lopes MG 10-12-2009 PCT/PT2009/055671 10-12-2009 Cerâmicos produzidos a partir de escórias de incineração de resíduos sólidos urbanos Fernandes MHF, Monteiro RCC, Davim EJCR, Figueiredo CFML, Aqueous Coating Compositions for Use in Surface Treatment of Cellulosic Substrates Lopes MG Pascoal Neto C, Gandini A, Silvestre A, Freire Barros C, Fernandes PPN 104861 07-12-2009 SCM PCT//IB2009/055622 09-12-2009 Aqueous Coating Compositions for Use in Surface Treatment of Cellulosic Substrates Process for the production of liquid poliols of renewable origin by the liquefaction of agro-forestry and agro-biomass Pascoal Neto C, Gandini A, Cruz Pinto JJ Pascoal Neto C, Gandini A, Silvestre A, Freire Barros C, Fernandes SCM PPN 104702 PCT/IB2009/053485 31-07-2009 08-07-2009 Método de sinterização reactiva de estruturas porosas vítreas ou semicristalinas para regeneração óssea com incremento da área superficial específica

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# **Projects finished during '09**

NMP3-CT-2007-SSA 032308 NANOCOFC - Nanotechnologies and Nanosciences, Knowledge Based Multifunctional Materials, New Production Processes and Devices Principal Researcher: Fernando Manuel Bico Marques Status: Participante Beginning Date: 01/11/2006 / 36 Months Funding: European Commission / UA Value: 32.650,00 STREP 033410

MATSILC-Novel materials for silicate based fuel cells Principal Researcher: Jorge Frade Status: Participante Beginning Date: 01/12/2006 / 36 Months Funding: EC-6º PROGRAMA QUADRO/ UA Value: 252.000,00

11783-2 MULTIPROTECT ou NMP3-CT-2005-011783 Advanced Environmentally Friendly Multifunctional Corrosion Protection by Nanotechnology Principal Researcher: Mikhail Zheludkevich Status: Participante Beginning Date: 01/03/2005 / 48 Months Funding: European Commission / UA Value: 282.203,00

> EuropeAid/120707/C/SER/Br nº PAIIPME-ATI-POA2-022 Principal Researcher: Rui Ramos Ferreira e Silva Status: Beginning Date: 01-02-2009 / 2 Months Funding: / UA Value: 11.340,00

> EuropeAid/120707/C/SER/Br nº PAIIPME-ATI-POA2-050 Principal Researcher: Rui Ramos Ferreira e Silva Status: Beginning Date: 2009 / Months Funding: / UA Value: 5.410,00

# international projects

Acção nº E-93/08, Procº AI-E/07 High-resolution solid-state NMR and powder diffraction two complementary techniques for the characterization of organic-inorganic hybrid nanomaterials based on metal phosphates Principal Researcher: Luis Miguel Monteiro Mafra national projects Status: Participante Beginning Date: 01/01/2008/ 24Months Funding:CRUP/ UA Value: 4.000,00 00286 28/02/2008, Proc. 4.4.1 Alemanha Characterization of the geometric and electronic structure of CNT supported vanadium oxides at the nanometer scale Principal Researcher: Marc Willinger Status: Proponente Beginning Date: 01/01/2008/ 24 Months Funding: FCT/DAAD (Germany)/ UA Value: 5.000,00 PTDC/QUI/58377/2004 NOVEL MULTIDIMENSIONAL LANTHANIDE-ORGANIC FRAMEWORKS: HYDROTHERMAL SYNTHESIS, STRUCTURAL CHARACTERISATION AND APPLICATIONS Principal Researcher: Filipe Alexandre Almeida Paz Status: Participante Beginning Date: 01/10/2005/ 42 Months Funding: FCT/ UA Value: 59.000,00 PPCDT/QUI/58377/2004 NOVEL MULTIDIMENSIONAL LANTHANIDE-ORGANIC FRAMEWORKS: HYDROTHERMAL SYNTHESIS, STRUCTURAL CHARACTERISATION AND APPLICATIONS Principal Researcher: Filipe Alexandre Almeida Paz Status: Proponente Beginning Date: 01/01/2007/ 27 Months Funding: FCT/ UA Value: 23.700,00 POCI/CTM/55648/2004 PERIODIC MESOPOROUS ORGANIC-INORGANIC HYBRIDS Principal researcher: Paula Celeste da Silva Ferreira Status: Proponente Beginning Date: 01/05/2006/ 36 Months Funding: FCT / UA value (€): 55.000,00 POCI/CTM/60064/2004 ELECTROPOLYMERIZED COATING USED AS PRE-TREATMENTS FOR ALUMINIUM ALLOYS Principal Researcher: Mário Guerreiro da Silva Ferreira Status: Participante Beginning Date: 15/07/2005 / 36 Months Funding: FCT / UA Value: 17.276,00 Estudo sobre o melhoramento da interacção tinta/papel na impressão offset e ink/jet Principal Researcher: Dmitry Victorovitch Evtyugin Status: Participante Beginning Date: 01/07/2007/ 24 Months Funding: RAIZ - Instituto de Investigação da Floresta e Papel/ UA Value: 25.000,00 REEQ/CTM/515/2005 Principal Researcher: José Pinto Status: Proponente Beginning Date: / Months Funding: FCT/ UA Value: 321.482,00 Produção de biocompósitos de valor acrescentado a partir do engaço e do folhelho da uva Principal Researcher: Dmitry Victorovitch Evtyugin Status: Participante Beginning Date: 01/04/2009 / 9 Months Funding: TAVFER/ UA Value: 13.200,00 A-14/07 Principal Researcher: Maria Helena Figueira Vaz Fernandes Status: Participante Beginning Date: Outubro de 2006/ 48 Months Funding: CRUP/ UA Value: 2.500,00 Programa PESSOA Luso-Frances Functional studies of the SOUL/ HBP family of heme.binding proteins Principal Researcher: Brian James Goodfellow Status: Proponente Beginning Date: 01/01/2008/ 36 Months Funding: FCT/ UA Value: 6.000,00 CIMAGO 14/06 Principal Researcher: Iola Melissa Fernandes Duarte Status: Proponente Beginning Date: 01/09/2006/ 36 Months Funding: CIMAGO/ UA Value: 5.000,00

# Projects in progress during '10

Marie Curie FP7-PEOPLE-2009-RG-256509 Oxalkanes - Sustainable catalytic oxidation of alkanes, FP7 Marie Curie Reintegration grant Principal Researcher: Ana Rosa Silva Status: Proponente Beginning Date: 01/04/2010/ 24 Months Funding: EU/ UA Value: 45.000,00

INTAS-05-1000008-8091 Polarization-driven self-assemply of organics and biomaterials using ultrathin ferroelectric polymers Principal Researcher: Andrei Kholkin Status: Proponente Beginning Date: 01/11/2006/ 30 Months Funding: INTAS/ UA Value: 16.000,00

NMP3-CT-2006-32616 MULTICERAL-Multifunctional Ceramics Layers with High Electro-magnetoelastic couplin in complex geometries Principal Researcher: Andrei Kholkin Status: Proponente Beginning Date: 01/11/2006/ 36 Months Funding: FP7 - European Commission/ UA Value: 263.000,00

> IP515960 ULCOS- Ultra Low CO2 Steelmaking Principal Researcher: Jorge Frade Status: Participante Beginning Date: 31/10/2004 / 70 Months Funding: European Commission / UA Value: 415.000,00

NMR3-LA-2008-214261 Multi-level protection of materials for vehicles by 'Smart' nanocontainers (MUST) Principal Researcher: Mikhail Zheludkevich Status: Participante Beginning Date: 01/06/2008 / 48 Months Funding: European Commission / UA Value: 824.769,00

RFSR-CT-2008-00028 Prediction of the kinetics of self-repaired of forming induced defects on thin functional primers for advances automotive applications (KINSREP) Principal Researcher: Mikhail Zheludkevich Status: Participante Beginning Date: 01/07/2008 / 36 Months Funding: European Commission / UA Value: 160.341,00

> COLL-CT-2006 030338 ADOPTIC ADOPTIC - ADDITIVE OPTIMISATION FOR IMPROVED CERAMICS Principal Researcher: José Maria da Fonte Ferreira Status: Participant Beginning Date: 01/09/2006/ 36 Months Funding: European Commission/ UA Value: 74.040,13

CP-IP 228589-2 AFORE – Forest Biorefinery: Added Value Chemicals and Polymers by new integrated separation, fractionation and upgrading technologies Principal Researcher: Armando Silvestre Status: Participante Beginning Date: Setembro de 2009/ 48 Months Funding: FP-7/ UA Value: 674.687,00

> 228802 SUNPAP - Scale-up of Nanoparticles in Modern Papermarking Principal Researcher: Carlos de Pascoal Neto Status: Participante Beginning Date: Junho de 2009/ 36 Months Funding: FP7/ UA Value: 226.000,00 B5–1000/03/000339

DOLCETA - Development of on-line consumer education tools for adults Principal Researcher: Maria Clara Ferreira Magalhães Status: Participante Beginning Date: Dezembro 2003/ Months Funding: European Commission/ UA Value: 120.000,00

## international projects

PTDC/CTM/73030/2006 Polarization-driven self-assembly of organic and biomaterials Principal Researcher: Andrei Kholkin Status: Proponente Beginning Date: 01/03/2008/ 36 Months Funding: FCT/ UA Value: 141.000,00

### national projects

PTDC/CTM/69316/2006 Multiferroic, magnetoelectric and metallic micro and nanocomposites base don electroactive polymers Principal Researcher: Andrei Kholkin Status: Participante Beginning Date: 01/01/2009/ 36 Months Funding: FCT/ UA Value: 10.000,00

PTDC/FIS/108025/2008 NOLEAD: Novel lead-free ferroelectric films by PLD for optoelectronics Principal Researcher: Andrei Kholkin Status: Participante Beginning Date: 02/01/2010/ 36 Months Funding: FCT/ UA Value: 51.966,00

PTDC/FIS/65233/2006 Ternary and quaternary nitride alloys for lattice matched heterostructures: novel materials for high efficiency field effect transistors and optoelectronic devices Principal Researcher: Sérgio Manuel Sousa Pereira Status: Participante Beginning Date: 01/04/2007/ 36 Months Funding: FCT/ UA Value: 59.520,00

PTDC/EQU-ERQ/66045/2006 Use of membrane reactores in the water-gas shift reaction Principal Researcher: Zhi Lin Status: Participante Beginning Date: 01/09/2007/ 36 Months Funding: FCT/UA Value: 25.919,00

PTDC/CTM/65667/2006 Synthesis and characterization of multiferroic nanostructures synthetised via novel non-aqueous sol-gel routes Principal Researcher: Nicola Allessandro Pinna Status: Proponente Beginning Date: 01/11/2007/ 36 Months Funding: FCT/ UA Value: 151.000,00

PTDC/CTM/73243/2006 Nanostructured Photoluminescent rare-earth nanotubes and microporous silicates Principal Researcher: João Rocha Status: Proponente Beginning Date: 01/12/2007/ 36 Months Funding: FCT/ UA Value: 60.456,00

PTDC/QUI/71198/2006 Ansa-bridged organorhenium(VII) oxides and their application as homogeneous and heterogeneous catalysts Principal Researcher: Isabel Maria Sousa Gonçalves Status: Proponente Beginning Date: 01/01/2008/ 36 Months Funding: FCT/ UA Value: 42.372,00

PTDC/QUI/65805/2006 Water nanodrops in microporouse and inorganic-organic hybrid materials Principal Researcher: João Carlos Matias Celestino Gomes da Rocha Status: Proponente Beginning Date: 01/01/2008/ 36 Months Funding: FCT/ UA Value: 61.000,00

PTDC/CTM/72093/2006 Self-patternable organic/inorganic hybrids for low cost integrated optics devices Principal Researcher: Maria Rute de Amorim e Sá Ferreira André Status: Proponente Beginning Date: 01/01/2008/ 36 Months Funding: FCT/ UA Value: 74.746,00

PTDC/QUI/67712/2006 Nanochemistry of magnetic/luminescent composites for in vitro medical diagnosis applications Principal Researcher: Tito da Silva Trindade Status: Proponente Beginning Date: 01/01/2008/ 36 Months Funding: FCT/ UA Value: 40.900,00

PTDC/CTM/73643/2006 Developing Novel Microporous Powders and Membranes Principal Researcher: Zhi Lin Status: Proponente Beginning Date: 01/02/2008/ 36 Months Funding: FCT/ UA Value: 78.000,00

PTDC/CTM/100468/2008 Structural and chemical characterization at the nanometer scale Principal Researcher: Marc Willinger Status: Proponente Beginning Date: 01/03/2010/ 36 Months Funding: FCT/ UA Value: 165.000,00

> PTDC/CTM/098361/2008 Nanotubes and Nanowires based hybrid nanostructures Principal Researcher: Nicola Allessandro Pinna Status: Participante Beginning Date: 01/04/2010/ 36 Months Funding: FCT/ UA Value: 180.000,00

NANO/NMed-SD/0140/200 Integrated lab on chip platforms for medical diagnosis Principal Researcher: Tito da Silva Trindade Status: Participante Beginning Date: 01/08/2009/ 24 Months Funding: FCT/CSIC/ UA Value: 20.040,00

PTDC/QUI/64770/2006 Catalytic oxidation reactions by transition metal complexes confined into mesoporous structured solids Principal Researcher: Ana Rosa Silva Status: Proponente Beginning Date: 01/02/2009/ 36 Months Funding: FCT/ UA Value: 64.638,00

PTDC/QUI/65142/2006 Recycling antimalarials: rational design of novel 8-aminoquinoline analogues with gametocytocidal and blood-schizontocidal activity Principal Researcher: José Richard Batista Gomes Status: Participante Beginning Date: 01/01/2009/ 36 Months Funding: FCT/ UA Value: 0,00

> PTDC/CTM/65718/2006 Fabrication of ordered mesoporous carbon networks for catalysts support Principal Researcher: José Richard Batista Gomes Status: Participante Beginning Date: 02/01/2008/ 36 Months Funding: FCT/ UA Value: 0,00

PTDC/QUI - QUI/100998/2008 Development of high-resolution 1H solid-state NMR methods and applications on materials and molecules of biological interest Principal Researcher: Luis Miguel Monteiro Mafra Status: Participante Beginning Date: 01/01/2010/ 36 Months Funding: FCT/ UA Value: 97.368,00

> PTDC/EQU-EQU/099423/2008 Intelligent Design of Mesoporous Organosilicas for Adsorptive Separation Processes Principal Researcher: José Richard Batista Gomes Status: Participante Beginning Date: 01/01/2010/ 36 Months Funding: FCT/ UA Value: 68.232,00

PTDC/QUI-QUI/098098/2008 Nano-sized Functional Metal-Organic Frameworks Based on Lanthanide Polyphosphonates Principal Researcher: Filipe Alexandre Almeida Paz Status: Proponente Beginning Date: 01/01/2010/ 36 Months Funding: FCT/ UA Value: 148.620,00

PTDC/CTM/108975/2008 Preparation and photoluminescence features of white-emitting single-phased phosphors for light emitting diodes Principal Researcher: Lianshe Fu Status: Proponente Beginning Date: 01/01/2010/ 36 Months Funding: FCT/ UA Value: 63.760,00 PTDC/CTM/101324/2008 Híbridos Orgânicos-Inorgânicos com Propriedades de Emissão Optimizadas para Aplicação na Nova Geração de Comunicações Ópticas Principal Researcher: Luís António Ferreira Martins Dias Carlos Status: Proponente Beginning Date: 2010 / 36 Months Funding: FCT/ UA Value: 77.878,00

PTDC/CTM/101453/2008 Novel light emitting heterostructures with plasmonic coupling to metal nanocrystals Principal Researcher: Sérgio Manuel Sousa Pereira Status: Proponente Beginning Date: 01/01/2010/ 36 Months Funding: FCT/ UA Value: 95.000,00

PTDC/FIS/100448/2008 Free-charge carrier properties and doping mechanisms of InN-based materials Principal Researcher: Sérgio Manuel Sousa Pereira Status: Participante Beginning Date: 01/01/2010/ 36 Months Funding: FCT/ UA Value: 21.720,00

PTDC/QUI-QUI/098892/2008 Study of intermolecular interactions in alternative solvents: A NMR based contribution to sustainable chemistry Principal Researcher: Luís Mafra Status: Participante Beginning Date: 01/01/2010/ 36 Months Funding: FCT/ UA Value: 0,00

PTDC/QUI/67612/2006 Nanochemistry of magnetic/luminescent composites for in-vitro medical diagnosis applications Principal Researcher: Tito da Silva Trindade Status: Participante Beginning Date: 01/01/2008/ 36 Months Funding: FCT/ UA Value: 56.200,00

PTDC/FIS/104310/2008 High-pressure synthesis and structure determination of novel nanostructured materials Principal Researcher: Leonel Marques Vitorino Joaquim Status: Proponente Beginning Date: 01/05/2010/ 36 Months Funding: FCT/ UA Value: 163.000,00

PTDC/QUI/65647/2006 Novas matrizes sólidas quelantes com hidroxipirimidinonas imobilizadas para aplicações ambientais e biológicas Principal Researcher: João Carlos Matias Celestino Gomes da Rocha Status: Participante Beginning Date: 01-12-2008 / 36 Months Funding: LNEG / UA Value: 9.300,00

RNRMN Rede Nacional de Ressonância Magnética Nuclear Principal Researcher: João Carlos Matias Celestino Gomes da Rocha Status: Participante Beginning Date: 01-01-2010 / 36 Months Funding: FCT / UA Value: 209.364,00

PTDC/CTM/71643/2006 Novel Aurivillus oxides for microelectronic applications Principal Researcher: Andrei Kholkin Status: Participante Beginning Date: 16/02/2008/ 36 Months Funding: FCT/ UA Value: 72.000,00

PTDC/CTM/68614/2006 Shear-induced solidification studies on polymers and polymer-clay nanocomposites Principal Researcher: Andrei Kholkin Status: Participante Beginning Date: 02/01/2008/ 36 Months Funding: FCT/ UA Value: 20.000,00

Nano/Nmed-SD/0156/2007 Smart joint implants using bionanocomposites Principal Researcher: Andrei Kholkin Status: Participante Beginning Date: 01/10/2009/ 24 Months Funding: FCT/ UA Value: 65.000,00

PTDC/CTM/81442/2006 Origin of polar state in relaxors via Scanning Probe Microscopy Principal Researcher: Andrei Kholkin Status: Proponente Beginning Date: 15/05/2007/ 36 Months Funding: FCT/ UA Value: 119.724,00

PTDC/CTM/73367/2006 Colossal permittivity perovskite films by chemical solution deposition methods for microelectronic and sensor applications Principal researcher: Aiying Wu Status: Proponente Beginning Date: 01/03/2008 / 36 Months Funding: FCT/ UA value (€): 85.000,00

> PTDC/QUI/72584/2006 Photocatalytic reduction of carbon dioxide into valuable hydrocarbon products Principal researcher: Paula Celeste da Silva Ferreira Status: Proponente Beginning Date: 01/01/2008/ 36 Months Funding: FCT/ UA value (€): 41.200,00

> > PTDC/CTM/71643/2006 Novel Aurivillius Oxides for microelectronic applications Principal researcher: Maria Elisabete Jorge Vieira Costa Status: Proponente Beginning Date: 01/02/2008/ 36 Months Funding: FCT/ UA value (€): 72.000,00

PTDC/CTM/64805/2006 Statics and dynamics of hight polarizable ultra-thin films and nano-layered superlattices Principal researcher: Paula Maria Lousada Silveirinha Vilarinho Status: Participante Beginning Date: Fevereiro de 2008/36 Months Funding: FCT/ UA value (€): 44.663,00

PTDC/CTM/67575/2006 PROCESSING AND CHARACTERIZATION OF MULTIFERROIC CERAMICS FOR SENSOR AND ACTUACTOR APPLICATIONS Principal researcher: Paula Maria Lousada Silveirinha Vilarinho Status: Participante Beginning Date: 02/01/2008/ 36 Months Funding: FCT/ UA value (€): 25.001,00

> PTDC/EQU-EQU/099423/2008 Intelligent Design of Mesoporous Organosilicas for Adsorptive Separation Processes Principal researcher: José Richard Batista Gomes Status: Participante Beginning Date: 01/01/2010 / 36 Months Funding: FCT/ UA value (€): 68.232,00

> > PTDC/CTM/98130/2008 Design of multifunctional films from porous thin films Principal researcher: Paula Celeste da Silva Ferreira Status: Proponente Beginning Date: 01/01/2010/ 36 Months Funding: FCT/ UA value (€): 100.000,00

NANO-NMed-SP/0156/2007 Smart joint implants using bionanocomposites – SIMBIO Principal researcher: Paula Maria Lousada Silveirinha Vilarinho Status: Participante Beginning Date : 01/03/2009/ 35 Months Funding: FCT/ UA value (€):

PTDC/CTM/104186/2008 Ferroelectric - carbon nanotube (CNT) composites towards the fabrication of advanced functional devices Principal researcher: Paula Maria Lousada Silveirinha Vilarinho Status: Proponente Beginning Date : 01-01-2010/ Months 36 Funding: FCT/ UA value (€):

PTDC/CTM/108319/2008 Low temperature synthesis of functional thin films towards compatibility with low cost substrates Principal researcher: Paula Maria Lousada Silveirinha Vilarinho Status: Proponente Beginning Date : 01-01-2010/ Months 36 Funding: FCT/ / UA value (€): PTDC/CTM/099415/2008 Multiferroics and magnetoelectrics for spintronics: barriers and interfaces Principal Researcher: Vitor Brás de Sequeira Amaral Status: Participante Beginning Date: 01/02/2010/ 36 Months Funding: FCT/ UA Value: 43.680,00

PTDC/FIS/105416/2008 MULTIFOX: Nanometric Probing and Modification of Multiferroic Oxides Principal Researcher: Vitor Brás de Sequeira Amaral Status Proponente Beginning Date: 01/02/2010 / 36 Months Funding: FCT / UA Value: 109.512,00

CERN/FP/83643/2008 Research on Magnetic and Multiferroic Oxides using Radioactive Isotopes at ISOLDE-CERN Principal Researcher: Vitor Brás de Sequeira Amaral Status Proponente Beginning Date: 02/01/2009 / 12 Months Funding: FCT / UA Value: 20.988.00

CERN/FP/109357/2009 Research on Magnetic and Multiferroic Materials using Radioactive Isotopes at ISOLDE-CERN Principal Researcher: Vitor Brás de Sequeira Amaral Status Proponente Beginning Date: 01/02/2010 / 12 Months Funding: FCT / UA Value: 17.216,00

CERN/FP/109325/2009 Local probe studies on Metal/Oxide junctions Principal Researcher: Armando António C. S. Lourenço Status: Participante Beginning Date: 01/01/2010/ 12 Months Funding: FCT / UA Value: 2.520,00

IS-487 Study of Local Correlations of Magnetic and Multiferroic Compounds Principal Researcher: Vitor Brás de Sequeira Amaral Status: Proponente Beginning Date: 01/01/2009 / 36 Months Funding: FCT/ UA Value:

I-81

Radioactive probe studies of coordination mechanisms of heavy metal ions from natural waters to functionalized magnetic nanoparticles Principal Researcher: Vitor Brás de Sequeira Amaral Status: Proponente Beginning Date: 01/01/2009 / 36 Months Funding: FCT/ UA Value:

NANO/NMed-AT/0042/2007 Avanço na área de entrega de fármacos: terapias dirigidas combinadas no tratamento do cancro da mama e leucemia (a rede Onco TargetNanoMed) Principal Researcher: Joaquim Vieira Status: Participante Beginning date: 01/07/2009 / 24 Months Funding: FCT /UA Value: 14.000,00

RME – REDE/1509/RME/2005 Rede Nacional de Microscopia Electrónica Principal Researcher: Joaquim Vieira Status: Proponente Beginning date: 01/01/2009/ 36 Months Funding: FCT /UA Value: 622.661,73

PTDC/CTM/64357/2006 NOVEL LAYERED FERRITE MATERIALS WITH MIXED IONIC-ELECTRONIC CONDUCTIVITY FOR APPLICATIONS IN ALTERNATIVE ENERGY SOURCES Principal Researcher: Vladislav Kharton Status: Participant Beginning Date: 01/01/2008 / 36 Months Funding: FCT/ UA Value: 76.760,00

PTDC/CTM/098486/2008 Nanocell Principal Researcher: Fernando Manuel Bico Marques Status: Proponente Beginning Date: 01/01/2010 / 36 Months Funding: FCT/ UA Value: 122.000.00 PTDC/CTM/66041/2006 Sensing the micro-distribution of chemical species in solution close to the active metal Principal Researcher: António Alexandre da Cunha Bastos Status: Proponente Beginning Date: 01/01/2008 / Months 36 Funding: FCT / UA Value: 82.425,00

PTDC/CTM/72223/2006 Anodic films on light metals obtained by novel high-voltage pulsed anodizing technique Principal Researcher: Mário Guerreiro da Silva Ferreira Status: Proponente Beginning Date: 01/01/2008 / 36 Months Funding: FCT / UA Value: 107.202,00

PTDC/CTM/65632/2006 Self-healing protective coating with 'intelligent' nanoreservoirs of corrosion inhibitors Principal Researcher: Mikhail Zheludkevich Status: Proponente Beginning Date: 01/03/2008 / 36 Months Funding: FCT / UA Value: 82.600,00

PTDC/CTM/66195/2006 Designing ultra-fine textured microstructures by laser floating zone – LaFlorZone Principal Researcher: Rui Ramos Ferreira e Silva Status: Participante Beginning Date: 01/01/2008 / 36 Months Funding: FCT / UA Value: 115.697,00

> PTDC/EME-TME/100689/2008 Principal Researcher: Filipe Oliveira Status: Participante Beginning Date: 01/03/2010 / 36 Months Funding: FCT / UA Value: 124.999,00

PTDC/CTM/66302/2006 DEVELOPMENT OF A SELF-FLOW REFRACTORY CASTABLE WITHOUT CEMENT FOR MONOLITHIC APPLICATIONS Principal Researcher: Ana Maria Segadães Status: Participante Beginning Date: 07/01/2007/ 36 Months Funding: FCT/ UA Value: 7.500,00

> PTDC/CTM/72318/2006 Ecopigments - Development of novel inorganic pigments from industrial wastes Principal Researcher: João António Labrincha Batista Status: Proponente Beginning Date: 01/01/2008/ 36 Months Funding: FCT/ UA Value: 62.880,00

> > PTDC/ECM/72104/2006 Study of functional mortars for a sustainable construction Principal Researcher: Victor Miguel de Sousa Ferreira Status: Proponente Beginning Date: 01/01/2007/ 36 Months Funding: FCT/ UA Value: 81.600,00

PTDC/CTM/65243/2006 EXREACT - Mitigação de reacções deletérias expansivas internas em estruturas de betão Principal Researcher: João António Labrincha Batista Status: Participante Beginning Date: 01/01/2008/ 36 Months Funding: FCT/ UA Value: 16.800,00

> PTDC/ECM /102154/2008 Principal Researcher: Victor Miguel de Sousa Ferreira Status: Beginning Date: 01/01/2010 / 36 Months Funding: FCT/ UA Value: 23.400,00

> PTDC/ECM /100234/2008 Principal Researcher: Victor Miguel de Sousa Ferreira Status: Beginning Date: 01/02/2010 / 36 Months Funding: FCT/ UA Value: 63.876,00

FCT/CNPq – biénio 2009-2010 Principal Researcher: Ana Maria Segadães Status: Proponente Beginning Date: 01/09/2009 / 24 Months Funding: FCT/ UA Value: 9.000,00

PTDC/CTM/102141/2008 Novos Vidros e compósitos vidro/ nanoparticulas cerâmicas sintetizáveis a baixas temperaturas Principal Researcher: Maria Helena Figueira Vaz Fernandes Status: Participante Beginning Date: 01/01/2010/ 36 Months Funding: FCT/ UA Value: 37.057,00

PTDC/QUI/68472/2006 Controlled chemical modification of polysaccharides for the development of novel materials/ Modificação químicas controlada de polissacarídeos para o desenvolvimento de novos materiais Principal Researcher: Carmen Sofia da Rocha Freire Barros Status: Participante Beginning Date: 01/01/2008 / 36 Months Funding: FCT/ UA Value: 69.300,00

PTDC/CTM/68614/2006 Shear Induced solidification studies in polymers and nanocomposites Principal Researcher: José Martins Status: Proponente Beginning Date: Junho de 2008 / 36 Months Funding: FCT/ UA Value: 12.931,00

PTDC/EQU-EQU/100476/2008 Síntese e Caracterização de Novas Membranas de Niobiossilicatos e Titanosilicatos Microporosos e sua Aplicação na Separação de Misturas Contendo Hidrogénio Principal Researcher: Carlos Manuel Santos da Silva Status: Proponente Beginning Date: 2010/ 36 Months Funding: FCT/ UA Value: 48.800,00

PTDC/CTM/67444/2006 Reversible Diels-Alder furan click chemistry at the service of novel functional materials based on renewable resources Principal Researcher: Alessandro Gandini Status: Proponente Beginning Date: 01/01/2009/ 36 Months Funding: FCT/ UA Value: 73.440,00

PTDC/CTM/71491/2006 OLIVEPOL – Espumas de Poliuretano e Compósitos Termoplásticos baseados em caroço de azeitona oxipropilado. Principal Researcher: Alessandro Gandini Status: Participante Beginning Date: Janeiro de 2009/ 35 Months Funding: FCT/ UA Value: 28.960,00

PTDC/QUI/101058/2008 Development of new polyesters derived from 2,5-furandicarboxylic acid Principal Researcher: Armando Silvestre Status: Proponente Beginning Date: 01/01/2010 / 36 Months Funding: FCT/ UA Value: 88.458,00

PTDC/AAC-AMB/101050/2008 Biopolymers production as a new concept on wastewater treatment - POLIBIO Principal Researcher: Luísa Alexandra Seuanes Serafim Leal Status: Participante Beginning Date: 01/01/2010 / 36 Months Funding: FCT/ UA Value: 152.976,00

PTDC/AAC-AMB/100790/2008 MICROBIAL CONTRIBUTION TO THE VALORIZATION OF WASTE/BY-PRODUCTS FROM BIOFUELS PRODUCTION Principal Researcher: Luísa Alexandra Seuanes Serafim Leal Status: Participante Beginning Date: 01/02/2010 / 36 Months Funding: FCT/ UA Value: 0,00

PTDC/AGR-AAM/104911/2008 Principal Researcher: Dmitry Victorovitch Evtyugin Status: Participante Beginning Date: 01/01/2010 / 48 Months Funding: FCT/ UA Value: 67.728,00

PTDC/QUI-QUI/100044/2008 Principal Researcher: Dmitry Victorovitch Evtyugin Status: Participante Beginning Date: 01/01/2010 / 48 Months Funding: FCT/ UA Value: 127.332,00

PTDC/EQU-FTT/102166/2008 Sweetening of natural gas using ionic liquids Principal Researcher: João Manuel da Costa e Araújo Pereira Coutinho Status: Proponente Beginning Date: 01/01/2010 / 36 Months Funding: FCT/ UA Value: 78.000,00

PTDC/QUI/72903/2008 Anchoring Basic Parameters for Fundamental Predictive Models in Liquid Salt Systems Principal Researcher: João Manuel da Costa e Araújo Pereira Coutinho Status: Proponente Beginning Date: 01/01/2009/ 36 Months Funding: FCT/ UA Value: 76.388,00

PTDC/EQU-FTT/65252/2006 Vapour Liquid Equilibrium of Pure Ionic Liquids and their Mixtures with Organic Solvent Principal Researcher: João Manuel da Costa e Araújo Pereira Coutinho Status: Proponente Beginning Date: 01/10/2007/ 36 Months Funding: FCT/ UA Value: 104.970,00

ERA-IB/BIO/0001/2008-ERA-NOEL Novel Enzyme Tools for Production of Functional Oleochemicals from unsaturated lipids (ERA-NOEL) Principal Researcher: Armando Silvestre Status: Participante Beginning Date: Março de 2009/ 36 Months Funding: ERA-NET/FCT/ UA Value: 129.943,00

PTDC/QUI/66523/2006 A Nuclear Magnetic Resonance (NMR)-based metabonomic study of health disorders of foetus and mother during pregnancy: towards biochemical characterisation and early diagnostics Principal Researcher: Ana Maria Pissarra Coelho Gil Status: Participante Beginning Date: 15/01/2008/ 36 Months Funding: FCT/ UA Value: 64.960,00

> PTDC/QUI/64203/2006 Structural and functional studies of the soul/hbp family of heme-binding proteins Principal Researcher: Brian James Goodfellow Status: Proponente Beginning Date: 01/01/2008/ 36 Months Funding: FCT/ UA Value: 55.950,00

PTDC/QUI/68017/2006 Metabolic profiling and biochemical differentiation of human lung tumours by nuclear magnetic resonance (NMR) methods Principal Researcher: Iola Melissa Fernandes Duarte Status: Proponente Beginning Date: 15/01/2008/ 36 Months Funding: FCT/ UA Value: 59.200,00

> PTDC/SAU-BEB/66896/2006 Implantable scaffolds for local osteo-sarcoma chemotherapy Principal Researcher: Rui Nunes Correia Status: Proponente Beginning Date: 01/09/2007/ 36 Months Funding: FCT/ UA Value:

PTDC/QUI/68582/2006 Molecular design of novel aza-bridged calixarene receptors for medicinal chemistry: encapsulation of lanthanide ions and resolution of racemic drugs Principal Researcher: Vitor Manuel Sousa Félix Status: Proponente Beginning Date: 01/01/2008/ 36 Months Funding: FCT/ UA Value: 24.060,00

PTDC/QUI-QUI/101022/2008 Development of azacalix(hetero)arene transporters for mediated anionic flux across membranes: a novel approach for studying ionic passive diffusion Principal Researcher: Vitor Manuel Sousa Félix Status: Proponente Beginning Date: 2010/ 36 Months Funding: FCT/ UA Value: 61.060,00 PTDC/QUI/69302/2006 Principal Researcher: Susana Braga Status: Proponente Beginning Date: 25/07/2009/ 17 Months Funding: FCT/ UA Value: 32.956,00

POCI/CTM/60207/2004 SIMULTANEOUS PRECIPITATION AND IN SITU STABILISATION OF CALCIUM PHOSPHATE POWDERS FOR BIOMEDICAL APPLICATIONS IN BONE REPAIR AND CONTROLLED DRUG DELIVERY SYSTEMS Principal Researcher: José Maria da Fonte Ferreira Status: Proponent Beginning Date: 01/01/2005/ 36 Months Funding: FCT/ UA Value: 29.510,40

F-131/10 Nanomateriais multifuncionais com propriedades ópticas e magnéticas Principal Researcher: Luís António Ferreira Martins Dias Carlos Status: Proponente Beginning Date: 2010/ 24 Months Funding: CRUP/ UA Value: 2.000,00

### Acção Integrada

Study of the constrained sintering of high Q low loss microwave dielectric thick films Principal researcher: Paula Maria Lousada Silveirinha Vilarinho Status: Participante Beginning Date : 01/01/2009/ 24 Months Funding: CRUP/ UA value (€): 2.500,00

Papéis de alto desempenho à impressão Principal Researcher: Dmitry Victorovitch Evtyugin Status: Participante Beginning Date: 01/10/2009 / 24 Months Funding: QREN / UA Value:189.676,00

Estudo da variável penetração de resina no papel e do fenómeno de crescimento em papéis decorativos, e respectivas relações causa-efeito com os processos de impregnação e de produção de termolaminados de alta pressão Principal Researcher: Dmitry Victorovitch Evtyugin Status: Proponente Beginning Date: 01/09/2008/ 19 Months Funding: Sonae - Indústria de Revestimentos SA/ UA Value: 29.000,00

E-85/09

Prediction of wax precipitation in flow assurance: Identification of limitations of current models and their improvement Principal Researcher: João Manuel da Costa e Araújo Pereira Coutinho

Status: Proponente Beginning Date: 01/01/2009 / 24 Months Funding: CRUP/ UA Value: 4.000,00



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European Union / ERDF – European Regional Development Fund

> SEVENTH FRAMEWORK PROGRAMME



CIENCIA





