3as Jornadas do CENIMAT

June 28th, 2013

Anfiteatro Leopoldo Guimarães

PROGRAM AND ABSTRACT BOOKLET

3as Jornadas do CENIMAT

June 28th, 2013

Organizing committee:

- **Hugo Águas**
- **Pedro Almeida**
- **Rui Igreja**

Following the two previous editions of "Jornadas do CENIMAT" in the year 2011 and 2012, the third edition of the same called "3as Jornadas do CENIMAT" will be held at CENIMAT-I3N on 28th June 2012 (Friday) involving all the researchers and the students from the center, along with the colleagues from the sister departments/ centers of FCT/UNL.
The main objective of the meeting is to discuss the research facilities and research activities done by the 3 different research groups in CENIMAT-I3N, on this particular day. As in the 2nd edition a poster session will be held in the CENIMAT main hall, dedicated to discuss the current research in the center. As well oral presentations are included where the 3 groups of CENIMAT will present their main scientific activities.

It is believed that the mutual exchange of information, knowledge and facilities might lead to several fruitful intra-cooperation in CENIMAT-I3N and inter-departmental research ventures in order to keep up the Live and Vibrant research atmosphere in the center.

The meeting is organized as follows:

9:00 – 9:15	Inaugural session
9:15 – 10:00	CENIMAT Groups Scientific Overview
10:00 – 10:35	Oral presentations from the ME Group
10:35 – 11:15	Coffee break
11:15 – 12:30	Oral presentations from the MPM Group
12:30 – 14:00	Lunch
14:00 – 16:05	Oral presentations from the MEON Group
16:05 – 17:00	Poster Session (along with Coffee break)
17:00	Closing Ceremony + Awards

Website address: http://eventos.fct.unl.pt/3jornadascenimat/

PROGRAM - 3as Jornadas do CENIMAT - 28 June

09:00	**Inaugural Session**		
	Director, CENIMAT/I3N		Prof. Dra. Elvira Fortunato
	President, DCM		Prof. Dr. Rodrigo Martins
	Dean, FCT/UNL		Prof. Dr. Fernando Santana
	E-MRS Tribute to Prof. Fernando Santana		

	CENIMAT Groups: Scientific Overview		
09:15	Braz Fernandes F.M.	3JC_SO1	Structural Materials: Scientific Overview
09:30	Godinho M.H.	3JC_SO2	A Bird's Eye View of the Polymeric and Liquid Crystal Group's Work
09:45	Martins R.	3JC_SO3	Electronic, Optoelectronic and Nanotechnology Materials: Scientific Overview

	Oral Session 1	*Chair person: Rui Igreja*	
10:00	Lima M.M.R. A.	3JC_01	Rare-earth doped phosphate glasses
10:20	Oliveira J.P.	3JC_O2	XRD Characterization Of Shape Memory Alloys Using Synchrotron Radiation

10:35	coffee break

	Oral Session 2	*Chair person: Pedro Almeida*	
11:15	Geng Y.	3JC_03	A soft motor from cellulose liquid crystal networks
11:40	Cidade M.T.	3JC_O4	Dendrimer growth followed by rheology
12:05	Soares P.	3JC_O5	Multifunctional nanoparticles for osteosarcoma theranostic

12:30	LUNCH

	Oral Session 3	*Chair person: Hugo Águas*	
14:00	Wojcik P.	3JC_O6	All-solid-state printed devices based on inorganic electrochromic films and thermosetting solid state electrolyte
14:25	Ferreira I.	3JC_O7	Thin Film Thermoelectric Materials
14:50	Pinto J.	3JC_O8	Towards Low Cost and Disposable Biosensors: Research at CENIMAT
15:15	Pereira L.	3JC_O9	Towards The Era of Paper Electronics
15:40	Filonovich S.	3JC_O10	2nd and 3rd generation solar cells

16:05	**POSTER SESSION** + coffe break

17:00	**Closing ceremony + Awards**

RESEARCH TOPICS OF THE STRUCTURAL MATERIALS GROUP

Braz Fernandes F.M.
*ME-CENIMAT-I3N, *fbf@fct.unl.pt*

The Structural Materials Research Group (SMRG) has been focusing his activity on the production of nanostructured materials (metals, ceramics and composites) as well as on techniques of micro/ nano-characterization. The development of new nanostructuring strategies and parameter optimization of already implemented techniques is envisaged. Members of this RG will continue to apply for synchrotron radiation (ESRF, DESY), aiming micro/ nano-characterization. Main topics comprise:

- Thermomechanical processing of shape memory alloys and its functional characterization aiming different engineering applications.
- Functionally graded alloys and composites through SPD, using ECAP and FSP methods.
- Development of functionally graded ceramic foams for biomedical and structural applications.
- Development of a problem solving environment, taking advantage of GPU-based computing, for materials structural characterization via tomography, with potential applications from micro- to nanotomography .
- Archaeometallurgy, studies focussing on micro/nano characterization (-XRF, OM, SEM-EDS and -XRD) of long term corrosion and metallic structures of archeological artifacts.
- Novel low temperature sinterable glasses and glass/nanoceramic particle composites and the study on the effect of experimental parameters on the final microstructure, thermal, electrical and optical properties.
- Innovative optical microsensors based on rare-earth doped phosphate glass and characterization of sol-gel prepared nanostructured glasses and films.
- Characterization of ceramic materials for dental restoration,
- protection of ceramic tiles through the development of new materials based on TiO2 nanoparticles.
- Development of Nanostructures to CO2 sequestration in eco-cements.
- Micro/nano characterization through the application of X-ray absorption spectroscopy techniques using synchrotron radiation.
- Study of ancient Portuguese tiles and implementation of conservation procedures using neutron beams.
- Theoretical crystal chemical approach to matter under extreme (P,T) conditions in the Earth's interior.

A BIRD'S EYE VIEW OF THE POLYMERIC AND LIQUID CRYSTAL GROUP'S WORK

M.H. Godinho
Polymeric and Mesomorphic Materials, mhg@fct.unl.pt

The Polymeric and Liquid Crystal group is much involved in the study of soft materials, which are easily deformable by external stresses, electric, magnetic fields, or even by thermal fluctuations. The materials in which we are interested on include liquid crystalline-based soft systems, foams, colloids, macromolecular and biological systems and elastomeric Janus particles. The structure of those materials as well as their dynamics at the mesoscopic scales determines their physical properties. The goal of our research has been dedicated to probe and understand this relationship. The techniques we used include light scattering, microscopy, rheology (Rheo), nuclear magnetic resonance (NMR), Rheo-NMR, magnetic resonance imaging (MRI), electrospinning and microfluidics.

ELECTRONIC, OPTOELECTRONIC AND NANOTECHNOLOGY MATERIALS: SCIENTIFIC OVERVIEW

Martins R.*, Fortunato E.
*MEON, *rm@uninova.pt*

The activities of the MEON group will focus on expanding existing research areas with novel materials/fabrication routes involving low-temperature processes and also on exploring new concepts based on the nanoscale properties of materials.

Main research topics will include:

- Solution-processed AOS TFTs and integration in CMOS circuits;
- Tunable nanostructures using cellulose derivatives for novel paper electronics applications;
- Electrochromic devices with solid-state and polymeric electrolytes;
- Bio-sensors and multipurpose lab on glass and lab on paper integrated detection platforms;
- Nano-devices with single-crystal nanostructures;
- Flexible and hybrid solar cells with incorporation of Si quantum dots;
- Piezoelectric energy harvesting, energy storage with ferroelectrics. Dielectric relaxation.

All these activities are being supported by 15 PhD students and 17 PhDs. A set of 10 national and 12 European projects, including an Advanced Grant from ERC, are running in the above described fields, most of them being industry or application-oriented ones, reinforcing our commitment towards an application-oriented research.

RARE-EARTH DOPED PHOSPHATE GLASSES

M.M.R.A.Lima*, J.P.Veiga, R.S.Soares, A.A.S.Lopes, R.C.C.Monteiro**
*Structural Materials, *mmal@fct.unl.pt; **rcm@fct.unl.pt*

Phosphate glasses, based on the $Li_2O–BaO–Al_2O_3–La_2O_3–P_2O_5$ system, and doped with samarium, europium and terbium trivalent ions, have been obtained by a wet non-conventional melt-quenching method. X-ray fluorescence (XRF) has been used to establish the elemental composition of these materials. The thermal stability of these glasses was assessed by differential scanning calorimetry (DSC). DSC curves for the three rare-earth-doped phosphate glasses, as bulk and powdered samples, showed Tg values in the range 435-450ºC. Bulk samples exhibited a very weak exothermic peak in the range 670- 685 ºC, while powdered samples showed two weak exothermic peaks, the first peak in the range 500-550 ºC and the second peak in the range 660-685 ºC. Microstructural analysis suggested that crystallization in heat-treated glasses started at the surface of the samples. X-ray diffraction indicated that the main crystalline phases present in heat-treated glasses are aluminium phosphate ($AlPO_4$) and aluminium metaphosphate ($Al(PO_3)_3$). These doped vitreous materials exhibit interesting photoluminescent characteristics (Fig.1), which indicates that they can be used as base components for optical sensors [1].

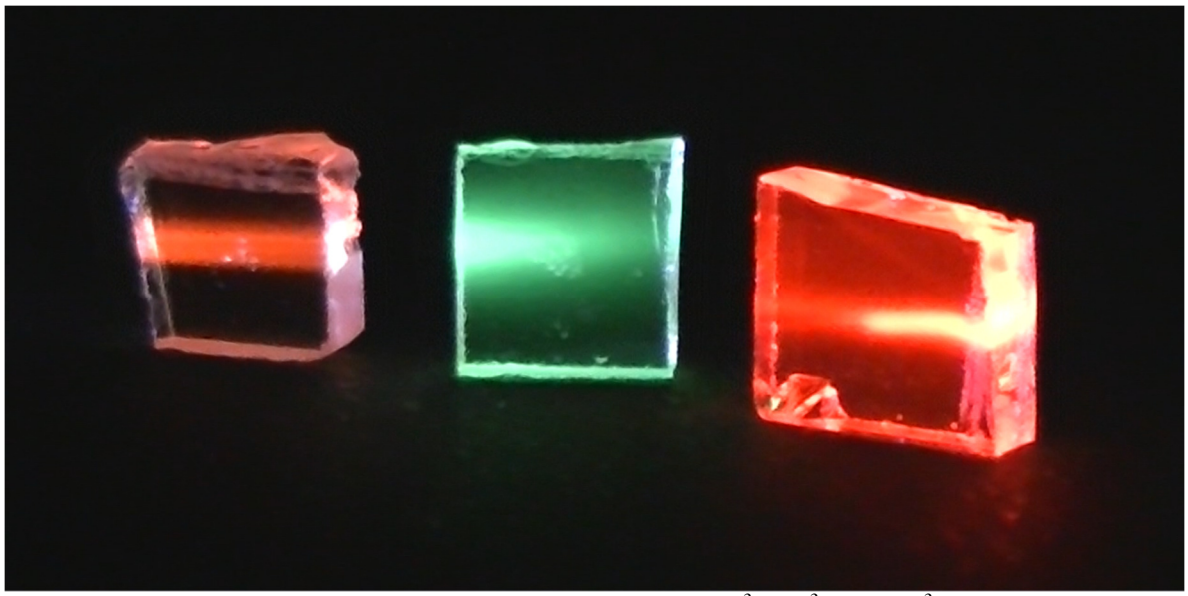

***Fig. 1** Photolumiescent phosphate glasses doped with Sm^{3+},$Tb^{3+}$and Eu^{3+} (from left to right)*

References:

[1] Elisa M., Sava B.,Vasiliu I.C., Monteiro R.C.C.,Veiga J.P.,Ghervase L.,Feraru I.,Iordanescu R., *Optical and structural characterization of samarium and europium-doped phosphate glasses*, J. Non-Cryst. Solids, **369** (2013) 55-60.

XRD CHARACTERIZATION OF SHAPE MEMORY ALLOYS USING SYNCHROTRON RADIATION

J. P. Oliveira*, F. Braz Fernandes, S. V. Correia, R. M. Miranda, N. Schell
*Structural Materials Group, *jp.oliveira@ampus.fct.unl.pt; **fbf@fct.unl.pt*

The use of synchrotron radiation for the structural characterization of materials is of great interest due to, amongst other features, the capability of using high energy X-rays, (greater penetration allowed) and high photons flux (giving finer time and spatial resolution). Recently, we took advantage of the use of synchrotron beam time in DESY to study laser welded NiTi shape memory alloys and NiTi endodontic files. Regarding the work performed on the laser welded NiTi samples, the use of synchrotron radiation is of great help since the dimensional extension of the heat affected zone (HAZ) and of the fusion zone (FZ) requires a very fine beam spot to identify the microstructural gradients. These microstrutctural features play a very important role on the mechanical behavior of the joints, in general, and open new application possibilities resulting from the microstructural gradients created during welding. These microstructural gradients (see Figure 1) are responsible for a change in the transformation temperatures of those regions giving rise to a functionally graded behavior. We also studied the effect of different post-weld heat treatments. NiTi endodontic files were studied under two different states: without any load applied and bent under a controlled curvature, using a glass tube, simulating their use in clinical practice. This study allowed us to perform a fine analysis of the files from tip to bottom. The regions where stress-induced martensite was formed were identified. The effect of the files geometry was also noticeable (Figure 2).

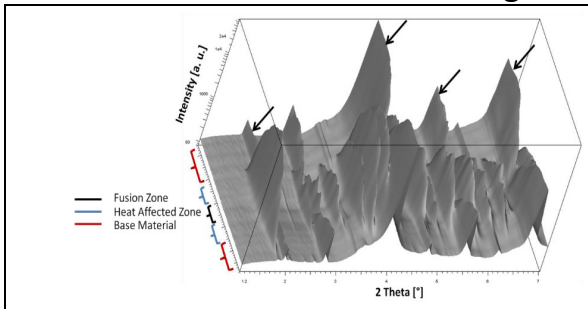

Fig. 1 XRD patterns along a welded NiTi sample. Black arrows mark the austenite peaks.

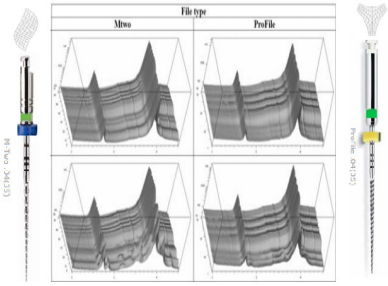

Fig. 2 XRD patterns for two different brands NiTi files under no stress (top), and under stress (bottom).

References:

[1] J. P. Oliveira, F. Braz Fernandes, R. M. Miranda, "Laser weldedNiTi. Correlation between mechanical cycling behavior and microstructure", LAP - Lambert Academic Publishing, Saarbrucken, 86 pp, 2013.

[2] F. Braz Fernandes, K. K. Mahesh, C. M. Craciunescu, J. P. Oliveira, N. Schell, R. M. Miranda, L. Quintino, J. L. Ocaña, "In situ structural characterization of laser welded NiTi shape memory alloys", Materials Science Forum, 738-739, pp. 338-343, 2012

[3] F. Braz Fernandes, S. V. Correia, J. P. Oliveira, N. Schell, "XRD Study of NiTi Endodontic Files Using Synchrotron Radiation", Shape Memory and Superelastic Technologies Conference, Czech Republic, May 2013

A SOFT MOTOR FROM CELLULOSE LIQUID CRYSTAL NETWORKS

Y. Geng*, P.L. Almeida, G.M. Feio, M.H Godinho**
*Polymeric And Mesomorphic Materials, *y. geng@fct. unl. pt; **mhg@fct.unl.pt*

Cellulose is the most common organic compound on earth. It is the structural component of the cell walls of green plants, constituting about a third of all plant matter. Because of cellulose ubiquity and importance, considerable attention has been given to its study and characterization.[1] HPC is a commercially available derivative of cellulose in which some of the hydroxyl groups in the repeating glucose units have been hydroxypropylated. It is well know that HPC can be solved in water at room temperature. HPC as other cellulose derivatives can generate lyotropic as well as thermotropic phases. Depending on polymer characteristics, molecular weight and degree of substitution, solvent and temperature a cholesteric phase with tunable pitch values can be obtained. From liquid crystalline cellulose solutions films and fibers can be produced. The main idea was to produce high modulus materials from cellulose with mechanical characteristics similar to Kevlar.

In this work we propose the use of cellulose liquid crystalline networks to produce responsive materials. A steam engine was made from a cellulose belt which (Fig. 1), transports water from regions of high chemical potential to low, gaining energy in the process.[2] To better understand the mechanism involved in the motor rotation we also studied the cellulose network by Rheo-NMR technique.[3]

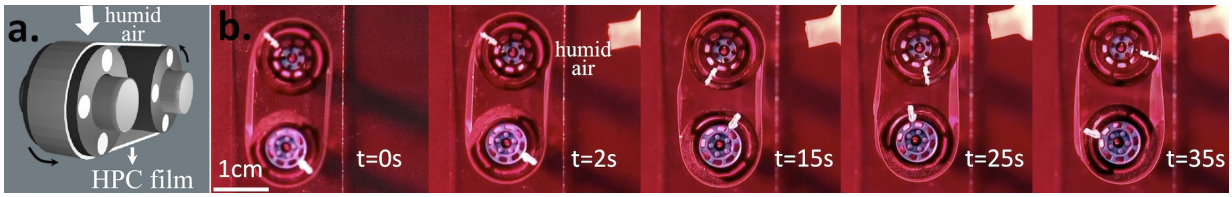

Fig. 1 *Soft motor made from cellulose liquid crystal network.*

Acknowledgments:

This research was supported by the Portuguese Science and Technology Foundation (FCT) through contracts SFRH/BD/63574/2009 PTDC/CTM/099595/2008, PTDC/CTM-POL/1484/2012 and PEst-C/CTM/LA0025/2011 (Strategic Project—LA 25-2011-2012).

References:

[1] Jarvis, M. *Nature* 2003, 426, 611-612.

[2] Geng, Y., Almeida, P. L., Fernandes, S. N., Cheng, C., Palffy-Muhoray, P. & Godinho, M. H. *Scientific Reports* 2013, 3, 1028.

[3] Geng, Y., Almeida, P. L., Feio, G., Figueirinhas, J. & Godinho, M. H. *Macromolecules*, 2013, 46 (11), pp 4296–4302.

DENDRIMER GROWTH FOLLOWED BY RHEOLOGY

Rita B. Restani[1], Ana Aguiar-Ricardo[1], Vasco D. B. Bonifácio[1] and Maria T. Cidade[2]
*PMM, * restanirita@gmail.com; ** mtc@fct.unl.pt*

The unique 3D architecture of dendrimers makes these polymers very interesting systems for enhanced guest solubilization and controlled release of molecular guests, which makes them interesting in many applications, particularly in Nanomedicine, for drug and gene delivery [1-3].

In this study we present the rheological characterization of PURE amine terminated dendrimers, which are particularly interesting due to their non-cytotoxic character. In particular, the increase of the molecular weight (generation) is easily followed by rheology measurements.

The rheological properties of the studied dendrimers depend mainly on the molecular weight (generation) and on their ability to establish intermolecular interactions through H-bonding. The flow curve shows that, for any generation, the dendrimer behaves like a Newtonian fluid in the experimental shear rate range and that the steady state shear viscosity, as expected, increases, linearly, with the molecular weight (generation). The dependence of the steady state shear viscosity with temperature follows an Arrhenius law, from which it was possible to determine the activation energy. Ea also increases with the molecular weight, as expected.

The elastic modulus $G'(\omega)$ and the viscous modulus $G''(\omega)$ were measured as a function of the angular frequency, showing a linear dependence, and the data obtained allowed us to conclude that $G''(\omega)$ increases with generation and that $G''(\omega) >> G'(\omega)$, showing a low elasticity of the dendrimers that correlates well with the properties of non-entangled polymer melts.

[1] Dendrimers in Medicine and Biotechnology – New Molecular Tools (Eds: U. Boas, J. B. Christensen, P. M. H. Heegaard), The Royal Society of Chemistry, UK, 2006.

[2] Dendrimer-Based Medicine (Eds: I. J. Majoros, J. R. Baker, Jr.), Pan Stanford Publishing, Singapore, 2008.

[3] J. A. Barreto , W. O'Malley , M. Kubeil , B. Graham , H. Stephan , L. Spiccia, Adv. Mater. 2011, 23, H18.

MULTIFUNCTIONAL NANOPARTICLES FOR OSTEOSARCOMA THERANOSTIC

Paula Soares*, Isabel Ferreira, Carlos Novo, João Paulo Borges
*MPM & MEON, *paulaipsoares@gmail.com*

Osteosarcoma is the most common primary bone tumor in children and adolescents, with a 5-year survival rate of 70%. It is characterized by an extremely aggressive clinical route with rapid development of metastases in 40-50% of patients, occurring mainly in lung. Current treatments for osteosarcoma have not resulted in improved prognosis during the last decade providing incentive for the development of new treatment options [1, 2].

A novel approach for osteosarcoma treatment includes multifunctional nanoparticles (MNPs) suitable for theranostics: "therapy" + "diagnostics". These MNPs are composed of a magnetite core, coated with an ammonium quaternary derivative of chitosan (*o*-HTCC), incorporated with an anti-cancer agent and grafted with a monoclonal antibody anti-CA IX specific for osteosarcoma cells. The mechanism of action of these MNPs include: (1) specific targeting through the monoclonal antibody; (2) killing cancer cells by hyperthermia; (3) drug delivery of the anti-cancer agent; (4) diagnostic and treatment monitoring through MRI.

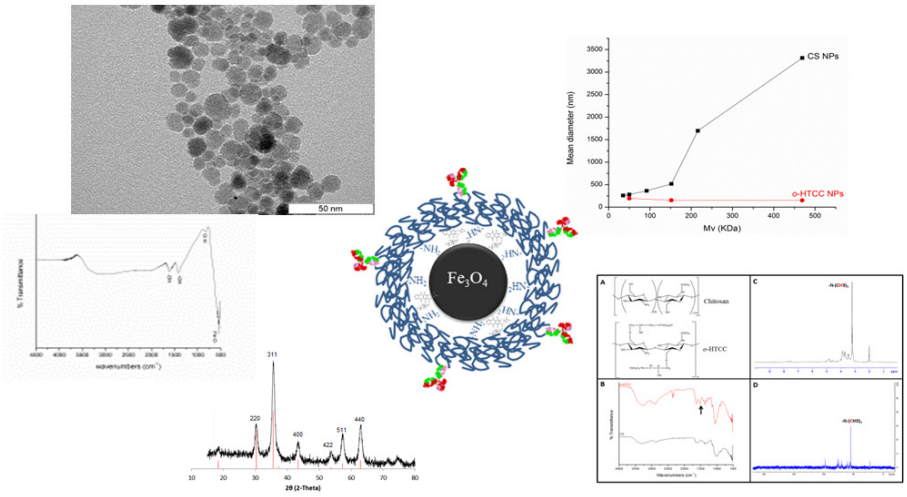

Fig. 1: *Preliminary results of the MNPs characterization.*

References:

[1] P. Soares, I. Ferreira, C. Novo, S. Dias and J. P. Borges, Doxorubicin vs. ladirubicin methods for improving osteosarcoma treatment, Mini-Reviews In Medicinal Chemistry, 12(12), 1239-49 (2012).

[2] P. Soares, I. Ferreira, R. Igreja, C. Novo and J. P. Borges, Application of Hyperthermia for Cancer Treatment: Recent Patents Review, Recent patents on anti-cancer drug discovery, 7(1), 64-73 (2012).

ALL-SOLID-STATE PRINTED DEVICES BASED ON INORGANIC ELECTROCHROMIC FILMS AND THERMOSETTING SOLID STATE ELECTROLYTE

P. Wojcik*, L. Santos, L. Pereira, R. Martins, E. Fortunato**

*MEON, *p.wojcik@campus.fct.unl.pt, **emf@fct.unl.pt*

We are demonstrating an effective and scalable to mass production strategy for creating high performance electrochromic (EC) devices that meets the demands of various applications such as transparent displays, smart windows, smart packaging, electronic paper and flexible displays. An innovative approach involves application of Printing Technologies (inkjet-, screen-printing) to deposit inorganic EC materials based on sol-gel technique, in which additionally the film crystallinity can be controlled in a low *T* process by addition of nanoparticles into liquid precursor. The grain size, crystallinity and stoichiometry of those particles are dependent only on the origin of crystals and are defined at the ink formulation stage. Those optically active films outperform their amorphous or nanocrystalline analogues presented in the state-of-the-art, owing to their superior switching time (<3s) optical density (0.7) and extremely low power consumption. Novel, solid state electrolytes were drop casted or screen printed and cured *in-situ*, using Succinonitrile as a solvent for lithium salt, thermosetting resin as a matrix and metal oxide nanoparticles as filler. We are also presenting experimental data related to ionic conductivity (10^{-6}-10^{-4} Scm^{-1}@RT), spectral response, mechanical strength and various structural characterizations. The combination of both components conveys excellent mechanical, electrical and optical properties of prototype displays and EC windows, which overall performance is also discussed.

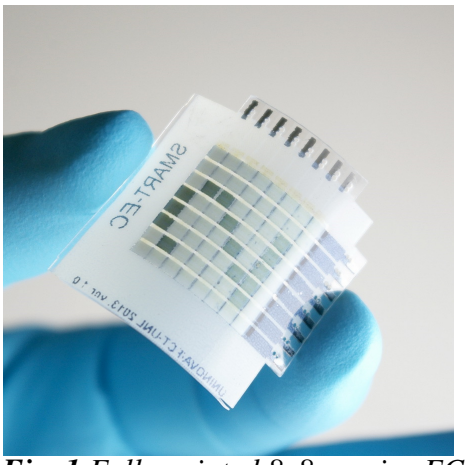

***Fig. 1** Fully-printed 8x8 passive EC matrix (Smart-EC FP7 project)*

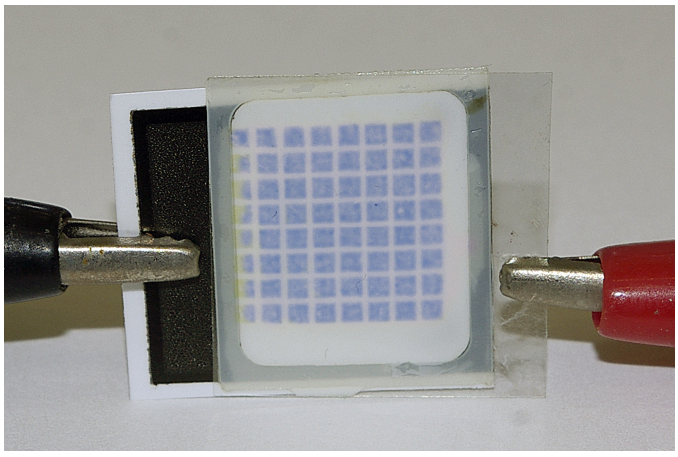

***Fig. 2** Prototype of printed EC display on paper (A3Ple FP7 project)*

THIN FILM THERMOELECTRIC MATERIALS

Joana Loureiro[1], João Rafael Santos, Adriana Nogueira, Joana Figueira, Alexandra Rodrigues, Lúcia Marisa Ferreira and Isabel Ferreira*
*MEON, [1]joa.loureiro@gmail.com; *imf@fct.unl.pt*

The efficient commercial application of thermoelectrics devices needs materials with simultaneously high Seebeck coefficient (S), low thermal conductivity (k) and low resistivity (ρ) to attain a high figure of merit ($ZT=S^2T/k\rho$). So far, the highest ZT values at low temperature (room temperature up to around 150°C) were obtained in Te based alloys[1]: ZT about 0.8 for n-type PbTe and 1 for p-type $Si_{0.8}$ $Ge_{0.2}$ or $Yb_{14}MnSb_{11}$ bulk materials. Nanostructured materials have achieved ZT over 1, at 300K, for instance p-type Bi_2Te_2/Sb_2Te_2SL with ZT of 2.5 and n-type PbSeTe of 1.5 for quantum wells of 4.5nm [2]. Although Te based materials achieved already a niche of market, their application to high volume market becomes a sustainable issue. For instance, Te is the ninth least abundant element [3, 4]. As the current Te modules require roundly 1kg to produce 1kW the cost reduction must be a problem. Environmental issues concerning the use of Pb and its end-life-cycle recyclability or re-use also leaves no merge for exploring commercialization of these materials[4]. Therefore more abundant and eco-friendly materials or alloys should be explored as thermoelectric materials. We study the TE characteristics of TF metal oxides such as $Zn_xM_yO_z$, $V_xM_yO_z$ (M is a metallic element) using physical deposition techniques such as thermal evaporation, rf and pulsed dc magnetron sputtering[5].

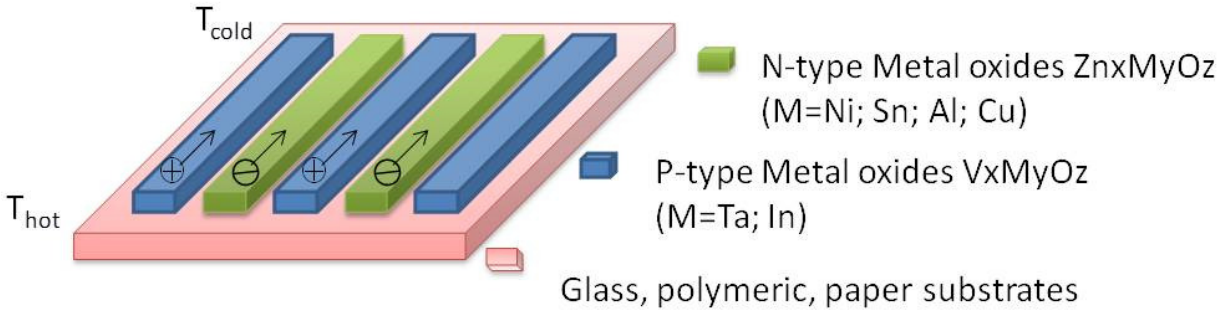

Figure 1: Schematics of the TF-TE under development.

References:

1. Toberer, G., *nature materials* **2008** 7.
2. Christopher J. Vineis , A. S., Arun Majumdar , and Mercouri G. Kanatzidis. *Adv. Mater.* **2010,** 22, 10.
3. Powell, P. V. a. A. V. *J. Mater. Chem.* **2010,** 20, 7.
4. Klar, G. H. a. P. J. *P hys. Status Solidi RRL* **2011,** 5, (9), 5.
5. R. Santos, J. Loureiro,A. Nogueira, E. Elangovan, J.V. Pinto, J.P. Veiga, T. Busani, E. Fortunato, R. Martins, I. Ferreira,Thermoelectric properties of V_2O_5 thin films deposited by thermal evaporation, http://dx.doi.org/10.1016/j.apsusc.2013.06.016

TOWARDS LOW COST AND DISPOSABLE BIOSENSORS: RESEARCH AT CENIMAT

J.V. Pinto*, M. Costa**, I. Bernacka-Wojcik***, R. Branquinho, B. Veigas, J. Neto, J. Chandra, F. Luigi, I. Martinho, F. Pereira, R. Borba, H. Aguas, J.Inácio, P. Baptista, R. Martins, E. Fortunato

*Field Effect Biosensors, *jdvp@fct.unl.pt,*

*Lab-on-Paper, **mafaldanscimentocosta@gmail.com*

*Microfluidics, ***iwonabernacka@gmail.com*

The combination of bio-recognition agents with a transducer device yields a powerful tool with applications in areas ranging from biomedicine to food industry and even bioterrorism prevention.

At CENIMAT several research teams are focused in the development of biosensors. The common ground is the production of low cost, disposable, easy to use and label free point-of-care devices using various types of detection mechanisms and methodologies. Electrochemical sensors based on field effect devices as potentiometric sensors and recently amperometric paper-based devices are being developed for the detection of diverse analytes, such as pH, enzyme substrates and DNA. Polymer based (cellulose and PDMS) devices allow the colorimetric diagnosis of several infection diseases based on DNA recognition or immunological response.

We intend to present an overview of the work performed within the biosensors area and highlight the main achievements in these transverse research lines.

Fig. 1 *Different type of biosensor devices produces at CENIMAT.*

TOWARDS THE ERA OF PAPER ELECTRONICS

Luís Pereira*, Diana Gaspar, Paulo Duarte, Pawel Wojcik, Evira Fortunato, Rodrigo Martins**
*MEON, *lmnp@fct.unl.pt; **rm@uninova.pt*

In this work we will present the concepts for paper-based electronic products (the lightest material and the most abundant biopolymer in the earth, fully recyclable) to be applied in a broad range of electronics commodities such as the intelligent packaging foldable displays (newspapers, disposable phones, etc.) smart labels in food, medical and pharmaceutical industries. All this is aimed using low cost technologies as ink-jet and flexography printing, using as key element multifunctional oxides processed at low temperatures and advanced organic or hybrid materials. We will show how to exploit the use of paper as a substrate or dielectric in which we can fabricate transistors; memories, displays, CMOS and logic circuits using functionalized materials [1-3]. This means that paper substrates for application in electronics have to be locally modified to present the right composition, fiber structure and chemical stability, function of the devices to be built-in. On other hand the transition from vacuum to printing deposition implies the development of printable functional materials as well as new devices' configuration.

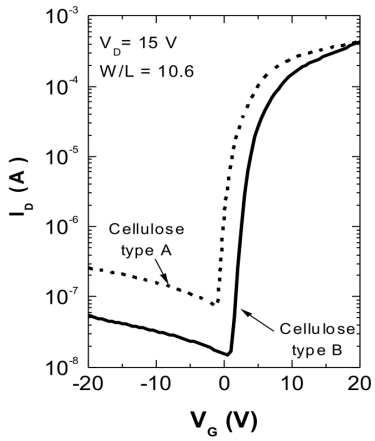

***Fig. 1** Transfer characteristics of transistors on paper*

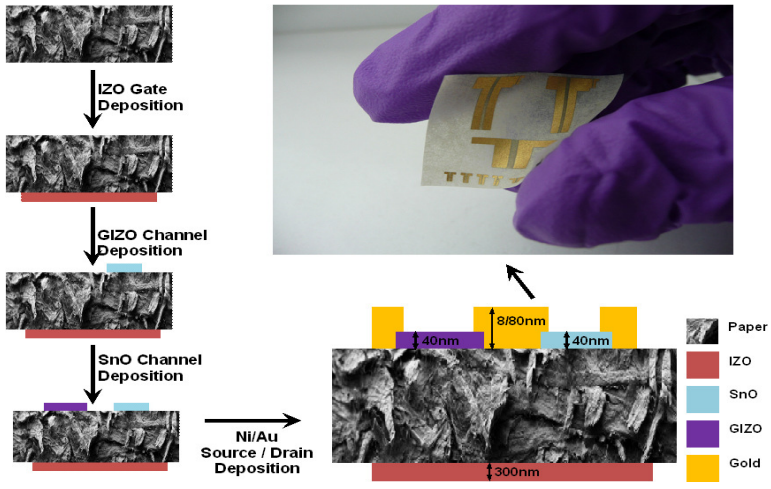

***Fig. 2** CMOS device on paper*

References:

[1] E. Fortunato, N. Correia, P. Barquinha, L. Pereira, G. Goncalves, R. Martins, *IEEE Electron Device Letters*, 29 (2008) 988-990
[2] R. Martins, A. Nathan, R. Barros, L. Pereira, P. Barquinha, N. Correia, R. Costa, A. Ahnood, I. Ferreira, E. Fortunato, *Advanced Materials*, 23 (2011), 4491
[3] R. Martins, A. Ahnood, N. Correia, L. Pereira, R. Barros, P. Barquinha, R. Costa, I. Ferreira, A. Nathan, *Advanced Functional Materials,* 23 (2013) 2153-2161

2ND AND 3RD GENERATION SOLAR CELLS

S.A. Filonovich*, H. Águas, T. Mateus, A. Araújo, A. Vicente, A. Riflet, B. Catela, I. Ferreira, E. Fortunato, R. Martins
*MEON, *filan@fct.unl.pt;*

The photovoltaic group of MEON works on creation and development of new concepts and fabrication methods of standard and novel materials which are used in solar cell of the present (2nd) and future (3rd) generations. The group members work on improvement of the standard silicon thin film solar cells by applying non-standard and novel technologies, such as use of extreme deposition conditions; use of plasmonic metallic nanoparticles for enhanced light capturing; fabrication of solar cells on non-conventional substrates (ceramics, paper, etc). Improved performance of the thin film solar cells achieved during the last year will be presented and discussed (Figure 1).

Novel concepts that are developed within CENIMAT include growth and application of silicon nanocrystals in the hybrid materials (i.e. organic/inorganic blends) and superlattices. The silicon nanocrystals of the sizes smaller than 10 nm exhibit quantum confinement effect which allows fabrication of complex structures (superlattices) with tunable opto-electronic properties. A newly started FCT/MEC project is dedicated to fabrication of such superlattices and superlattice-based solar cells (Figure 2) by a new method, proposed by researchers of MEON, at low substrate temperatures (200ºC). Typically such superlattices are fabricated by employing high temperatures (1100ºC) thus limiting their applicability.

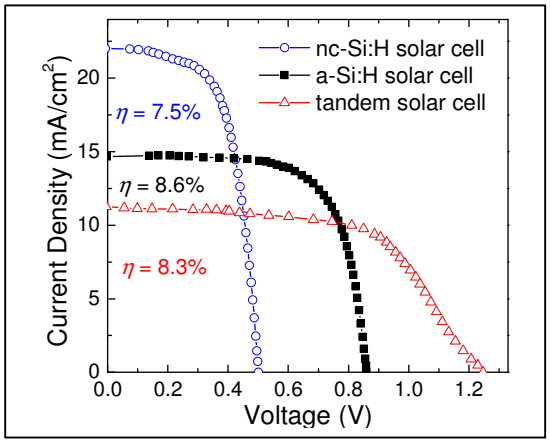

Fig. 1 *JVs of best thin film silicon solar cells.*

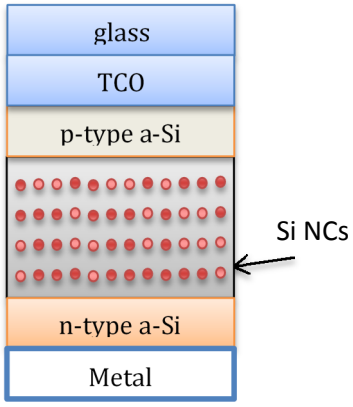

Fig. 2 *A concept of solar cell structure with superlattice as an active layer.*

INNOVATIVE MATERIAL FOR DENTAL RESTORATION BASED ON FLUORCANASITE GLASS-CERAMIC

M.S. Nunes*, R.S. Soares**, R.C.C. Monteiro
*Structural Materials, *md.nunes@campus.fct.unl.pt; **r.soares@campus.fct.unl.pt*

Glass-ceramics are increasing their popularity in all-ceramic dental restorations due to their excellent mechanical, chemical and aesthetical properties comparing with the traditional metal-ceramic restorations. An innovative glass-ceramic based on fluorcanasite ($K_2Na_4Ca_5Si_{12}O_{30}F_4$) has proven to be a worthy substitute for leucite ($KAlSi_2O_6$) and lithium disilicate ($Li_2Si_2O_5$) glass-ceramics, because of its unique mechanical properties [1, 2]. Three compositions based on the stoichiometric formula $60SiO_2$-(x)Na_2O-(10-x)K_2O-$15CaO$-$10CaF_2$, where x varied from 5 to 10, were investigated with the aim of improving the chemical durability and mechanical strength. The preparation of these glass-ceramics includes different steps: a melt-quenching process, to obtain a transparent bulk glass; and a ceramization process that induces controlled crystallization, resulting in an opaque glass-ceramic, as shown in Fig.1. To investigate the properties of the produced material, various characterization techniques have been used such as differential thermal analysis, x-ray diffraction, scanning electron microscopy (Fig.2), density and Vickers microhardness measurements. The results of this study confirmed the possibility of obtaining a glass-ceramic with satisfactory properties for use in dental restoration.

Fig. 1 *Glass (top) and glass-ceramic (bottom).*

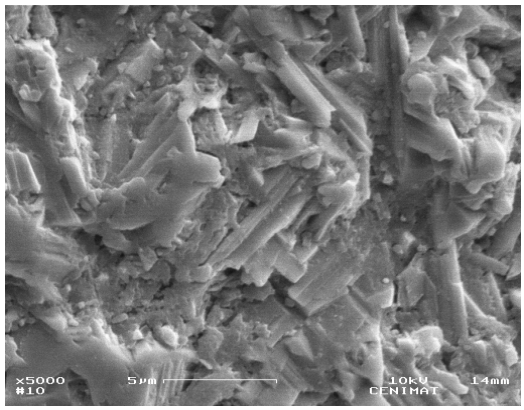

Fig. 2 *SEM image of a fluorcanasite glass-ceramic.*

References:

[1] Pollington S., Van Noort R. "*Manufacture, characterization and properties of novel fluorcanasite glass-ceramics*", J. Dentistry, **40** (2012) 1006-1017.

[2] Stokes C.W., Van Noort R., Hand R.J. "*Investigation of the chemical solubility of mixed-alkali fluorcanasite forming glasses*", J. Non-Crystalline Solids, **352** (2006) 142-149.

FILLING THE GAPS OF DINOSAUR EGGSHELL PHYLOGENY

R. Araújo[1,2(*)], R. Castanhinha[2,3], R.M.S. Martins[2,4,5(**)], C. Hendrickx[2,6], O. Mateus[2,6], F. Beckmann[7], N. Schell[7], L.C. Alves[5]

[1]*Huffington Department of Earth Sciences, SMU, 75275-0395 Dallas, Texas, USA*
[2]*Museu da Lourinhã, Rua João Luis de Moura 95, 2530-158 Lourinhã, Portugal*
[3]*Instituto Gulbenkian de Ciência, Rua da Quinta Grande 6P-2780-156 Oeiras, Portugal*
[4]*CENIMAT/I3N, FCT/UNL, Quinta da Torre, 2829-516 Caparica, Portugal*
[5]*IST/CTN - Campus Tecnológico e Nuclear, EN10, 2696-953 Sacavém, Portugal*
[6]*CICEGe, FCT/UNL, Quinta da Torre, 2829-516 Caparica, Portugal*
[7]*Helmholtz-Zentrum Geesthacht (HZG), Max-Planck-Str. 1, 21502 Geesthacht, Germany*

Structural Materials Group, [*]rmaraujo@smu.edu; [**]rmsm@fct.unl.pt

We report a dinosaur clutch containing several crushed eggs and embryonic material ascribed to the megalosaurid theropod *Torvosaurus*. It represents the first associated eggshells and embryos of megalosauroids, thus filling an important phylogenetic gap between two distantly related groups of saurischians. These fossils represent the only unequivocal basal theropod embryos found to date. The assemblage was found in early Tithonian fluvial overbank deposits of the Lourinhã Formation in West Portugal. The morphological, microstructural and chemical characterization results of the eggshell fragments indicate very mild diagenesis. Furthermore, these fossils allow unambiguous association of basal theropod osteology with a specific and unique new eggshell morphology.

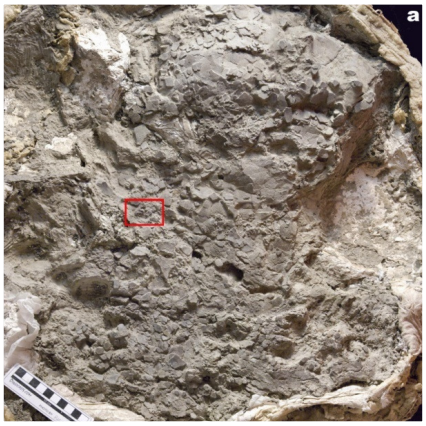

Fig. 1 *Clutch of Torvosaurus eggs (65 cm in diameter) [1]*

Fig. 2 *SR-μCT image of a fossilized eggshell fragment collected at Porto das Barcas (thickness ≈ 1.23 mm)[2]*

References:

[1] Araújo R., Castanhinha R., Martins R.M.S., Mateus O., Hendrickx C., Beckmann F., Schell N. and Alves L.C. *Sci. Rep.* **3** (2013) 1924.

[2] Martins R.M.S., Castanhinha R., Mateus O., Araújo R., Beckmann F., Schell N., Ciência & Tecnologia dos Materiais, **24** 3/4 (2012) 153.

METALLURGICAL PRODUCTION EVIDENCES IN OUTEIRO REDONDO, SESIMBRA (PORTUGAL)

Maria João FURTADO, Filipa PEREIRA, António MONGE SOARES, Maria Fátima ARAÚJO*, Rui SILVA** and João Luis CARDOSO
*Structural Materials Group, *faraujo@ctn.ist.utl.pt; **rjcs@fct.unl.pt*

The settlement of Outeiro Redondo (OR) located near Sesimbra (Portugal) [1] is an important and representative fortified site occupied during the second half of the third millennium BC, during the Chalcolithic period of the Portuguese Estremadura region [2].

The present study focuses on the elemental and microstructural characterization of a diversified set of artefacts from the OR collection [3]: 12 copper-based artefacts (or fragments of artefacts) such as saws, fish-hooks and awls, and 1 crucible fragment, aiming to contribute to a better comprehension of the copper-based early metallurgy of Central Portugal.

The combination of different analytical techniques - EDXRF and micro-EDXRF spectrometry, optical microscopy and SEM-EDS - has been applied in previous interdisciplinary studies [4], allowing the determination of alloy compositions and structures, as well as the identification of the thermomechanical processes applied to the manufacturing of artefacts. Elemental composition of the OR artefact collection shows that it is mainly composed of coppers or arsenical coppers, consistent with alloy artefact production from the same region and chronological period [5].

Further analysis, involving optical microscopy and SEM-EDS, will help to determine if these remains are related to melting or smelting operations (of copper ores or copper with arsenic ores) in crucibles.

References:

[1] Cardoso J.L. *Revista Portuguesa de Arqueologia* **12** (2009) 1.
[2] Cardoso J.L., Soares A.M.M. and Martins J.M.M. *E.A.O.* **18** (2010/2011).
[3] Cardoso J.L. in *Transformação e Mudança no Centro e Sul de Portugal: o quarto e o terceiro milénios a.n.e.* (V. Gonçalves & A.C. Sousa, Eds.), Câmara Municipal de Cascais, (2010).
[4] Furtado M.J., Silva R.J.C., Araújo M.F., Braz Fernandes F.M. *Mat. Sci. Forum* **636-637** (2010).
[5] Pereira F., Silva R.J.C., Monge Soares A.M., Araújo M.F. *J. Arch. Sci.* **40** (2013).

This research work has been financed by the Portuguese Science Foundation (FCT-MCTES) through the EarlyMetal project (PTDC/HIS-ARQ/110442/2008) and the grant SFRH/BD/78107/2011 to FP. The financial support of CENIMAT/I3N through the Strategic Project-LA25-2011-2012 (PEst-C/CTM/LA0025/2011) is also acknowledged.

SYNTACTIC FUNCTIONALLY GRADED CERAMIC FOAMS PRODUCED BY FREEZE-CASTING

Fonseca, J.*,Borges, J. P. **, Velhinho, A. ***
*MPM: **jpb@fct.unl.pt; ME: * jv.fonseca@campus.fct.unl.pt,***ajv@fct.unl.pt*

Syntactic functionally graded ceramic foams, consisting of a skeleton formed from hollow microspheres, are materials that evoke significant interest in two very distinct areas: biomaterials and composites. This work aims to carry out a structural and mechanical characterization of such materials, whose production is performed by a freeze-casting technique, where the introduction of the microspheres is effected with resource to a microfluidic system.

LIGHT SHUTTERS FROM NANOCRYSTALLINE CELLULOSE RODS IN A NEMATIC LIQUID CRYSTAL

Y. Geng*, M.H Godinho, P.L. Almeida**
*Polymeric And Mesomorphic Materials, *y. geng@fct. unl. pt;*
**palmeida@adf.isel.pt*

The search for efficient, scalable and low cost light shutters is an active area of research in Liquid Crystals (LC) in view of applications in the field of architecture. While Liquid Crystals have been so successful in the field of high tech displays for computer and TV screens, the penetration in the field of architecture for large area windows is not fully developed yet.

Recently another polarizer free type of LC optical shutter based on cellulose derivatives with equivalent electro-optical performance and production advantages was proposed.8 In this device the cellulose derivatives are deposited as nonwoven nano and microfiber mats onto the conductive substrates by electrospinning and the cell is filled up by capillarity with a nematic liquid crystal.[1]

This work reports a recently developed electro-optical device that can potentially be used as a light shutter or a privacy window (Fig. 1). By using nanocrystalline cellulose rods we were able to improve some of the most relevant parameters characterizing the electro-optical behavior.[2]

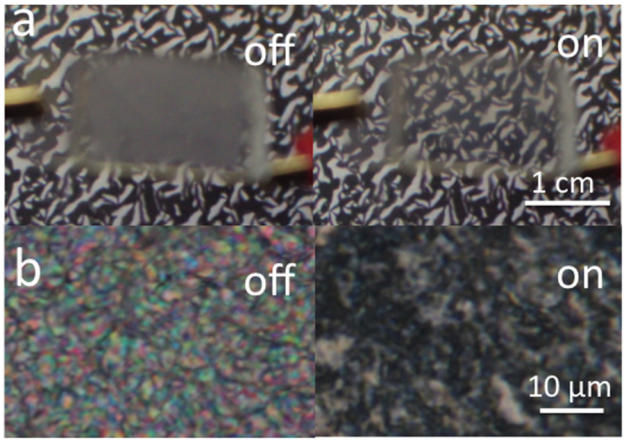

Fig. 1 *a) Macroscopic and b) POM (between cross polars) photographs of the ON and OFF states.*

Acknowledgments:

This research was supported by the Portuguese Science and Technology Foundation (FCT) through contracts SFRH/BD/63574/2009 PTDC/CTM/099595/2008, PTDC/CTM-POL/1484/2012 and PEst-C/CTM/LA0025/2011 (Strategic Project—LA 25-2011-2012).

References:

[1] P.L. Almeida, S. Kundu, J.P. Borges, M.H. Godinho, J.L. Figueirinhas, Appl. Phys. Lett., 95, 043501, (2009).

[2] Y. Geng, P. Brogueira, J.L. Figueirinhas, M.H. Godinho and P.L. Almeida, *Liquid Crystals*, 2013, **DOI:** 10.1080 / 02678292. 2013. 783137)

NECKLACES OF LIQUID CRYSTAL BEADS

Y. Geng*, P.L. Almeida, M.H. Godinho**
*Polymeric And Mesomorphic Materials, *y. geng@fct.unl.pt; **mhg@fct.unl.pt*

Liquid crystal droplets dispersed in a continuous matrix have important applications in electro-optical devices[1]. They also produce intriguing topological defect structures due to the confinement of the liquid crystal by closed boundaries that impose alignment at the interface.

In this work we use a simple method to generate stable liquid crystal droplets topologically equivalent to a toroid by depositing tiny volumes of a liquid crystals (nematic and cholesteric) on cellulosic micro-fibers (1 μm diameter) suspended in air.[2,3]

This system can exhibit different structures depending on the liquid crystal types, droplet size, anchoring condition, and also external stimuli like temperature and electric field (Fig.1).

The necklaces of such liquid crystal drops constitute excellent systems for fundamental studies and open new perspectives for applications[2], such as tunable photonic and waveguide applications.

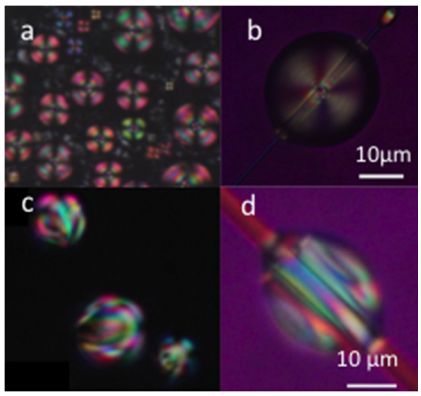

Fig. 1 *a. the nematic droplets dispersed in isotropic liquid with homeotropic anchoring condition, b. Nematic droplet confined on thin fiber, c. cholesteric drops dispersed in glycerol with planner anchoring condition,d Cholesteric beads textures observed by POM with planner anchoring condition.*

Acknowledgments:

This research was supported by the Portuguese Science and Technology Foundation (FCT) through contracts SFRH/BD/63574/2009 PTDC/CTM/099595/2008, PTDC/CTM-POL/1484/2012 and PEst-C/CTM/LA0025/2011 (Strategic Project—LA 25-2011-2012).

References:

[1] M. Humar, M. Ravnik, S. Pajk, M. Musevic, S. Pajk and I. Musevic, *Nat. Photonics*, 3, 595–600 (2009).

[2] Y. Geng, P. L. Almeida, J. L. Figueirinhas, E. M. Terentjevd and M. H. Godinho, *Soft Matter,* 8, 3634-3640 (2012).

[3] Y. Geng, D. Seč, P.L. Almeida, O.D. Lavrentovich, S. Žumer, M.H. Godinho, *Soft Matter*, (2013) DOI: 10.1039/c3sm50900a. (Cover of that issue)

INFLUENCE OF THE LIPIDS IN RHEOLOGICAL BEHAVIOUR OF AMIMULSION – A NEW SAFE COSMETIC EMULSION

J. Marto, E. Oliveira, A.J. Almeida, H.M. Ribeiro and M.T. Cidade
*MPM, jmmarto@ff.ul.pt; **mtc@fct.unl.pt*

Cosmetic water in oil emulsions are complex multiple-phase systems which may contain a number of interacting surfactants, fatty amphiphiles (e.g.alchols), polymers and other excipients as structuring agents.

In this work the rheological behaviour and the microscopic analysis of two w/o semi-solid emulsion, differing only in lipid used [Emulsion A (lipophilic emollient - triglycerides) and Emulsion B (occlusive agent - hydrocarbons)], intended for topical application and prepared using a modification of a cold emulsification process, as described elsewhere [1], will be presented.

Oscillatory and steady state shear measurements were performed for angular frequencies (□) between 1 and 100 rad s-1 and shear rates ($\dot{\gamma}$) between 1 and 1000 s-1, for two different temperatures, 25 and 37 ºC, and the samples were examined by brightfield light microscopy.

For the two emulsions, G' is must higher than G'', meaning a dominant elastic behavior of both emulsions, and the steady state shear viscosity decreases with the increase of the shear rate, showing a shear-thinning behavior. G' and G'' also decreases with the increase of the temperature, as expected.

In both cases, the slope of the curve G'vs □ is very small meaning that both systems are well structured.

Emulsion B presents higher G' and G''modulus and steady state shear viscosity than emulsion A.

The relationship between the rheological behaviour of both emulsions and the microscopic observations (particle sizes, shapes and distribution) will be presented.

References:

[1] – S. Raposo et. al., Cold Processed Oil-in-Water Emulsions for Dermatological Purpose: Formulation Design and Structure Analysis, Pharm. Dev. Tech., in press 2013.

ELASTOMERIC JANUS FIBERS

A.C. Trindade*, J.P. Canejo, M.H. Godinho**
*MPM Group, *acrt@fct.unl.pt; **mhg@fct.unl.pt*

The excellent properties of elastomers are exploited to trigger wrinkling instabilities in curved shells. Micro- and nano-fibres are produced by electrospinning and UV-irradiated: each fibre consists of a soft core and a stiff outer half-shell. Upon solvent de-swelling the fibres curl because the shell and the core have different natural lengths. Wrinkling only starts after the fibre has attained a well-defined helical shape. This new instability is also found in the tendrils of climbing plants as they dry and lignify.

New perspectives on biomimetic materials, as additional functionalities can be added by having "young" (smooth, small-surface-area) and "old" (wrinkled, large-surface-area) regions co-habit in the same material. In a very recent paper it was argued that the wrinkling of skin on fingers due to immersion in water increases the human ability to grip wet objects [1]. The kind of fibre network studied in our work allows a fine control of the degree of wrinkling, and as such might enable the production of fibre-based micromanipulators [2]. A micro- or nano-sized object would be grabbed and carried by an array or wrinkled fibres, then released at a very precise location by just adjusting the pattern.

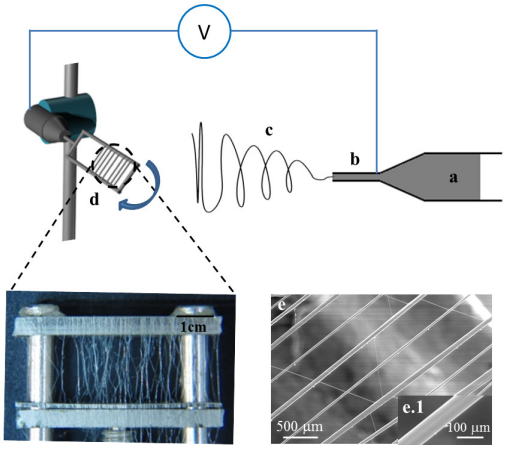

Fig. 1 *Schematics of electrospun fibre production.*

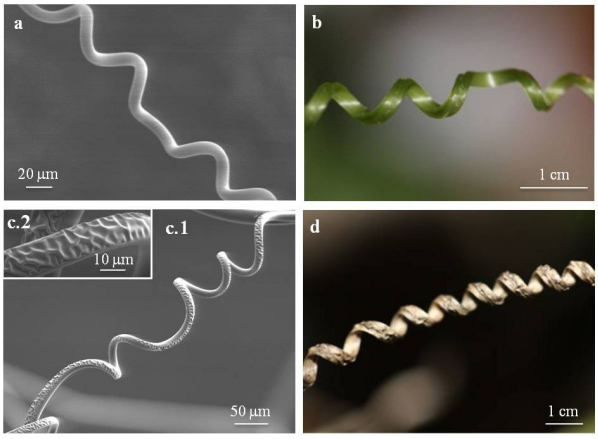

Fig. 2 *Electrospun fibres mimicking young and old plant tendrils.*

References:

[1] Kareklas K., Nettle D. and Smulder T.V. *Biol. Lett.* (2013), 20120999.

[2] Tokudome Y., Suzuki K., Kitanaga T. and Takahashi M. *Sci. Rep.* (2012), 2, 683.

UNUSUAL BEHAVIOR INQUERY BY NMR OF SUPERPARAMAGNETIC NP AND OF STRANGE LIFE FORMS

Alexandra Carvalho[*], Clara Gonçalves[**], Sofia Reboleira[***]

MPM, [*]amfc.carvalho@fct.unl.pt,[**]clara.goncalves@ist.unl.pt,
[***]sofiarbola@gmail.com

In this poster two very recent work themes under development in the CENIMAT NMR Lab are presented, in both the unique characteristics of the CENIMAT NMR spectrometer allowed the observation of new and puzzling behaviors.

One system is a aqueous solution of silica and organically modified silica nanoparticles with and without superparamagnetic iron oxide nanoparticles cores and diameters in the range 30-100nm. The diffusion of water molecules in these environment was measured by Pulse Field Gradient Stimulated -Echo NMR (PFGSE) [1] in a high gradient field up to 1700 G/cm. The measured diffusion coefficients showed peculiar behavior that we will presented and discussed.

The other system where two subterraneans animals: *Squamatinia algharbica* (Zygentoma: Nicoletiidae) a giant subterranean thysanuran recently described, endemic from caves along the Algarve [2] and *Porcellio cavernicolus* (Isopoda: Porcellionidae) the largest cave-dwelling terrestrial isopod from Sicó caves, Portugal. MR micro-images were collected and a localized NMR spectroscopy study of these animals was preformed for the first time.

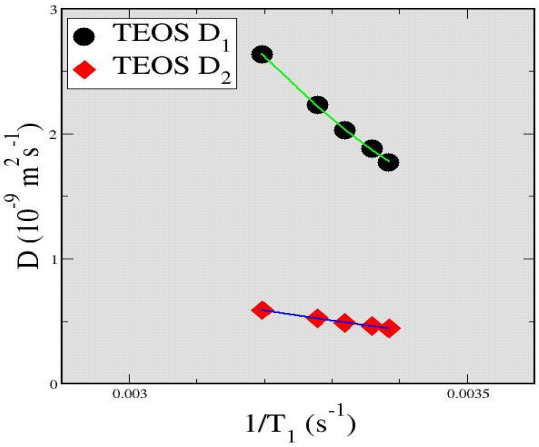

Fig. 1 *Temperature evolution of the two diffusion coefficients of TEOS_a*

Fig. 2 *Squamatinia algharbica*

References:

[1] Veith S. R., Hughes E., VuatazG., Pratsinis S.E., J. Coll. Inter. Sci., (2004) 274 ,216–228.

[2] Reboleira A.S.P.S., Gonçalves F., Oromi P., Mendes L.F.,Zootaxa, (2012) 3260,33-46.

BIOMATERIALS: TECHNOLOGIES & APPLICATIONS

Ana Almeida, Ana Baptista, Ana Espiga, Ana Pedrosa, Ana Nicolau, Ana Rebelo, Beatriz Romba, Carlos João, Carlos Marques, Daniela Flórido, Francisco Ferreira, João Fonseca, Joana Vasconcelos, Paula Soares, Ricardo Ribeiro, João Paulo Borges*

*Polimeric and Mesomorphic Materials, *jpb@fct.unl.pt*

Biomaterials are nonviable materials used in a medical device, intended to interact with biological systems [1]. Since this definition by Williams in 1986 different technologies applying these materials have been developed, resulting in extraordinary applications in the field of medicine, biology, tissue engineering and materials science.

Fibers (Fig.1), blocks, spheres, cements, membranes, 3D structures (Fig.2) have been produced by us with technologies like electrospinning, forcespinning, wet-spinning, freeze-casting, freeze-drying, microfluidic. Based on these technologies we have found outstanding applications such as bone substitutes, drug delivery systems, bio-batteries, skin repair/replace devices, dental membranes, etc.

In this poster we summarize the current technologies and applications that are being explored in the field of biomaterials, in the Polimeric and Mesomorphic Materials group of CENIMAT/I3N.

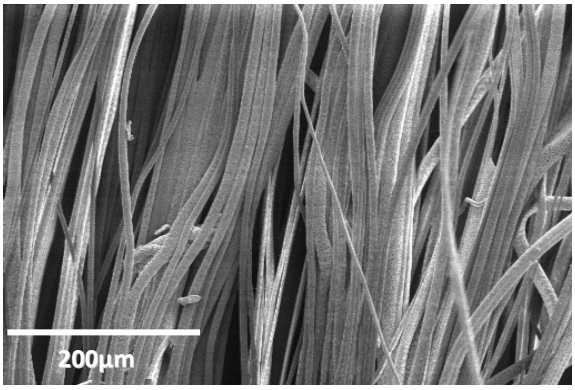

***Fig. 1** Policaprolactone fibers produced by Forcespinning.*

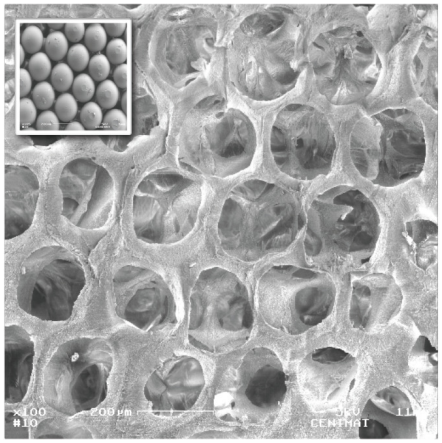

***Fig. 2** Chitosan 3D structure produced by Inverse replication of microspheres.*

References:

[1] D. F. Williams, *Definitions in Biomaterials. Proceedings of a Consensus Conference on the European Society for Biomaterials*, Chester, England, 3-5 March 1986, Vol. 4, Elsevier, New York

ELECTRICAL AND DIELECTRIC MEASUREMENTS APPLIED TO BIO AND ECOMATERIALS

M. C. Lança*, A.S. Pedrosa, J: P. Borges, E.R. Neagu, C.J. Dias, J. Marat-Mendes
*MPM, *mcl@fct.unl.pt*

Two of the most common techniques used for studying electrical dipoles and space charge in insulating materials are isothermal measurements of DC charging and discharging currents (ICC/IDC) and thermally stimulated discharge currents (TSDC). A common technique to study the dielectric properties is Dielectric Relaxation Spectroscopy (DRS). The combined results of the three methods allow better understanding of the electrical dipoles and space charge trapping/detrapping characteristics.

Hydroxyapatite (HA) is a calcium phosphate (CaP) that in its natural form is the main constitute of hard tissue (bones and teeth). Together with other CaP (like β-Tricalcium phosphate (β -TCP)) it is used in hard tissue replacement, either has coating of metallic prosthesis, porous blocks or injectable materials. It is known that the bone remodeling is related with its piezoelectric properties and there is an important role played by the coupling of mechanical stresses vs electrical response. Also since the last decade of the XX century, bioactivity tests on polarized HA showed enhanced apatites growth pointing to a faster and better osteointegration. In our work, studies were carried on HA, HA with added piezoelectric materials (barium titanate) and HA/ β-TCP biphasic composites so that the best charging/polarizing conditions could be selected. After the *in vitro* bioactivity tests performed, SEM analysis reveal faster apatites growth on the negative surface of charged samples. However the positively charged surfaces showed less growth than the control (non-charged/polarized) samples.

Portugal is one of the main producers of cork in the world and is the main manufacturer. Recently a major effort is being made to find new cork based materials with new applications. Some years ago, a composite was developed in order to recycle both cork and TetraPak® containers. Its properties have been studied in order to control the humidity in the material and its influence on the ability to store charge. To lower the water content a hygroscopic material was added (paraffin) to the composite. At the same time a thermal treatment was made on some of the powders which were dried before sample preparation. After the samples were kept at higher temperature until measurements were made. The results were compared with previous published for different types of the cork/TetraPak® composite, natural cork and cork agglomerates.

SOLID STATE ELECTROLYTE GATED TFT'S

Lídia Santos*, Pawel Wojcik, Luís Pereira, Rodrigo Martins, Elvira Fortunato**
*MEON, *ls.santos@campus.fct.unl.pt; **emf@fct.unl.pt*

Solution-processed field-effect transistors are important building blocks for flexible electronics but many challenges have still to be overcome in order to achieve high-performance transistors. Low temperature, reproducibility, large areas and cost effectiveness are the main concerns.

The concept of electrolyte-gating is based on the redistribution of ions in an electrolyte when a voltage is applied to the gate electrode. This leads to the formation of electric double layers (EDL) at the surface of the gate electrode and the semiconductor. The bulk remains neutral and thus the applied gate voltage drops almost entirely over the few nm thick double layers resulting in a very high effective capacitance. Electrolyte-gating transistors are particularly interesting for rough surface such as nanoparticles since it promotes a more efficient and uniform gating effect [1].

In this work we used hydrothermal synthesized GIZO nanoparticles dispersed in water with ethylene glycol as semiconductor and solid state electrolyte is based on aqueous dispersions of vinyl acetate stabilized with cellulose derivatives, an aqueous dispersion in styrene of an acrylic acid ester and lithium perchlorate (dispersions provided by RESIQUÍMICA). Both layers were deposit by spin coating and the semiconductor was annealed at 450 °C for 1 hour.

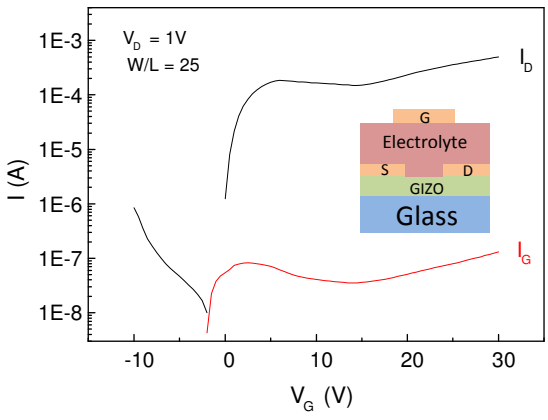

Fig. 1 *Transfer curve of electrolyte gated TFT with GIZO NP's semiconductor*

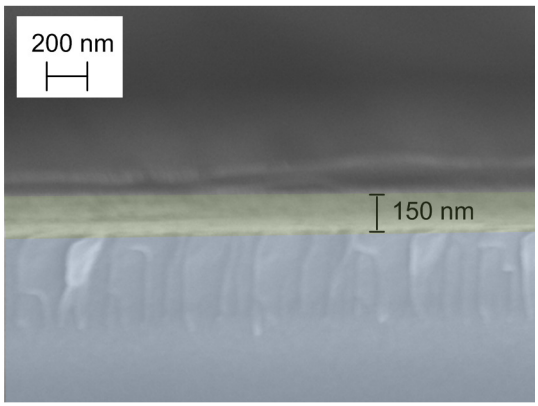

Fig. 2 *SEM cross-section of GIZO NP's layer*

References:

[1] Thiemann, S., Gruber, M., Lokteva, I., Hirchmann, J., Halik, M., Zaumseil, J., *ACS applied materials and interfaces* **5** (2013) 1656.

ZnO NANOSTRUCTURE SYNTHESIS ASSISTED BY MICROWAVE RADIATION

A. Pimentel*, D. Nunes, R. Martins, E. Fortunato**
*MEON, *acgp@campus.fct.unl.pt; **emf@fctunl.pt*

One important aspect of Zinc oxide (ZnO) is the fact that both the physical and chemical properties vary as a function of size, shape, morphology and crystalline structures. Several techniques have been tested including, electrodeposition, electrospinning and hydrothermal method [1-3]. Yet, precursors and solvents also play an import role in the nanostructure outcome. Thus, new synthesis strategies are vital for the development of novel nanomaterials.

Conventional heating is known to be inefficient, time and energy consuming. Microwave irradiation seem to be an option as it is relatively cheap and presents short reaction time, enhanced reaction selectivity, energy saving, homogeneous volumetric heating and high reaction rate. By the fact that microwaves can transfer energy directly to the reactive species, so-called "molecular heating", it promotes transformations that are currently not possible with conventional heat. Power and heating frequency are the main parameters of a microwave system, and each of them is expected to have great influence on the structure and properties of ZnO [4].

ZnO nanostructures with hexagonal structure have been synthesized by hydrothermal method assisted by microwave radiation. Different solvents and microwave power have been tested, allowing obtaining ZnO with different structures.

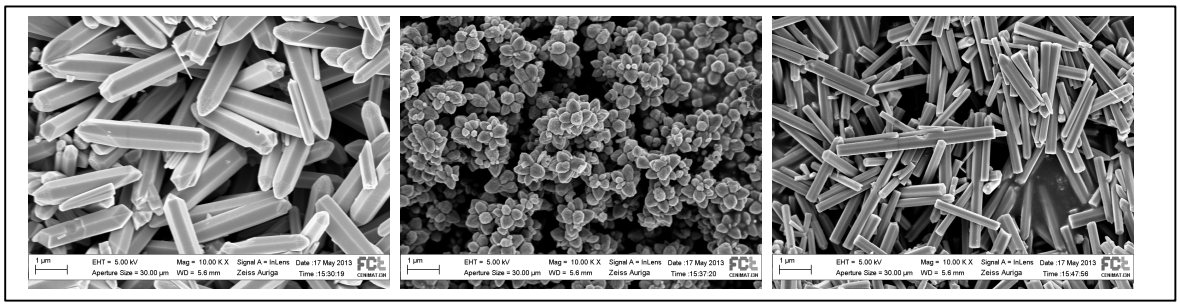

Fig. 1 *Scanning Electron Microscopy of ZnO nanostructures produces by hydrothermal synthesis assisted by microwave radiation, using different solvents: (a) water, (b) ethylenglycol, (c) 2-ethoxyethanol*

References:

[1] L. Li, S. Pan, X. Dou, Y. Zhu, X. Huang, Y. Yang, G. Li, L. Zhang, J. Phys. Chem. C, 111 (2007) 7288-7291.

[2] H. Wu, W. Pan, J. Am. Ceram. Soc., 89 [2] (2006) 699-701.

[3] S. Baruah, J. Dutta, Science and Technology of Advanced Materials, 10 (2009) 1-18.

[4] P. Zhu, J. Zhang, Z. Wu, Z. Zhang, Crystal Growth & Design, 8 (2008) 3148-3153.

RECYCLABLE AMORPHOUS SOLAR CELL DEPOSITED ON PAPER

António Vicente*, Tiago Mateus**, Sergej Filonovich, Hugo Águas, Rodrigo Martins and Elvira Fortunato.

*MEON, *amv17109@campus.fct.unl.pt; **tp.mateus@gmail.com*

Solar energy is probably the source of renewable energy that better perspectives presents to endow any object with truly autonomous and self sufficiency performance. To achieve such energetic revolution the manufacturing cost of solar cells has to be minimized while flexibility and simplified implementation are mandatory conditions. In order to decrease substrate related costs, paper seems to be a viable option. Cellulose is the most abundant natural biopolymer on earth and besides its low cost, it is renewable, biodegradable, as well as non-toxic, making paper even more interesting for the scientific community and the industry as the material of excellence for the production of inexpensive and disposable electronic devices. Here, we show that *TetraBrik*®, (the beverage packaging material based on paper, produced by the Swedish company *TetraPak*®) and a paper based substrate, *Smart paper type 2* which as a hydrophilic nanoporous surface. These substrates provide a flexible, renewable and extremely cheap support for the deposition of amorphous hydrogenated silicon (a-Si:H) solar cells by plasma enhanced chemical vapor deposition (PECVD). We furthermore report a single solar cell deposited on *TetraBrik*® with a conversion efficiency of 4%, fill factor of 0.54, open circuit voltage of 0.8V and short circuit current of 9mA; while our cell on *Smart paper type 2* has a conversion efficiency of 3.4% with a fill factor of 0.40, open circuit voltage of 0.82V and short circuit current of 10.2mA. The transversal cut of the *Smart paper type 2* cells was observed on SEM (Fig.1). Such results demonstrate the viability of applying the traditional PECVD technology to this original substrate and produce solar cells with the best cost/efficiency relation.

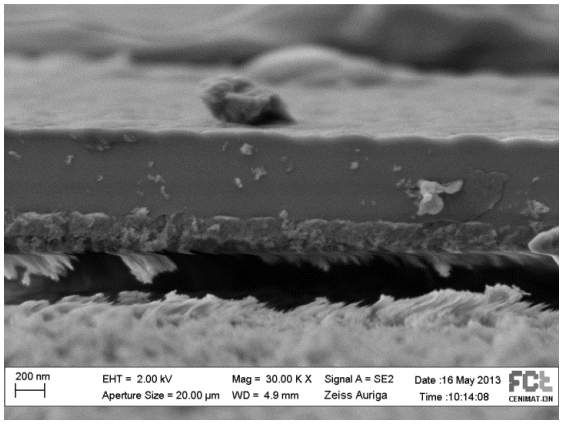

Fig. 1- *SEM image of the a-Si:H solar cell deposited over the Smart paper type 2 substrate.*

BIO-BATTERIES BASED ON ELECTROSPUN MEMBRANES

Ana Baptista*, Joana Neto, José I. Martins, Elvira Fortunato, Rodrigo Martins, João P. Borges and Isabel Ferreira
*MEON, *anacbaptista@campus.fct.unl.pt*

The present work proposes the development of a flexible and lightweight electrochemical device which takes advantage of the ionic content of the physiological fluids to generate electric energy to power biomedical devices. A biocompatible polymer membrane was produced by electrospinning forming a flexible and highly porous nonwoven mats with a high surface area. By depositing thin metal films electrodes onto both sides of the electrospun membrane, the original flexibility and surface area is preserved leading to a highly flexible and foldable electrochemical device (Fig.1). For instance, a cellulose-based device covered with silver and aluminum thin films, provides power density higher than 3µW.cm-2 under simulated physiological fluid [1]. This is a promising achievement concerning biomedical applications since the typical power required for a pacemaker operation is around 1µW.

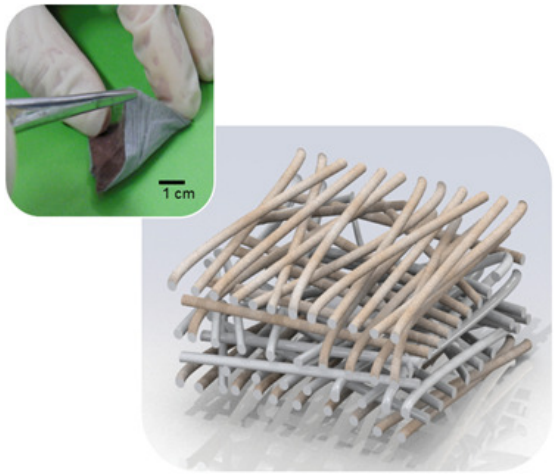

Fig. 1 *Electrochemical device based on biocompatible electrospun membrane.*

References:

[1]Baptista A.C., Martins J.I., Fortunato E., Martins R., Borges J.P. and Ferreira I., *Biosensors and Bioelectronic* **26** (5), 2742 (2011).

ALL OXIDE PHOTOVOLTAICS: CUPROUS OXIDE THIN FILMS BY SPRAY PYROLYSIS TO BE USED AS P-TYPE LAYERS IN ALL OXIDE HETEROJUNCTION FOR SOLAR CELL APPLICATIONS

M. Pavan*, J. Deuermeier, A. Gonçalves, R. Martins, E. Fortunato**
*MEON, *m.pavan@fct.unl.pt; **emf@fct.unl.pt*

AllOxidePV project aim to make low cost solar cells using inexpensive MOs . To overcome the limiting properties of the known oxides AllOxidePV project aim to develop novel materials like multi-component MOs thus enabling efficient, durable solar conversion to electricity at extremely low cost.

Low cost solar cells need deposition technologies easy to upscale and spray pyrolysis technique is one of the cheaper ones that allow to deposit compact oxides on large areas.

Low cost and nontoxic cuprous oxide (Cu_2O), is a spontaneous p-type semiconductor with a direct energy gap of 2.1 eV, that is a very attractive semiconductor material to solar cells application.

Cu_2O thin films can be obtained by spray pyrolysis of aqueous solutions that include copper(II) acetate, glucose, and 2-propanol. The presence of glucose makes possible the reduction of copper cation (II) to metallic copper, that is subsequently oxidized to Cu_2O allowing the formation of the thin film.

Depositions around 300°C of solution without glucose lead instead to cupric oxide (CuO) thin films. In that case the reduction stage of the previous reaction is avoided, allowing the formation of the copper oxide from the aqueous copper cation (II). Cupric oxide is a natural p-type semiconductor with a band gap of 1.5 eV, that is also a good candidate as p-type layer in all oxide heterojunction for solar cells application.

The deposition conditions, based on the phase relations of the films, were investigated in terms of substrate temperature. Thin films were characterized to determine phases, electrical and optical properties.

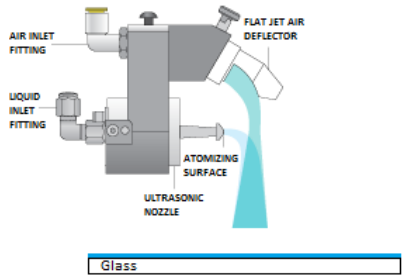

Fig. 1 *Nozzle of SONOTEK spray pyrolysis system*

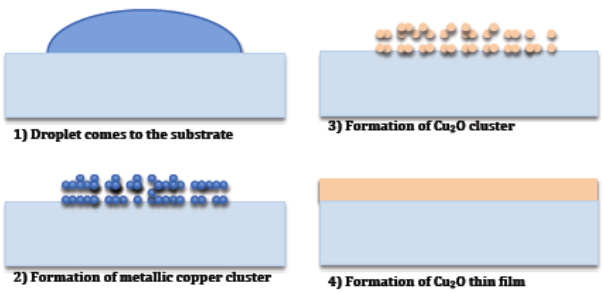

Fig. 2 *Schematic flow diagram of the Cu2O film formation process*

METAL NANOPARTICLES FOR PLASMON - ENHANCEMENT IN SI SOLAR CELLS AND RAMAN SPECTROSCOPY

Araújo A.[1*], Riflet A[1]., Mendes M. J.[2], Gaspar D[1]., Salazar C[3]., Franco R[3]., Vicente A. [1], Filonovich S. A[1]., Fortunato E.[1], Ferreira I[1]., Águas H.[1]. and Martins R.[1**]

[1]Cenimat / I3N - Cemop / Uninova, [2] MATIS CNR-IMM and Dipartimento di Fisica e Astronomia, Università di Catania, [3]Bionano@REQUIMTE
[*]andreiajoiaraujo@hotmail.com; [**]rm@uninova.pt

Metallic nanostructures (Figure 1) supporting surface plasmons have been proposed as an alternative method to achieve enhancement in Si solar cells and also surface Raman spectroscopy (SERS). When metal nanoparticles (NPs) are excited by electromagnetic radiation of appropriate energy, their conduction electrons oscillate collectively exhibiting a localized surface plasmon resonance (LSPR). The incident light near the resonance frequency can be resonantly absorbed or scattered by the nanoparticles, creating localized near-field and propagating far-field, depending on their physical parameters (size, shape and the distances between them) and the surrounding environment. When the particle distances are less than the incident wavelength, the particle interaction will be dominated by the near-field effects, and when the particle distances are larger than the incident wavelength only the far-field effects can play a role. Far-field phenomena appear to be advantageous for silicon based devices while near-field is beneficial for SERS (figure 2). In this work we make use of both phenomena, exploring the physical properties of the metal nanoparticles.

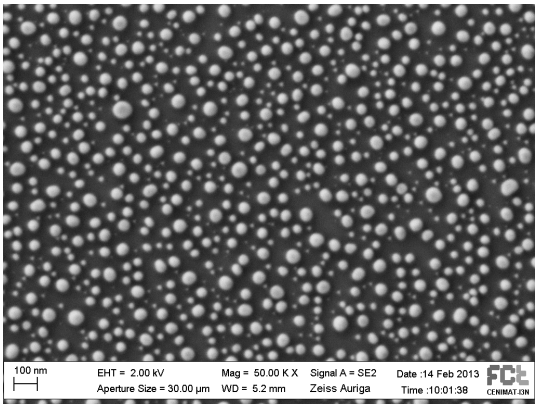

Fig. 1 SEM images of Ag NPs

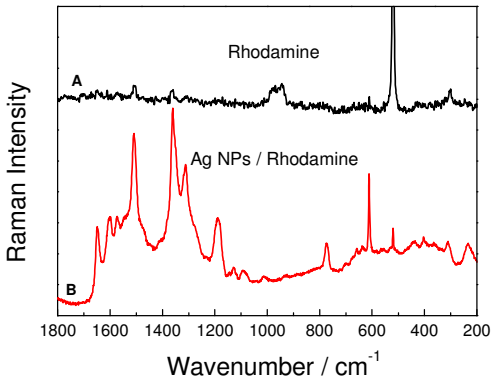

Fig. 2 SERS spectra of Rhodamine formed on Ag NPs(enhancement ≈ 238672.4)

AMORPHOUS Ga-Zn-Sn-O THIN FILM TRANSISTORS VIA COMBUSTION PROCESSING

Salgueiro, D.*, Duarte, P., Gaspar, D., Pereira, L.**, Fortunato, E., Martins, R.
*MEON, *d.salgueiro@fct.unl.pt; **lmnp@fct.unl.pt*

Oxide semiconductors can be deposited using solution processes, which is a viable alternative to vacuum deposition methods due to its simplicity and low processing cost [1].

In this work, we developed amorphous semiconductors layers of gallium-zinc-tin oxide (GZTO) by solution combustion processing using annealing temperatures of 250, 300 and 350 ºC. The molar percentage of Zn:Sn on the precursor was always kept at 2:1, while Ga molar percentage was varied from 0.1 to 0.2. Besides, two different solvents (2-methoxyethanol and ethanol) were used to prepare the precursor.

Bottom-gate TFTs were fabricated by spin coating deposition of *a*-GZTO films on Si/SiO_2 wafers using the different precursors and annealing temperatures. Even if further tests are need in order to perform a complete study, the most promising results were obtained using GZTO solutions with 2-methoxyethanol as solvent where the saturation mobility is approximately 2 $cm^2V^{-1}s^{-1}$ and the on/off ratio is between 10^6-10^7.

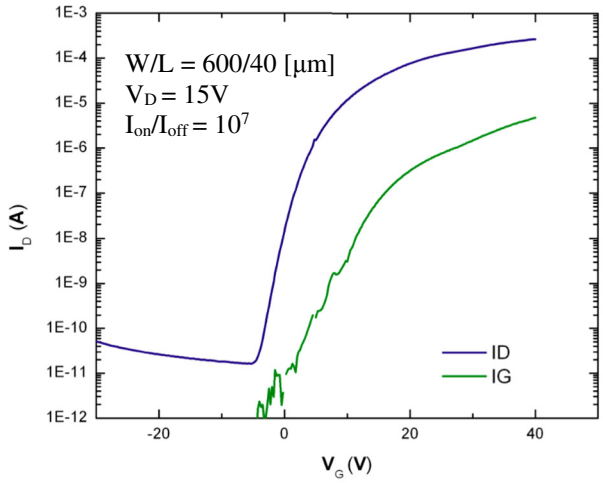

Fig. 2 *Transfer characteristics of transistor based on GZTO (0.1:2:1) in 2-methoxyethanol, annealed at 250ºC*

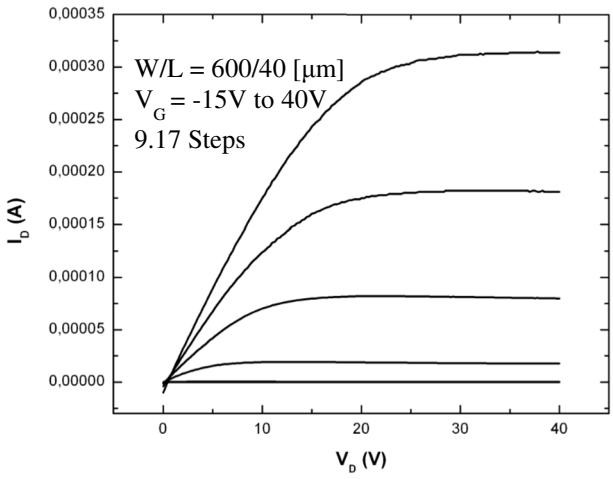

Fig. 1 *Output characteristics of transistor based on GZTO (0.1:2:1) in 2-methoxyethanol, annealed at 250ºC*

References:

[1] Jeong Y., Song K., Jun T., Jeong S., Moon J., *Thin Solid Films*, **519** (2011) 6164-6168.

HIGHLY CONDUCTING AND INFRARED TRANSPARENT GZO THIN FILMS PREPARED BY ULTRASONIC SPRAY PYROLYSIS

Kasra Kardarian*, Luis Pereira, Rodrigo Martins, Elvira Fortunato **
*MEON, *k.kardarian@fct.unl.pt; **emf@fct.unl.pt*

Different methods have been employed to produce Gallium-doped zinc oxide films, including sol-gel, pulsed laser deposition, radio-frequency magnetron, sputtering, and spray pyrolysis.

Herein we report the preparation of Gallium-doped zinc oxide (GZO) films by an automatic high precision ultrasonic spray pyrolysis system (Fig. 1).

The effect of increase in Ga/Zn atomic ratio from 1 to 4%, in the starting solution, and annealing in hydrogen for 30 min, 1 h and 2 h at 400ºC on structural, optical and electrical properties of the GZO films were investigated by various characterization methods.

The X-ray diffraction analysis indicated that the films were polycrystalline with (002) plane as preferential orientation. However, Increments of annealing time led to decrease in crystallinity of the films. Scanning electron microscopy (SEM) measurements revealed that the surface morphology of the films change by annealing in hydrogen atmosphere with elimination of grain boundaries.

The results show that the doping affects the thin films properties and mainly the electrical ones. The film doped with 3 at% of Gallium presented the lowest value of resistivity (5.5×10^{-1} Ω.cm) among the other films which was further decreased after annealing in hydrogen for 1 h to 7.4×10^{-3} Ω.cm without significant changes in optical properties (transparency of 80-90% in the visible and IR wavelength). Nevertheless, figure of merit and haze factor suggest 2 at% of Gallium as the most adequate doping concentration for the solar cells applications.

Fig. 1 *Sono-Tek® ultrasonic spray pyrolysis system*

STUDY AND APPLICATIONS OF PVDF MEMBRANES

Igreja R.*, Monteiro T.**, Sanguino P.*, Busani T.*, Fortunato E*., Martins R.*, Franco R.** Dias C.J.*

**MEON-CENIMAT/I3N, DCM, FCT-UNL,cmd@fct.unl.pt, rni@fct.unl.pt;*
***REQUIMTE, DQ, FCT-UNL rft@fct.unl.pt*

Biosensor application - We have explored for the first time the feasibility of using PVDF Immobilon-P membranes, attached to interdigitated capacitor microelectrodes, as 3-dimensional matrixes for the immobilization and distribution of antibodies that perform as affinity probes for the antigen of interest. The membranes allow for the distribution of antibodies across the entire region probed by the electric field.

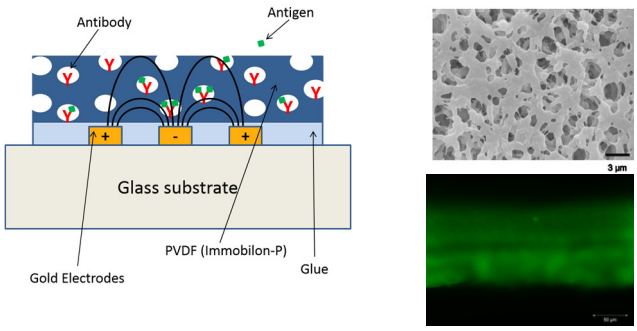

Fig. 1 *Schema of the biosensor cross-section.*

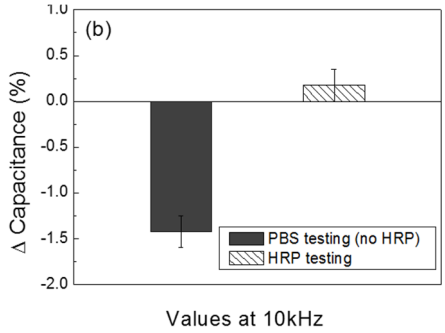

Fig. 2 *Capacitive response*

Modeling of dielectric and ferroelectric properties of PVDF - Spin coat membranes of PVDF of 2.5 and 5µm were obtained in β-phase, which is the ferroelectric phase of this polymer, through an appropriate procedure and without further treatment. Ferroelectric switching measurements were undertaken in order to confirm the ferroelectric properties of these films (Fig. 3). In Fig. 4, modeling of these measurements can be observed leading to the conclusion that the 2.5µm thick membranes had a polarization of 9.9mC/m^2 with an activation field of 42MV/m.

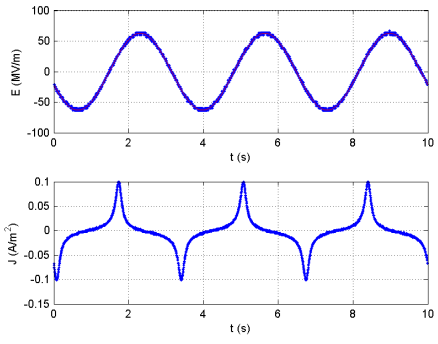

Fig. 3 *Measurements of ferroelectric switching of PVDF membrane*

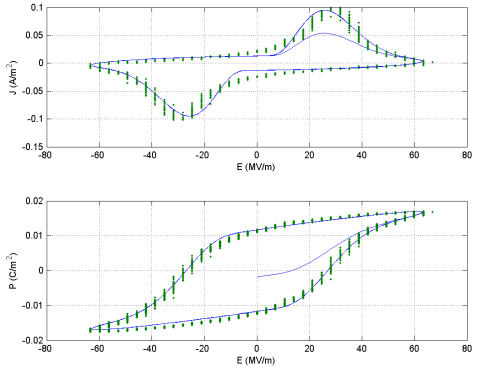

Fig. 4 *Modeling of ferroelectric hysteresis of a 2.5um thick film*

SYNTHESIS OF ZINC STANNATE NANOPARTICLES: HYDROTHERMAL VS. MICROWAVE

Alicja Elzbieta Kownacka*, Daniela Nunes, Rodrigo Martins, Pedro Barquinha, Elvira Fortunato **

CENIMAT/I3N, Departamento de Ciência de Materiais, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa and CEMOP/UNINOVA, Campus da Caparica, 2829-516 Caparica, Portugal

**a.kownacka@fct.unl.pt; **emf@fct.unl.pt*

Zn_2SnO_4 (zinc stannate) has been attracting a growing attention in the last decade owning to its flexibility and wide variety of applications.Several methods for the zinc stannate synthesization have been published over the years. Summarizing all of available processes, the hydrothermal and microwave method have sparked much interest due to operational simplicity, cost-efficiency and capability for a large-scale production. In order to achieve a variety of shapes like cubes, spheres and rods the chemicophysical parameters of the system, as temperature, reaction duration or mineralizers can be varied to easily control the kinetics and thermodynamics in the nucleation and growth of nanocrystals. In order to understand the influence of used synthesis technique and different reaction conditions on the ZTO nanoparticles creation, numerous tests have been performed, as like by X-ray diffraction (XRD), Fourier Transform Infrared (FT-IR), scanning electron microscope (SEM) equipped with energy dispersive X-Ray spectroscopy (EDS), transmission electron microscopy (TEM) and by differential scanning calormetry (DSC).

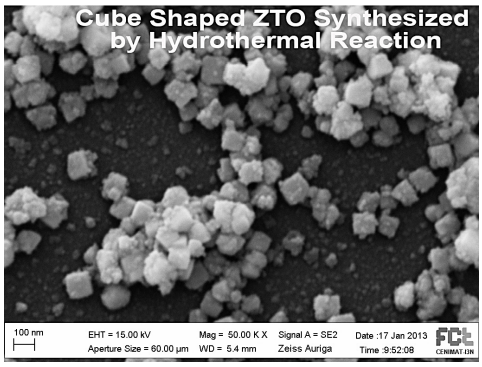

***Fig. 1** Cube shaped ZTO*

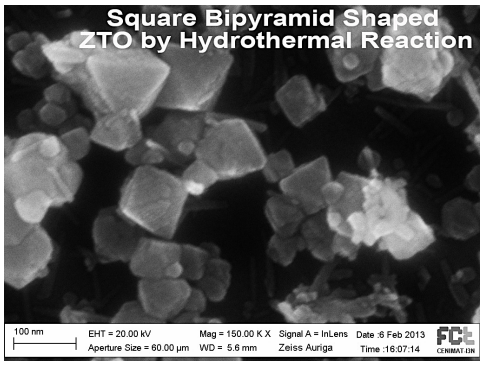

***Fig. 2** Bipyramid shaped ZTO*

List of Participants

Name	email	group
Aguas, Hugo	hma@fct.unl.pt	MEON
Almeida, Pedro	Pla@fct.unl.pt	MPM
Almeida, Ana	ana.almeida@fct.unl.pt	MPM
Baptista, Ana	anacbaptista@campus.fct.unl.pt	MEON
Barros, Raquel	arxbarros@campus.fct.unl.pt	MEON
Bernacka-Wojcik, Iwona	ib@uninova.pt	MEON
Borges, João	jpb@fct.unl.pt	MPM
Braz Fernandes, Francisco Manuel	fbf@fct.unl.pt	ME
Canejo, João	jpgc@campus.fct.unl.pt	MPM
Cardoso, Andreia	Andreiajoiaraujo@hotmail.com	MEON
Carvalho, Alexandra	amfc.carvalho@fct.unl.pt	MPM
Catela, Bruno	b.catela@campus.fct.unl.pt	MEON
Cidade, Maria Teresa	mtc@fct.unl.pt	MPM
Contreras, Javier	ja@uninova.pt	MEON
Costa, Mafada	mafaldanascimentocosta@gmail.com	MEON
Dias, Carlos J.	cmd@fct.unl.pt	MEON
Echeverria, Coro	coro@fct.unl.pt	MPM
Feio, Gabriel	gf@fct.unl.pt	MPM
Fernandes, Susete	sm.fernandes@fct.unl.pt	MPM
Ferreira, Isabel	imf@fct.unl.pt	MEON
Ferreira, Francisco	ferreira.r.kiko@gmail.com	MPM
Ferreira, Lúcia	lm.ferreira@campus.fct.unl.pt	MEON
Figueira, Joana	joanarsfigueira@msn.com	MEON
Figueiredo, Elin	elinfigueiredo@gmail.com	ME
Filonovich, Sergej	filan@fct.unl.pt	MEON
Fonseca, João	jv.fonseca@campus.fct.unl.pt	ME
Fortunato, Elvira	emf@fct.unl.pt	MEON
Furtado, Maria	mjfurtado@itn.pt	ME
Garcia Merino, Esther	e.merino@campus.fct.unl.pt	MPM
Gaspar, Diana	dfpgaspar@gmail.com	MEON
Geng, Yong	y.geng@fct.unl.pt	MPM
Godinho, Maria Helena	mhg@fct.unl.pt	MPM
Gomes, Daniela	ddsn.gmes@campus.fct.unl.pt	MEON
Gonçalves, Alexandra	amfg@fct.unl.pt	MEON
Igreja, Rui	rni@fct.unl.pt	MEON
João, Carlos	carlosfcjoao@gmail.com	MPM
Kardarian, Kasra	k.kardarian@fct.unl.pt	MEON
Kownacka, Alicja Elżbieta	a.kownacka@fct.unl.pt	MEON
Lança, M Carmo	mcl@fct.unl.pt	MPM

Name	email	group
Leal, Catarina	cleal@adf.isel.pt	MPM
Lima, M. Margarida	mmal@fct.unl.pt	ME
Lopes, Andreia	keyalopes@gmail.com	ME
Loureiro, Joana	joa.loureiro@gmail.com	MEON
Machado, Angela	amp.machado@campus.fct.unl.pt	ME
Martins, Rui	rmsm@fct.unl.pt	ME
Martins, Assis	asfm@fct.unl.pt	MPM
Martins, Rodrigo	rm@uninova.pt	MEON
Mateus, Tiago	tp.mateus@gmail.com	MEON
Monteiro, Regina	rcm@fct.unl.pt	ME
Nandy, Suman	snandy_ju@yahoo.co.in	MEON
Neves, Nuno	nuno.neves@campus.fct.unl.pt	MEON
Nogueira, Adriana	adrianatiagonogueira@gmail.com	ME
Nunes, Marcelo	marcelo_snunes@hotmail.com	ME
Oliveira, João Pedro	jp.oliveira@campus.fct.unl.pt	ME
Pavan, Michele	m.pavan@fct.unl.pt	MEON
Pedrosa, Ana Sofia	ana.sofia.mota.pedrosa@gmail.com	MPM
Pereira, Sónia	sp@uninova.pt	MEON
Pereira, Luis	lmnp@fct.unl.pt	MEON
Pimentel, Ana	acgp@campus.fct.unl.pt	MEON
Rodrigues, Alexandra	xana.rodrigues@hotmail.com	MEON
Rovisco, Ana	a.rovisco@campus.fct.unl.pt	MEON
Salgueiro, Daniela	d.salgueiro@fct.unl.pt	MEON
Santos, Ana Catarina	acg.santos@campus.fct.unl.pt	MEON
Santos, Lídia	ls.santos@campus.fct.unl.pt	MEON
Santos, Rafael	jrs18241@campus.fct.unl.pt	MEON
Silva, Pedro	pess@ua.pt	MPM
Silva, Rui	rjcs@fct.unl.pt	ME
Soares, Paula	paulaipsoares@gmail.com	MPM
Soares, Roque	roque.saldanha.soares@gmail.com	ME
Trindade, Ana Catarina	acrt@fct.unl.pt	MPM
Vasconcelos, Joana	joanamarta7@gmail.com	MPM
Vaz Pinto, Joana	jdvp@fct.unl.pt	MEON
Veiga, João Pedro	jpv@fct.unl.pt	ME
Velhinho, Alexandre	ajv@fct.unl.pt	ME
Vicente, Antonio	amv17109@campus.fct.unl.pt	MEON
Wojcik, Pawel	p.wojcik@campus.fct.unl.pt	MEON

NOTES

Sponsors:


CENIMAT
i3N
CENTRO DE INVESTIGAÇÃO DE MATERIAIS


FCT
FACULDADE DE
CIÊNCIAS E TECNOLOGIA
UNIVERSIDADE NOVA DE LISBOA


UNINOVA
INSTITUTO DE DESENVOLVIMENTO DE NOVAS TECNOLOGIAS


sumol+compal


VICARTE