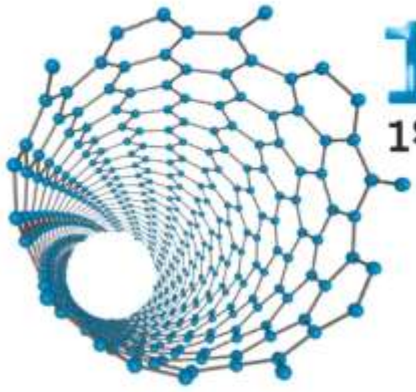

1-CLUSTERMN

1st CLUSTER Workshop in Materials
and Nanotechnology

Platform for Nanotechnology and Materials
of Instituto Superior Técnico (IST-NM)

BOOK OF ABSTRACTS

1st CLUSTER Workshop in Materials and Nanotechnology

IST Lisbon, 4th-6th December 2013

1st Cluster Workshop in Materials and Nanotechnology

Dear Colleagues,

We are delighted to welcome you to the 1st Cluster Workshop in Materials and Nanotechnology, organized by the Platform of Nanotechnologies and Materials of Instituto Superior Técnico (IST-NM).

The meeting is intended to foster the ties between researchers working in the areas of Materials Science and Nanotechnology at IST and other national institutions with their international Cluster fellows, launching a forum for exchanging the latest developments in these areas of research.

The workshop includes 15 inspiring invited lectures by researchers from IST, Cluster schools, and other Portuguese Universities, expected to promote fruitfull discussions during the two and a half days of the meeting and behond. It is especially rewarding to see such a strong participation by young researchers, which will present most of the 15 oral and over 50 poster communications in the program.

We thank all the authors for their contributions and wish you an active and stimulating participation in this event.

The Organizing Committee

Organizing Committee

Rui Vilar
José Paulo Farinha
Amélia Almeida
Carlos Baleizão
Fátima Montemor
Catarina Santos
Darya Snihirova
Liliana Cangueiro

Sponsors

Venue

The workshop will take place at the Instituto Superior Tecnico Congress Center (IST, Alameda Campus).

Program

December 2013		
4 (Wednesday)	**5 (Thursday)**	**6 (Friday)**
	09:00 IC 4	**09:00** IC 12
	09:40 IC 5	**09:40** IC 13
	10:20 Coffee / Posters	**10:20** Coffee / Posters
	10:50 IC 6	**10:50** IC 14
	11:30 IC 7	**11:30** OC 5
		11:50 OC 6
	12:10 OC 2	**12:10** OC 7
	12:30 Lunch	**12:30** Lunch
14:00 Opening	**14:00** IC 8	**14:00** IC 15
14:20 IC 1		
	14:40 IC 9	**14:40** OC 8
15:00 IC 2		**15:00** OC 9
	15:20 IC 10	**15:20** OC 10
15:40 OC 1		**15:40** OC 11
16:00 Coffee / Posters	**16:00** Coffee / Posters	**16:00** Coffee
		16:20 OC 12
16:30 IC 3	**16:30** OC 3	**16:40** OC 13
	16:50 OC 4	**17:00** OC 14
17:10 Round Table	**17:10** IC 11	**17:20** OC 15
		17:40 Closing
	20:00 Workshop dinner	

1st Cluster Workshop in Materials and Nanotechnology

Wednesday 4th

13:30-14:00	Workshop Registration
14:00-14:20	Opening
SESSION 1	*Chairman*: François Weiss (Grenoble-INP, France)
14:20-15:00	**IC1**: Alain M. Jonas (Université Catholique de Louvain, Belgium) “Hybrid Nanostructured Functional Layers: From Confined Polymer Crystallization to Plastic Memory Devices”
15:00-15:40	**IC2**: José Gaspar Martinho (CQFM, IST, ULisboa) “Photochromic Materials Activated by Two-Photon Excitation”
15:40-16:00	**OC1**: Frederico Ferreira (IBB, IST, ULisboa) “Electrospun Nanofiber Based Scaffold Platform for Stem Cell Alignment”
16:00-16:30	Coffee Break / Poster Session
SESSION 2	*Chairman*: Rui Vilar (IST-MN, IST, ULisboa)
16:30-17:10	**IC3**: Pedro L. Granja (INEB/ICBAS, UPorto) “Engineering Cell-Material Interactions at the Molecular Level”
17:10-18:00	**Round Table**: “New opportunities in Materials Science education at post graduated level” - François Weiss (Grenoble-INP, France) - Wolfgang Donner (TU Darmstad,Germany) - João Carlos M. Bordado (IST, ULisboa) - António Sousa Correia (Ordem dos Engenheiros) - Rui Vilar (IST-MN, IST, ULisboa)

Thursday 5th

SESSION 3	*Chairman*: Manuel Almeida (CTN, IST, ULisboa)
9:00-9:40	**IC4**: João Carlos M. Bordado (IST, ULisboa) "Antifouling Surfaces: New Immobilized Biocide Systems"
9:40-10:20	**IC5**: Jorge Morgado (IT, IST, ULisboa) "Molecular Wires Based on Zinc-Porhyrins: Preparation and Electrical Properties Assessed by STM"
10:20-10:50	Coffee Break / Poster Session
SESSION 4	*Chairman*: Rui Almeida (ICEMS, IST, ULisboa)
10:50-11:30	**IC6**: Albano Cavaleiro (SEG-CEMUC, UCoimbra) "The Importance of Structural Arrangement on the Friction Performance of Transition Metal Dichalcogenides Sputtered Films"
11:30-12:10	**IC7**: Manuel Freitas (Dep. Mechanical Engineering, IST, ULisboa) "AZ31 Magnesium Alloy Elastoplastic Behavior Under Multiaxial Loading Conditions"
12:10-12:30	**OC2**: Nuno Silvestre (Dep. Mechanical Engineering, IST, ULisboa) "Computational Modelling of the Compressive Behaviour of CNT-Reinforced Aluminium Composites"
12:30-14:00	Lunch
SESSION 5	*Chairman*: José Gaspar Martinho (CQFM, IST, ULisboa)
14:00-14:40	**IC8**: João Rocha (CICECO, UAveiro) "Light at the End of the Tunnel"
14:40-15:20	**IC9**: Rui Almeida (ICEMS, IST, ULisboa) "YAG:Ce^{3+} Photoluminescence Tuned by 1-D Photonic Crystal Microcavity for White Light Generation"
15:20-16:00	**IC10**: Manuel Almeida (C2TN, IST, ULisboa) "Metals Based on Neutral Molecular Species: The New Paradigm and its Application to Plastic Electronics"
16:00-16:30	Coffee Break / Poster Session

SESSION 6	*Chairman*: Jorge Morgado (IT, IST, ULisboa)
16:30-16:50	**OC3**: Elena Tatarova (IPFN, IST, ULisboa) "Free Standing Graphene Synthesis Using Microwave Plasmas"
16:50-17:10	**OC4**: António Gonçalves (CTN, IST, ULisboa) "New Thermoelectric Materials: The Disorder Paradigm"
17:10-17:50	**IC11**: Paulo Freitas (INESC-MN/INL, IST, ULisboa) "Magnetoresistive Sensors: from Industrial to Biomedical Applications"
20:00	Workshop Dinner: Museu da Cerveja (Terreiro do Paço)

Friday 6th

SESSION 7	*Chairman*: Pedro Granja (INEB, UPorto)
9:00-9:40	**IC12**: Laura Ilharco (CQFM, IST, ULisboa) "The Versatility of Sol-gel Processing in Tailoring Silica-Based Materials for Specific Applications"
9:40-10:20	**IC13**: Verónica Bermudez (CQ-VR, UTAD) "Self-Directed Assembly in Non-Bridged Silsesquioxanes"
10:20-10:50	Coffee Break / Poster Session

SESSION 8	*Chairman*: Albano Cavaleiro (SEG-CEMUC, UCoimbra)
10:50-11:30	**IC14**: Elvira Fortunato (CENIMAT/I3N, FCT, UNL) "Thin Film Transistors Based on Metal Oxide Semiconductor Thin Films and Nanoparticles"
11:30-11:50	**OC5**: Tânia Ribeiro (CQFM, IST, ULisboa) "Highly Photostable Fluorescent Silica Particles for Laser Scanning Imaging Applications"
11:50-12:10	**OC6**: Pedro Paulo (CQE, IST, ULisboa) "Large Fluorescence Enhancements of Phthalocyanine in (Lipid Bilayer)-Polyelectrolyte Coated Gold Nanoparticles"
12:10-12:30	**OC7**: Rui Pinto (INESC-MN/CQFM, IST, ULisboa) "Exciton Dynamics in Organic Materials: High Quantum Efficiency in Charge-Transfer Interfaces"
12:30-14:00	Lunch

SESSION 9	*Chairman*: Fátima Montemor (ICEMS, IST, ULisboa)
14:00-14:40	**IC15**: François Weiss (Grenoble-INP, France) "Chemical Routes for Coatings by Design. From "Paint and Heat" to Today"
14:40-15:00	**OC8**: Tiago Monteiro (INESC-MN, IST, ULisboa) "Silicon Probes as Biosensors for Intra- and Extracellular Measurement of pH for Early Detection of Dysplasia"
15:00-15:20	**OC9**: Vânia André (CQE, IST, ULisboa) "Bio-MOFs As Potential Drug Delivery Materials – A New Approach To Traditional MOFs"
15:20-15:40	**OC10**: Sónia Eugénio (ICEMS, IST, ULisboa) "Electrodeposition of Dendritic Transition Metal Films and Their Application as Electrodes for Supercapacitors"
15:40-16:00	**OC11**: Graça Brotas (IT, IST, ULisboa) "Synthesis of Cross-linkable P3HT Derivatives and Applications in Photovoltaic Cells"
16:00-16:20	Coffee Break
SESSION 10	*Chairman*: Amélia Almeida (ICEMS, IST, ULisboa)
16:20-16:40	**OC12**: Nikolay Polushkin (ICEMS, IST, ULisboa) "Current-Induced Magnetization Switching in a Single Ferromagnetic Element"
16:40-17:00	**OC13**: António Maurício (CERENA/CEPGIST, IST, ULisboa) "X-ray MicroCT: Non-Destructive Tool for Material Characterization in Art and Science"
17:00-17:20	**OC14**: Reinhard Schwarz (ICEMS, IST, ULisboa) "Raman Spectroscopy, XPS and XRD of Ferroelectric Domains in Pulsed Laser Deposited Na0.5K0.5NbO3 Films"
17:20-17:40	**OC15**: Maria Norberta Pinho (ICEMS, IST, ULisboa) "Sub-Micron Tailoring of Bi-Soft Segment Asymmetric Polyurethane Membrane Surfaces with Enhanced Hemocompatibility Properties"
17:40-18:00	Closing

Invited Communications

IC1. Hybrid Nanostructured Functional Layers: From Confined Polymer Crystallization to Plastic Memory Devices

Alain M. Jonas

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Advanced applications often require combining functional materials with a high degree of control over their morphology at the scale of a few tens of nanometers. This is especially the case for polymers used in electronics, e.g., when fabricating heterojunctions for solar cells, or when integrating different components to fabricate a transistor device.

It is therefore highly desirable to develop methodologies able to design hybrid nano-morphologies combining multiple functional polymers, while simultaneously controlling essential attributes of semicrystalline polymers such as crystal orientation and size. Indeed, functional polymers such as used in plastic electronics are most often semicrystalline or liquid crystalline. Unfortunately, when polymers are crystallized from the quiescent melt, they typically adopt complex spherulitic morphologies. Spherulites are generally nucleated by an impurity (heterogeneous nucleation), from which stacks of crystalline lamellae grow more or less radially. This gives rise to a random crystalline orientation, which is detrimental for applications, especially in the field of organic electronics.

Recently, we have reported on the combination of nucleation control and graphoepitaxial alignment, by crystallizing thin polymer films in the nanocavities of hard silicon molds such as used in nanoimprint lithography (NIL) [1-3]. This process was applied to a variety of functional polymers, including semiconducting [4], electroluminescent [4] or ferroelectric polymers [5]. As a side benefit of this process, the polymer is also shaped in an array of nanoobjects separated by regularly spaced cavities. This provides a unique opportunity to fabricate hybrid multifunctional layers, by filling the so-created cavities by another material synergetically interacting with the first one.

In this lecture, I will review the effect of NIL on the morphology of functional semicrystalline polymers, and show an example of multifunctional layer obtained by this process, combining ferroelectric and semiconducting polymers in a hybrid memory device able to store and read electrical information with a high storage density [6].

References

[1] Hu, Z.; Baralia, G.; Bayot, V.; Gohy, J. F.; Jonas, A. M., Nanoscale control of polymer crystallization by nanoimprint lithography. *Nano Letters* **2005**, *5*, 1738-1743.

[2] Hu, Z.; Jonas, A. M., Control of crystal orientation in soft nanostructures by nanoimprint lithography. *Soft Matter* **2010**, *6*, 21-28.

[3] Hu, Z.; Jonas, A. M., Patterning and Ordering with Nanoimprint Lithography. *In Handbook of Nanophysics. Nanoelectronics and Nanophotonics, Sattler, K. D., Ed. CRC: Boca Raton*, **2011**; Vol. 6, pp 18.1-18.8.

[4] Hu, Z.; Muls, B.; Gence, L.; Serban, D. A.; Hofkens, J.; Melinte, S.; Nysten, B.; Demoustier-Champagne, S.; Jonas, A. M., High-throughput fabrication of organic nanowire devices with preferential internal alignment and improved performance. *Nano Letters* **2007**, *7*, 3639-3644.

[5] Hu, Z.; Tian, M.; Nysten, B.; Jonas, A. M., Regular arrays of highly ordered ferroelectric polymer nanostructures for non-volatile low-voltage memories. *Nature Materials* **2009**, *8*, 62-67.

[6] Nougaret, L.; Kassa, H. G.; Nysten, B.; van Breemen, A. J. J. M.; Gelinck, G. H.; de Leeuw, D.; Marrani, A.; Hu, Z.; Jonas, A. M., Nanoimprinted ferroelectric/semiconduting polymer layers for high-density low-voltage non-volatile memory diodes, *submitted*

IC2. Photochromic Materials Activated by Two-Photon Excitation

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The ever growing demand for high capacity/reduced volume storage devices awaits the development of new materials and concepts that are able to meet the challenge. Nonlinear three-dimensional excitation combined with holographic recording are exciting concepts to explore in this context. [1] At the heart of optical storage devices are photochromic compounds that when activated by light of adequate energy suffer a molecular transformation that can be reversed by another source of light of different energy. The best photochromic compounds are diarylethenes owing to their excellent fatigue resistance, high conversion rates and absence of thermal isomerization. However, they are not effective nonlinear absorbing compounds at wavelengths required to induce the photoisomerization processes at high depths within the photosensitive material.

In order to overcome this limitation we combine the photochromic unit with a high nonlinearly absorbing dye in the NIR able to transfer the excitation energy by a Förster Resonance Energy Transfer (FRET) mechanism to the photochromic molecules. The antenna dye a polymer containing 2,4,6-tris(thiophen-2-yl)-1,3,5 triazine units bridged by 9,9-dihexyl-pH-fluorene with a very high two-photon absorption cross section (6930 GM at 740 nm) that efficiently transfers the excitation energy to the closed form of a diarylethene derivative (1,2-bis(2-methylbenzo[b]thiophen-3-yl) hexafluorocyclopentene) initiating the writing process [2]. The excitation by a two-photon absorption process with wavelengths in the red to the near-IR allows a better localization and deeper penetration of the excitation light in the support medium [3]. The reading process was performed with excitation light of shorter wavelengths (400 nm) at which the closed form absorbs inducing the isomerization into the open form. It was shown using as support an ethylcellulose film that a large number (>30) of writing-reading cycles can be performed without a significant loss of performance at a considerably faster speed compared to previously reported polymer composites [4].

References

[1] Walker E.; Rentzepis P. M. *Nat. Photon.* **2**, 406 - 408 (2008)
[2] Mariz, I. F. A.; Maçoas, E. M. S.; Martinho, J. M. G.; Zou, L.; Zhou,P.; Chen, X.; Qin, J. *J. Mater. Chem. B.* **1**, 2169-2177(2013).
[3] Zou, L.; Liu, L.; Ma, N.; Maçoas, E.; Martinho, J. M. G.; Pettersson, M.; Chen, X. G.; Qin, J. U. *Phys. Chem. Chem. Phys.* **13 (19)** 8838-8846 (2011).
[4] Corredor, C. C.; Huang, L.-Z. ; Belfield, K. D.; Morales, A. R. ; Bondar, M. V. *Chem. of Materials* **19**, 5165-5173 (2007)

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IC3. Engineering Cell-Material Interactions at the Molecular Level

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The potential of cell therapies to produce functional substitutes capable of restoring, maintaining or improving tissue function is being widely investigated, in combination with new and more efficient cell delivery vehicles. Progenitor and stem cells provide improved possibilities for *in situ* tissue regeneration. New material structures are required not only to provide the physical and mechanical support to cells, but also to play the role of insoluble and soluble components of the extracellular matrix (ECM), thus assuring their signalling properties to promote cell growth and restore differentiated function. Our research efforts are currently focused on the biofunctionalization of hydrogels, mainly polysaccharides, to improve their interaction with biological systems.

Several distinct cell types have been entrapped within hydrogels conjugated with the Arg-Gly-Asp (RGD) peptide sequence to modulate the process of cell adhesion. For the creation of cell-instructive matrices, hydrogels were also modified with the protease-sensitive and osteogenic peptidic sequences. Strategies were also optimized to promote cell proliferation, differentiation and migration within the hydrogels as well as to promote angiogenesis and to recruit cells from the surrounding environment.

References

Guerreiro SG, Brochhausen C, Negrão R, Barbosa MA, Unger RE, Kirkpatrick CJ, Soares R, Granja PL. Implanted neonatal human dermal fibroblasts influence the recruitment of endothelial cells in mice. Biomatter 2012;2:1-10.

Bidarra SJ, Barrias CC, Barbosa MA, Soares R, Granja PL. Evaluation of injectable in situ crosslinkable alginate matrix for endothelial cells delivery. Biomaterials 2011;32:7897-904.

Munarin F, Guerreiro S, Grellier M, Petrini P, Tanzi MC, Barbosa MA, Granja PL. Pectin-based injectable biomaterials for bone tissue engineering. Biomacromolecules 2011;12:568-77.

Fonseca KB, Bidarra SJ, Oliveira MJ, Granja PL, Barrias CC. Molecularly-designed alginate hydrogels susceptible to local proteolysis as 3D cellular microenvironments. Acta Biomaterialia 2011;7:1674-82.

IC4. Antifouling Surfaces: New Immobilized Biocide Systems

E. R. Silva,[a, b] O. Ferreira,[b] J. C. M. Bordado,[b] M. J. Calhorda [a]

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Water is the basis of all living micro and macroorganisms. In aqueous environments there is a wide range of organisms' species, which use flowing water not only to provide them with nutrients but also to transport them to other locations that can offer better conditions to their survival. However, this natural process also promotes a spontaneous unwanted colonization on submerged artificial surfaces, known as biofouling. This unwanted bio-attach can cause serious detrimental effects on such surfaces leading to subsequent economic and environmental penalties. For instance, it is responsible for hydrodynamic drag increasing in ships and thereby fuel consumption and greenhouse gas emissions [1]. It also becomes of particular alarm on fluid transport systems, such as water purification, since the fluid contact with biofouling will promote its contamination and further transmission into the environment (e.g. human infections). Protection methods against this biological attack have been extensively exploited. Hitherto, antifouling biocide-releasing coatings [2], i.e, coatings that elute biocides to kill microorganisms, or direct chemical treatments seem to be the most effective methods. However, the intrinsic ecotoxicity and continuous releasing of such antifouling agents have led to dangerous side-effects and thus to regulatory restrictions of their use. New alternatives are sought to provide greener and safe solutions.

In this work a new approach, consisting on the immobilisation of bioactive potential compounds in a polymeric based matrix through a chemical bond and/or physical retention in the polymer framework, is proposed. Comercial biocides, such as Irgarol and Econea, have been derivatised in order to be immobilised using this approach. The obtained derivatised biocide showed 10 to 12% (m/m) incorporation of the functional group, corresponding to reaction conversions up to 95 ± 5 %. No damage on biocides structures was identified from FTIR spectra analysis. Bacteriologic analysis revealed potential bioactivity of these derivatives when compared to the non-derivatised. Further binding of derivatised biocides with a conventional polyurethane (PU) paint system (provide by HEMPEL A/S) revealed successful linkage. Steel metal prototypes were coated with PU based paint containing different biocide compositions, and are currently placed in Peniche for field seawater tests. Leaching tests are being also conducted with freshwater and artificial seawater.

References

[1] Banerjee, I.; Pangule R. C.; Kane R. S. *Adv. Mat.* **2011**, *23*, 690-718.
[2] Lejars, M.; Margaillan, A.; Christine, B. *Chem. Rev.*, **2012**, *112*, 4347-4390.

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IC5. Molecular Wires Based on Zinc-Porhyrins: Preparation and Electrical Properties Assessed by STM

Jorge Morgado,[a,b] **Ana M. Bragança,**[a] **Quirina Ferreira,**[a] **Luis Alcácer**[a]

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Self-assembly is a key process in the bottom-up approach in nanotechnology. We now have the tools to manipulate and characterize materials organization at the nanoscale, such as atomic force microscopy (AFM) and scanning tunnelling microscopy (STM). This is allowing us to better understand materials properties and their relation with chemical composition.

One of the areas where this approach is being intensively used is the nanoelectronics. While preparation of simple nanodevices is a challenging task, which is providing highly interesting results, the characterization of their electrical behaviour has been shown to be quite a difficult task. Taking for instance the electrical characterization of single molecular wires, various techniques are available, providing results that are not always easy to replicate and interpret. In spite these difficulties, this is a step we need to overtake, if we want to establish a solid fundamental knowledge in this area, required to proceed to more complex systems.

In this communication we report on our efforts in this area of the unimolecular electronics. In particular, we have been studying the controlled formation of molecular wires combining a zinc-porphyrin and bipyridine, following by STM the molecular organization at every growth step of such wires [1]. The electrical properties of these wires have been studied by STS, to assess the influence of the wire length on the dominating electrical transport mechanism. The obtained results will be discussed in the context of the results reported by other research groups.

References

[1] Ferreira, Q.; Alcácer, J.; Morgado, J. *Nanotechnology* **2011**, 435604.
[2] Ferreira, Q.; Bragança, A. M.; Moura, N. M. M.; Faustino, M. A. F.; Alcácer, J.; Morgado, J. *Appl. Surf. Sci.* **2013**, *220*, 273.

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IC6. The Importance of Structural Arrangement on the Friction Performance of Transition Metal Dichalcogenides Sputtered Films

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The utopia of achieving frictionless mechanical contacts through the use of materials with optimized surface properties is the driving force for extensive research studies performed in the field of coatings tribology. Transition metal dichalcogenides (TMD) due to their layered structure and weak inter-layer bonding, has been a traditional solution for lowering the friction in mechanical contacts. As friction and wear is a materials surface problem, the focus of research in this field has been on the deposition of coatings of this family using sputtering techniques. The two main drawbacks which have impeded a widespread application of TMD coatings for reducing friction are the low loading bearing capacity and the high sensibility to moisture. Alloying TMD has been largely used for improving their tribological behavior, allowing to overcome those drawbacks. Our approach that goes beyond the state of the art is to control the deposition parameters, including the type and amount of alloying element, in order to tailor the structure at nanometer level allowing a suitable self-adaption phenomenon at the contact surface, for achieving a quasi-perfect TMD crystal at the coating surface, assuring very low friction in all atmospheres. The selection of the appropriate alloying element will permit to reach a high loading bearing capacity to sustain contact stresses over 1 GPa.

The aim of this talk is to present the latest developments within alloying of TMD-based magnetron sputtering deposited coatings, with either carbon and nitrogen. The focus will be directed to the importance of the alloying element on the control of the structure at nanometer level either in achieving amorphous or nanocomposite structures consisting of TMD crystals of different shapes embedded in C-based amorphous matrixes.

IC7. AZ31 Magnesium Alloy Elastoplastic Behavior Under Multiaxial Loading Conditions

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This work deals with obtaining an improved understanding of the deformation processes under multiaxial conditions of magnesium alloys. The magnesium offers a lightweight industrial material but with the drawback of HCP ductility issues. The particular mechanical behavior inherent to this kind of materials, hexagonal closed pack microstructures, leads to conclude that it is necessary to have a numeric elastoplastic model based on experimental data to estimate the inherent constitutive behavior. This numeric tool offers a useful contribution towards the production of useful knowledge for incorporation into several industrial sectors.

In order to implement an elastoplastic numeric model, it is studied here the low-cycle behavior of the magnesium alloy AZ31-B at several total strains amplitudes under uniaxial cyclic loading conditions. It is presented a first iteration for a numerical model which modulates the several physical mechanisms inherent to the magnesium elastoplastic behavior under uniaxial loading conditions. The ultimate goal is to achieve an elastoplastic numerical model suitable to estimate the magnesium alloys mechanical behavior under uniaxial and multiaxial loadings, which can account for mean stress, out-of-phase loading and sequential loading effects.

In order to validate the work already done, the numeric estimations were compared with the uniaxial data and with the Jiang & Sehitoglu plasticity model. The numeric results from the implemented model where acceptable however the Jiang & Sehitoglu model shows some shortcomings on the magnesium hysteresis loops modulation.

References

[1.] Barnett, M. R. "Twinning and the ductility of magnesium alloys: Part I:“Tension” twins." Materials Science and Engineering: A 2007, 464.1, 1-7.

[2.] Barnett, M. R. "Twinning and the ductility of magnesium alloys: Part II.“Contraction” twins." Materials Science and Engineering: A 2007, 464.1, 8-16.

[3.] Albinmousa, J.; H. Jahed; S. Lambert, Cyclic behaviour of wrought magnesium alloy under multiaxial load, International Journal of Fatigue 2011, 33, 1127-1139.

[4.] Jiang, Y.; Kurath, P. "A Theoretical Evaluation of the Incremental Plasticity Hardening Algorithms for Cyclic Nonproportional Loadings," ACTA Mechanica 1996, 118, 213-234.

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IC8. Light at the End of the Tunnel

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The frameworks of zeolites and other crystalline microporous oxides, such as aluminophosphates, encompass tetrahedrally coordinated (Si, Al, P) atoms. Materials possessing mixed octahedral-pentahedral-tetrahedral microporous oxide frameworks have been comprehensively studied since the early 1990s, and encompass silicates of Ti, Zr, Nb, V, Cu, Sn, Ca. In the last decade, the constituent elements of heteropolyhedral silicates were extended to lanthanides and, thus, important properties, such as photoluminescence (PL), became available [1].

Inorganic-organic hybrid solids known as coordination polymers or metal-organic frameworks (MOFs) are of considerable interest because the combination of inorganic and organic fragments produces a large number of new crystal architectures allowing the design of solids with specific functions. Only 10% or so of MOFs are effectively microporous, exhibiting zeolite-type behavior, and photoluminescent [2,3]. The combination of porosity and light emission allows the design of intriguing new types of chemical species [4] and temperature sensors [5].

Here, I shall review some of the main achievements in the field of heteropolyhedral silicates in the last fifteen years or so (including light emission [1,6] and release of biological amounts of NO [7]), and draw attention to the enormous potential of MOFs for engineering properties such as photoluminescence [2-5, 8].

References

[1] Ananias, D.; Ferreira, A.; Rocha, J.; Ferreira, P.; Rainho, J. P.; Morais, C.; Carlos, L. D. *J. Am. Chem. Soc.*, **2001**, *123*, 5735.

[2] Rocha, J.; Carlos, L. D.; Paz, F. A. A.; Ananias, D.; *Chem. Soc. Rev.* **2011**, *40*, 926.

[3] Shi, F. N.; Cunha-Silva, L.; Ferreira, R. A. S.; Mafra, L.; Trindade, T.; Carlos, L. D.; Paz, F. A. A.; Rocha, J. *J. Am. Chem. Soc.*, **2008**, *130*, 150.

[4] Harbuzaru, B. V.; Corma, A.; Rey, F.; Atienzar, P.; Jordá, J. L.; García, H.; Ananias, D.; Carlos L. D.; Rocha, J. *Angew. Chem. Int. Ed.*, **2008**, *47*, 1080.

[5] Cadiau, A.; Brites, C. D. S.; Costa, P. M. F. J.; Ferreira, R. A. S.; Rocha, J.; Carlos, L. D. *ACS Nano*, **2013**, ***7***, 7213.

[6] Ananias, D.; Kostova, M.; Paz, F. A. A.; Neto, A. N. C.; DE Mora, R. T.; Malta, O. L.; Carlos, L. D.; Rocha, J. *J. Am. Chem. Soc.*, **2009**, *131*, 8620.

[7] Pinto, M. L.; Rocha, J.; Gomes, J. R. B.; Pires, J. *J. Am. Chem. Soc.*, **2011**, *133*, 6396.

[8] Abdelhameed, R. M.; Carlos, L. D.; Silva, A.; Rocha, J. *Chem. Commun.*, **2013**, *49*, 5019.

Acknowledgements: I thank COMPETE, FEDER and FCT (PEst-C/CTM/LA0011/2013) for funding.

IC9. YAG:Ce^{3+} Photoluminescence Tuned by 1-D Photonic Crystal Microcavity for White Light Generation

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A sol-gel process for the preparation of thick YAG:Ce3+ films was developed and different photonic bandgap (PBG) structures, consisting of a YAG:Ce^{3+} layer embedded within two three-period Bragg mirrors, have been prepared by sol-gel processing, forming Fabry–Perot microcavities whose defect peak position moved from red to green [1]. The refractive index of the deposited YAG films (~ 1.85 @ 633 nm and ~ 1.80 @ 1540 nm) was very close to that of YAG single crystal. Under irradiation of blue Ar^{+} laser light, the typical broad YAG:Ce^{3+} photoluminescence (PL) emission band was drastically narrowed in these samples, with the new position of the modified PL peaks corresponding to the resonance wavelength of each microcavity, while the corresponding colour changes could be easily observed by the human eye. The PL efficiency of the prepared films was strongly related to the degree of YAG phase formation and the rate of YAG phase evolution strongly depended on the film thickness. The adjustable PL range here demonstrated was wide enough to generate white light with color temperatures from warm white (~ 2700 K) to daylight white (~ 5600 K), by mixing the modified PL with light from any common blue Light Emitting Diode (LED) excitation source. This result provides a novel technique to solve the red-deficiency problem in the white LED industry: instead of relying on the development of new phosphors, the well known PL of YAG:Ce^{3+} can be conveniently adjusted by 1-D PBG (or photonic crystal) structures. The current modification technology is based on optical structures, rather than on any specific materials or fabrication processes, thus having good potential for application in white light generation for domestic lighting based on LED lamps.

References

[1] Li, Y.; Almeida, R.M., *J. Phys. D: Appl. Phys.* ***2013***, 46, 165102.

IC10. Metals Based on Neutral Molecular Species: The New Paradigm and its Application to Plastic Electronics

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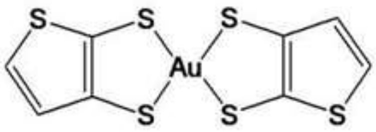
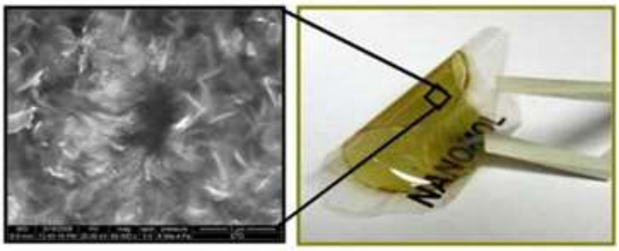
Thanks to continuous and significant reserch efforts during the last decades that a large number of molecule based compounds with electrically conducting properties of metals or even of superconductors are presently known. Until recently all these these molecular conductors were charge transfer salts based on the partial electronic transfer from electronic donor or acceptor molecular species. The metallic properties in these compounds are therefore associated with the formation of partially filled bands of extended networks of electroactive species, upon electronic transfer towards suitable counter ions. However a new paradigm of molecular metals, based on neutral species, emerged during the last decade. In these systems the partially bands associated with the metallic properties are achieved by band overlapping as in elemental semimetals.

In in the first part of this presentation it will be reviewed the contribution of our group to the preparation of what are the still rare examples of metallic systems based on neutral molecules, starting with [Au(α-tpdt)$_2$], the first of such examples[1, 2]. In the last part of the presentation a strategy for the application of these compounds in the preparation of conducting bilayer films suitable for applications in plastic electronics [3] will be described.



Au(α-tpdt)$_2$



References

[1] Belo, D; Alves, H.; Lopes, E. B.; Duarte, M. T.; Gama, V.; Henriques, R. T.; Almeida, M.; Ribera, E.; Rovira, C.; Veciana J. *Chemistry: Eur. J.*, **2001,** *7*, 511.

[2] Nunes, J. P. M.; Figueira, M. J.; Belo, D.; Santos, I. C.; Ribeiro, B.; Lopes, E. B.; Henriques, R.T.; Vidal-Gancedo, J.; Veciana J.; Rovira, C.; Almeida, M. *Chemistry Eur. J.*, **2007**, *13*, 9841.

[3] Laukhina, E.; Lebedev, V.; Laukhin, V.; Pérez Del Pino, A.; Lopes, E. B.; Neves, A. I. S., Belo, D.; Almeida, M.; Veciana, J.; Rovira, C. *Organic Electronics*, **2012**, *13*, 894.

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IC11. Magnetoresistive Sensors: From Industrial to Biomedical Applications

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Magnetoresistive sensors based on spin valve and magnetic tunnel junction stacks are discussed, starting with working principles, biasing techniques, optimized stacks, magnetic annealing procedures, noise limits and sensor architectures. Where necessary, magnetic flux guides or hybrid configurations combining sensors with MEMS structures can be implemented to increase field detectivity or decrease 1/f noise. It is shown that magnetoresistive sensor architectures can be fabricated with field detectivities down to few pT (above 1/f knee) to few tens pT at 1-10 Hz, with controlled field spans, and low coercivities (< 0.1mT). Thermal stability can be tuned in optimized stacks to close to 300C. Applications are discussed including scanning heads for non destructive testing (micro-defect detection in welding joints), for magnetic NP detection in security applications, and for fault detection in IC circuits. Examples for current and power monitoring applications will also be given. In the biochip area, examples are given of static and dynamic lab-on-chip platforms where integrated magnetoresistive sensors detect bio analytes (DNA, proteins, cells) that are labelled with magnetic NPs [1]. These platforms can also provide magnetophoretic separation capability where required. In the neuroelectronics area, magnetoresistive sensors are fabricated in thin Si (down to 50um thick) or polyimide microelectrodes in order to check in vitro (brain slices) or in vivo, magnetic fields generated by single and bundled neurons. Magnetoresistive sensors in proper architectures can also be used to probe NMR/MRI signals in integrated devices, and to monitor the magnetic fields coming out from the heart (magneto cardiography).

References

[1] Spintronic platforms for biomedical applications, Freitas, P.P., Cardoso, F.A., Martins, V.C., et al, Lab On Chip, 12, 546-557 (2012)

IC12. The Versatility of Sol-Gel Processing in Tailoring Silica-Based Materials for Specific Applications

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The sol-gel process is a soft and green synthesis process for producing inorganic, organic or hybrid materials from precursor solutions [1]. The technology is known since the XIX century, but the chemical principles of the sol-gel processing were only clarified in the early 1990s [1]. It has the advantage of an extraordinary versatility that has contributed to broaden the fields of application of sol-gel materials. The products may be in the form of monoliths, powders, particles or films, and their properties may be tailored according to the specific application, just by tuning the processing parameters.

In the present work some examples are given of this unique characteristic of the sol-gel processing regarding silica-based materials, namely:

- the capability of producing extremely light gels (aerogels) under sub critical conditions, either as monoliths, as flexible blankets or as powders, that may be used as high value thermal insulators.
- the capability of producing functionalized nanoparticles, either bulk or hollow (nanocapsules) that may be used as drug vectors for delivery and diagnostics;
- the capability of producing nanocomposite catalysts by encapsulating metal nanoparticles within organically modified silica gels (ORMOSILs), with extremely high stereoselectivity and yield;
- the capability of producing superhydrophobic films that may be used as anti-wetting or anti-icing coatings.

References

[1] C. J. Brinker, G. W. Scherer, *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing,* Academic Press Inc, San Diego, USA, 1990.

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IC13. Self-Directed Assembly in Non-Bridged Silsesquioxanes

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In recent years the combination of sol-gel chemistry [1] with self-directed assembly (SDA) [2] has attracted considerable interest for the development of hierarchically structured ordered silsesquioxane hybrids [3] (mainly bridged [2,4,5]) exhibiting a wide range of morphologies and tunable properties. SDA operates in the absence of a template and is governed by weak interactions, such as van der Waals interactions solely or van der Waals and hydrogen bonding interactions simultaneously. In the latter situation the cross-links that bond the organic components to the inorganic counterparts include a functional group comprising hydrogen donor and hydrogen acceptor moieties (typically a urea, an amide or a urethane group).

The first organized non-bridged silsesquioxane incorporating cross-links obtained via SDA was a complex hierarchically structured lamellar bilayer hybrid (named mono-amidosil) obtained from a mono-amide cross-linked *n*-alkyltriethoxysilane [6]. This material (m-A(14), where 14 represents the number of CH_2 repeat units) is a photoluminescent bilayered suprastructure displaying nanoscopic sensitivity. In m-A(14) the self-assembly driving forces determine the emergence of a thermally-actuated optical memory effect induced by the reversible order/disorder phase transition of the alkyl chains. The recovery of the emission energy is time-dependent.

The investigation of the shorter chain analogue mono-amidosil AC-m-A(8) (where AC stands for acid catalysis) with water-mediated tunable structure followed [7]. Hierarchically structured lamellar bilayer mono-urethane cross-linked alkyl/siloxanes (mono-urethanesils, m-Ut(Y)-ac with Y = 14, 16 and 22, where Y is the number of CH_2 repeat units and ac represents acid catalysis) displaying intricate morphologies mimicking cabbage leaves or the desert rose were also developed [8]. More recently lamellar m-A(14)-based mono-amidosil hybrids incorporating K^+ [9], Mg^{2+} [9] and Eu^{3+} [9,10] ions and exhibiting textures that resemble cabbage leaves, foliated schist and sea sponges, respectively, were produced. Lamellar m-A(14)-based materials doped with monomethinecyanine dyes were also obtained [11].

References

[1] Brinker, C. J.; Scherer, G. W. *Sol-gel Science: The Physics and Chemistry of Sol-Gel Processing,* Academic Press, San Diego, CA, 1990.

[2] Moreau, J. J. E.; Vellutini, L.; Wong Chi Man, M.; Bied, C.; Bantignies, J.-L.; Dieudonné, P.; Sauvajol, J.-L. *J. Am. Chem. Soc*. **2001**, *123*, 7957-7958.

[3] Gomez-Romero, P.; Sanchez, C. *Functional Hybrid Materials*, Wiley Interscience, New York, 2003.

[4] Moreau, J. J. E.; Vellutini, L.; Wong Chi Man, M.; Bied, C. *Chem. Eur. J.* **2003**, *9*, 1594-1599.

[5] Moreau, J. J. E.; Pichon, B. P.; Wong Chi Man, M.; Bied, C.; Pritzkow, H.; Bantignies, J.-L.; Dieudonné, P.; Sauvajol, J.-L. *Angew. Chem. Int. Ed.* **2004**, *43*, 20 3-206.

[6] Carlos, L. D.; de Zea Bermudez, V.; Amaral, V. S.; Nunes, S. C.; Silva, N. J. O.; Ferreira, R. A. S.; Santilli, C. V.; Ostrovskii, D.; Rocha, J. *Adv. Mater*. **2007**, *19*, 341-348.

[7] Nunes, S. C.; Silva, N. J. O.; Hümmer, J.; Ferreira, R. A. S.; Almeida, P.; Carlos, L. D.; de Zea Bermudez, V. *RSC Adv*. **2012**, *2*, 2087-2099.

[8] Fernandes, M.; Cattöen, X.; Ferreira, R.A.S.; Carlos, L.D.; Wong Chi Man, M.; de Zea Bermudez, V. *J. Sol-Gel Sci. & Tech.* **2013**, *65*, 61-73.

[9] Nunes,S.C.; Ferreira,R.A.S.; Carlos,L.D.; Almeida,P.; de Zea Bermudez, V. *J. Phys. Chem. B* **2013**, *117*, 14529-14543.

[10] Nunes, S. C.; Planelles-Aragó, José; Ferreira, R. A. S.; Carlos, L. D.; de Zea Bermudez, V. *Eur. J. Inorg. Chem.* **2010**, *18*, 2688-2699.

[11] Nunes, S. C.; Ferreira, C. B.; Hümmer, J.; Ferreira, R. A. S.; Carlos, L. D.; Almeida, P.; de Zea Bermudez, V. *J. Mater. Chem. C* **2013**, *1*, 2290–2301.

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IC14. Thin Film Transistors Based on Metal Oxide Semiconductor Thin Films and Nanoparticles

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Metal oxide conductors/semiconductors exhibit an intriguing combination of high optical transparency, high electron mobility, and in some cases amorphous microstructures.

Transparent electronics has arrived and is contributing for generating a free real state electronics that is able to add new electronic functionalities onto surfaces, which currently are not used in this manner and where silicon cannot contribute [1]. The already high performance developed n- and p-type TFTs have been processed by physical vapour deposition (PVD) techniques like rf magnetron sputtering at room temperature which is already compatible with the use of low cost and flexible substrates (polymers, cellulose paper, among others). Besides that a tremendous development is coming through solution-based technologies very exciting for ink-jet printing, where the theoretical limitations are becoming practical evidences. In this presentation we will review some of the most promising new technologies for n- and p-type thin film transistors based on oxide semiconductors either in the form of thin films or nanoparticles.

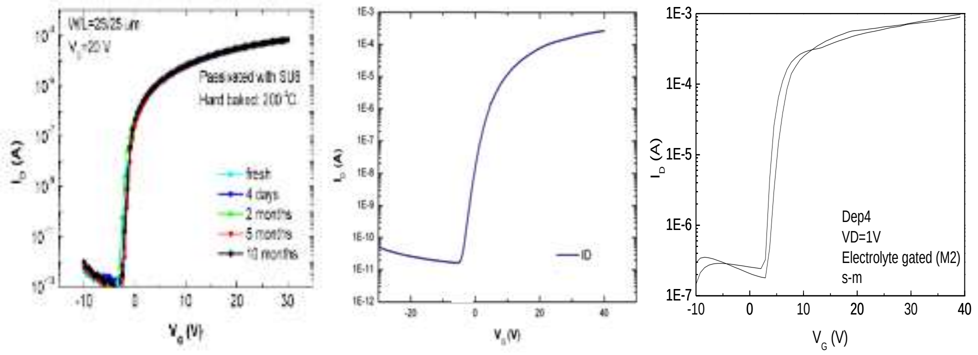

Figure 1. a) GIZO TFT produced by rf sputtering at room temperature; b) GZTO TFT produced by combustion synthesis at 250 °C; c) Electrolyte-gated TFT based ZnO nanoparticles annealed at 250 °C.

References

[1] E. Fortunato, P. Barquinha, and R. Martins, "Oxide Semiconductor Thin-Film Transistors: A Review of Recent Advances," Advanced Materials, vol. 24, pp. 2945-2986, Jun 2012.

Acknowledgements: This work was funded by the Portuguese Science Foundation (FCT-MEC) through the projects EXCL/CTM-NAN/0201/2012 and PEst-C/CTM/LA0025/2013-14, and the European projects: ERC 2008 Advanced Grant (INVISIBLE contract number 228144), ORAMA CP-IP 246334-2 and POINTS NMP 263042.

IC15. Chemical Routes for Coatings by Design. From "Paint and Heat" to Today.

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Issued from the development of thin films and in relation with the continuous reduction in size of electronic systems and smart devices, multifunctional nanostructures face today very challenging questions in materials science: ultimate size reduction, integration of heterogeneous functions, system characterisation or process control at an atomic scale.

We present here different studies devoted to solid state oxide systems, where in a privileged direction the atomic organisation decreases down to a few nanometers. These systems are primarily containing functional oxides for active devices, read-write memories, storage memories, optoelectronics or photovoltaics. Indeed, as soon as dimensions of a system become lower than a characteristic dimension of a physical phenomenon, very original physical phenomena can occur; they are particularly enhanced in multi-layers or superlattices, nanowires or dots, where strain, surfaces and interfaces play a crucial role and can tune the physical properties.

We approach these phenomena by using MOCVD and combined chemical routes for the synthesis and present in this study specific considerations on the synthesis techniques and the growth conditions used to design complex 3D, 2D and 1D smart structures.

Selected case studies will finally be presented, illustrating the powerful development of different oxide nanostructures based on superconducting oxides (YBa2Cu3O7..), dielectric or ferroelectric oxides (Pb(Zr1-xTix)O3, BaTiO3/SrTiO3..), manganites and nickelates, as well as smart films or nanowires for photonic or photovoltaic devices.

Oral Communications

OC1. Electrospun Nanofiber Based Scaffold Platform for Stem Cell Alignment

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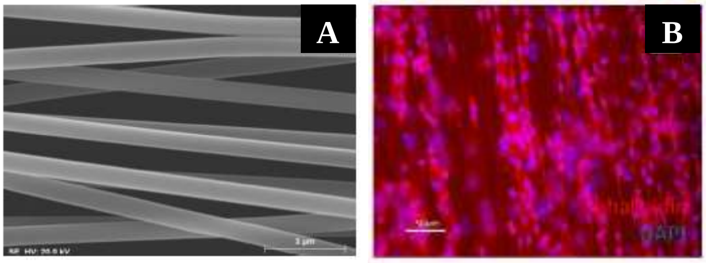
Stem cells (SCs) hold great potential for several regenerative therapies. However, SCs are anchorage dependent, requiring large surface areas with appropriate topology for cultivation in clinically relevant numbers. An interesting system for mimicking the natural niche where SCs inhabit is the use of electrospun fibers with diameters of 200-500nm (the dimensions of niche fibrous proteins, such as collagen I and III), which can provide the mechanical properties and high contact areas required for cell adhesion.[1] The electrospinning technique is a simple and convenient electrostatic force-driven approach to draw polymer fibers of sub-micrometer diameters, with controllable bulk network properties (chemical structure, phase behavior, morphology, thermal and mechanical properties) and surface properties (composition, topography and surface hydrophilicity/hydrophobicity). According with the collector system used, nanofibers can also be produced aligned or randomly oriented.[2] The use of aligned fibers as polymeric scaffolds to confer anisotropy to stem cell organization is particularly interesting for applications envisaging regeneration of skeletal muscle and neuronal tissue, using respectively mesenchymal stem cells and neural stem cells. Results for both systems will be presented.

Figure 1. SEM image of the fibers (A) and neuronal stem cells cultivated in the fibers



functionalized with laminin, an adhesion protein (B).

References

[1] Lim S. H.; Mao H. Q. *Adv Drug Deliv Rev*, **2009**, 61(12), 1084-1096
[2] Monteiro, B. J.C. ; Guerreiro, J. D. T. ; dos Santos, F. ; Cabral, J.S.M.; da Silva, C. L. ; Ferreira, F. C., *2013 IEEE 3rd Portuguese Meeting in Bioengineering*, **2013** 1-6.

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OC2. Computational modelling of the compressive behaviour of CNT-reinforced aluminium composites

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This paper presents a Molecular Dynamics (MD) study on the characterization of the compressive behavior of an aluminium (Al) material reinforced with carbon nanotubes (CNTs). Firstly, a detailed literature review of recent experimental and numerical works dedicated to the characterization and mechanical enhancement of CNT-Al composites is presented. Then, the paper describes a computational approach based on MD simulations used to analyze the mechanical behavior of the CNT-Al composite material under compression. Finally, the paper presents and discusses several results that comprise (i) curves relating the energies (total, Al, CNT, interface) with the imposed axial shortening displacement, (ii) plots of deformed shapes and failure modes of CNT-Al specimen and (iii) curves relating the acting stress with the imposed strain. In this study, we adopted two limit cases for bonding between the CNT and Al matrix, one in which the displacements are imposed to the Al atoms (case A) and another in which displacements are imposed to both Al and C atoms (case B). In comparison with pure Al, the Young's modulus increases about 50% in case A and 100% in case B. These increases are not only due to the CNT intrinsic stiffness but also to the interface slip stresses, which are about 16 MPa (case A) and 75 MPa (case B). In opposition, it is seen that both yield stress and yield strain do not increase. This evidence is mostly due to premature failure of the CNT-Al composite due to CNT local buckling. This study not only confirms previous results obtained by other researchers but also provides some understanding on the compressive behavior of CNT-based composites, which might be different to standard tensile behavior.

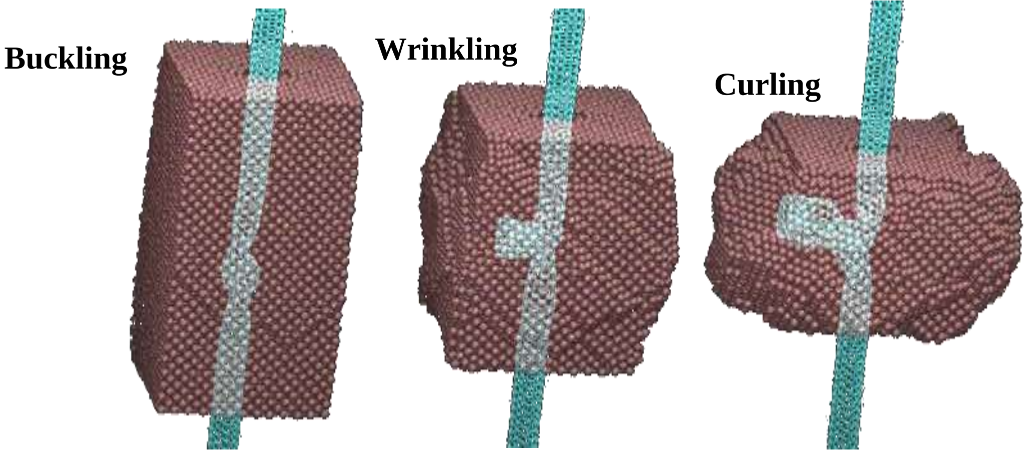

Figure 1. Deformed configurations of CNT-reinforced aluminium sample.

OC3. Free Standing Graphene Synthesis Using Microwave Plasmas

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Presently, the outstanding capabilities of plasma-based nanofabrication tools and processes are widely accepted. Many applications rely on the plasma ability to break down complex molecules, because plasma systems provide simultaneously high temperatures and a highly reactive environment that is a source of many long lived active particles, which may strongly influence the assembly pathways across different temporal and space scales, including the atomic ones. In this way, the remarkable potential of plasmas permits to implement singular assembly pathways and unique atomic-level arrangements of nanostructures.

In the present work, microwave atmospheric plasmas have been used to generate self-standing graphene sheets at atmospheric pressure conditions. The method is based on sending vaporized molecules containing carbon through a microwave argon plasma environment, where decomposition of the molecules takes place and carbon atoms are created. Gas-phase carbon atoms diffuse into colder plasma zones both in the radial and axial directions, and as a result gas-phase carbon is transformed into solid carbon.[1]A part of the solid carbon is deposited on the discharge tube wall while the main part is gradually withdrawn from the hot region of the plasma in the outlet gas stream, where graphene sheets are assembled. Since the temperature of the outlet stream is a key parameter for the nucleation and growth processes, externally forced heating has been applied in this zone to control the thermodynamic conditions there[2]. The synthesized graphene sheets have been analyzed by Raman spectroscopy, scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM) and X-ray photoelectron spectroscopy (XPS). The synthesized graphene sheets are stable and highly ordered. The sheets disorder can be reduced/increased by increasing/decreasing the gas temperature in the outlet plasma stream. This control can be done by changing the microwave power or/and the externally forced heating of the nucleation zone. The obtained sheets exhibit a structural quality comparable to that of existing graphene materials, but they are synthesized here without the need of metal or crystal substrates. The microwave plasma-based method developed is a single step method at ambiance conditions that does not require transient metals and complex processing conditions.The results demonstrate that this method paves a reliable, versatile way toward scalable production of graphene structures for numerous applications.

References

[1] Tsyganov, D.; Bundaleska, N.; Tatarova, E.; and C.M. Ferreira, *Int. J. Hydrogen Energy* **2013**, *38*, 14512-14530.

[2] Tatarova, E.; Henriques, J.; Luhrs, C.C. ; Dias, A.; Phillips, J.; Abrashev, M.V. and C. M. Ferreira, *Appl. Phys. Lett*. **2013,** *103*, 134101-5.

OC4. New Thermoelectric Materials: The Disorder Paradigm

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The expected future energy demands strongly induce the development of new and optimized green energy sources. A huge potential energy source is the waste heat, which drive the development of high-performance thermoelectric materials that can directly convert such heat in electrical energy. The need to obtain high efficiency thermoelectric materials has recently leaded to new approaches for their development. The decrease of the thermal conductivity has been one of the main issues to increase the thermoelectric figure of merit of a material, zT. Disorder can play an important role on the thermal conductivity decrease, as it allows an effective scattering of a significant part of the phonon spectrum.

Herein we present how disorder, from nano to atomic scale, can be used to increase zT. Special emphasis will be made on chalcogenide glasses, which present some of the lowest thermal conductivities observed. The challenges of using chalcogenide glasses for thermoelectrics will be examined. The possibility for enhance the thermoelectric performance on chalcogenide-based glass-ceramics will be also discussed.

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OC5. Highly Photostable Fluorescent Silica Particles for Laser Scanning Imaging Applications

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We describe the preparation of two types of fluorescent silica particles for application in laser scanning confocal microscopy (LSCM), one emitting in the visible and the other in the near infrared (NIR) region of the spectrum.[1] The particles were prepared by incorporating modified perylenediimide (PDI) dyes (containing alkoxysilane groups) onto the silica nanostructure, with different diameter (30 – 300 nm) and low size dispersity. One of the dyes (PDIvis) can be excited at 488 nm (argon laser) and used for imaging at wavelengths in the green,[2,3] while the other (PDInir) can be excited in the red (for example, at 633 nm, using an HeNe laser) and emits in the NIR.[1] Silica particles containing these dyes, SiP-PDIvis and SiP-PDInir respectively, were efficiently internalized in HEK293 cells with low toxicity, showing very good potential for use as a platform for *in vivo* bioimaging applications. The NIR emitting particles in particular can be used even in cells expressing high levels of fluorescent proteins and/or co-stained with different fluorescent dyes, both of which commonly emit at wavelengths lower than the NIR. The *in vivo* photostability of the fluorescent particles during laser scanning is much higher than that of usual commercial dyes.

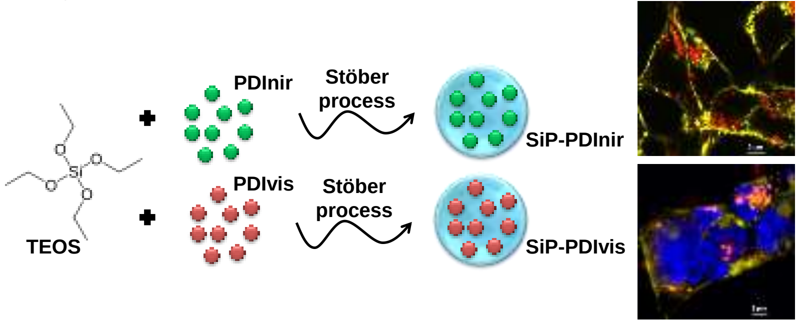

Figure 1. Incorporation of PDI derivatives in silica nanoparticles (SiNPs) network during synthesis by a modified Stöber method. LSCM images of HEK293 cells with internalized silica particles appearing in the cytosol (red). SiNP-PDInir were excited at 633 nm (up) and SiNP-PDIvis were excited at 488 nm (bottom).

References

[1] Ribeiro, T.; Raja, S.; Rodrigues, A. S.; Fernandes, F.; Farinha, J. P. S.; Baleizão, C. *RSC Advances* **2013**, *3*, 9171-9174.
[2] Ribeiro, T.; Baleizão, C.; Farinha, J. P. S. *J. Phys. Chem. C* **2009**, *113*, 18082-18090.
[3] Rodrigues, A. S.; Ribeiro, T.; Fernandes, F.; Farinha, J. P. S.; Baleizão, C. *Microscopy and Microanalysis* **2013**, *19*, 1216-1221.

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OC6. Large Fluorescence Enhancements of Phthalocyanine in (Lipid Bilayer)-Polyelectrolyte Coated Gold Nanoparticles

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Fluorescence enhancement by plasmonic nanoparticles is an appealing way to improve the detection of fluorescent molecules, e.g. for imaging and sensing applications. The enhancement factor depends on specific features of the molecule-nanoparticle assembly, such as spectral overlap, distance and relative orientation, etc. Many reports have contributed to a better understanding of this phenomenon, in particular experiments of single-molecule and single-particle microscopy.[1,2] The maximum enhancements reported in those studies were, respectively, 8- and 20-fold increase in detected emission. Since then, larger enhancements in the order of thousands have been achieved with bowtie nanoantennas [3] or nanorods.[4]

In this contribution, we report on large fluorescent enhancements, also in the order of thousands, obtained in small gold nanoparticle clusters assembled with layer-by-layer polyelectrolyte coating. The fluorescent molecule, a phthalocyanine, was incorporated in a lipid bilayer surrounding the gold nanoparticles. The distance between the gold nanoparticles and the lipid bilayer containing the phthalocyanine was tuned by increasing the number of polyelectrolyte layers in between them. Fluorescence lifetime imaging microscopy revealed that an optimum number of polyelectrolyte layers was needed to obtain a maximum fluorescence enhancement. On the other hand, the fluorescence lifetime distribution shifts progressively to longer lifetimes, as the number of separating polyelectrolyte layer increases. These results will be compared to those of a previous study, in which the gold nanoparticles were first immobilized on a surface and then coated with polyelectrolyte layers before phthalocyanine deposition.[5]

References

[1] Anger, P.; Bharadwaj, P.; Novotny, L. *Phys. Rev. Lett.* **2006**, *96*, 113002-4.

[2] Kühn, S.; Håkanson, U.; Rogobete, L.; Sandoghdar, V. *Phys. Rev. Lett.* **2006**, *97*, 017402-4.

[3] Kinkhabwala, A.; Yu, Z.; Fan, S. et al. *Nature Photon.* **2009**, *3*, 654-657.

[4] Yuan, H.; Khatua, S.; Zijlstra, P. et al. *Angew. Chem. Int. Ed.* **2013**, *52*, 1217-1221.

[5] Teixeira, R.; Paulo, P. M. R.; Viana, A. S.; Costa, S. M. B. *J. Phys. Chem. C* **2011**, *115*, 24674-24680.

Acknowledgements: The authors acknowledge Fundação para a Ciência e a Tecnologia for financial support through the Projects REEQ/115/QUI/2005 and PEst-OE/QUI/UI0100/2011 (Portugal). P.M.R.P. acknowledges Program Ciência 2008.

OC7. Exciton dynamics in organic materials: high quantum efficiency in charge-transfer interfaces

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With the widespread use of organic materials in photonic applications, such as solar cells, photodiodes and light-emitting devices, interfacial excitonic processes are under the spotlight of materials R&D. Complete understanding of exciton generation, diffusion, separation and recombination in bilayer or bulk heterojunction (BHJ) devices is challenging, since it implies precise knowledge of several key-factors: structure, interfacial morphology and electronic structure landscape across the heterojunction [1].

Our work focuses on fabricating devices based on bilayer charge-transfer interfaces with long-range order, using single-crystals (SCs) of organic semiconductors. In 5,6,11,12-tetraphenyltetracene/tetracyanoquinodimethane (rubrene/TCNQ) SC interfaces fabricated via lamination, a high quantum efficiency has been measured [2], with responsivity values reaching ~1 A/W between 400-550 nm. Photocurrent generation has been attributed to the separation of rubrene excitons at the rubrene/TCNQ junction, enhanced by interfacial band-bending and polarization [3]. In a related study on SC rubrene/PCBM film interfaces [4], it was found that photocurrent arises from the separation of both donor (rubrene) and acceptor (PCBM) excitons, yielding a very high responsivity over 400-700 nm.

These studies highlight the overwhelming importance of structure to charge-separation and collection, by exploring the enhanced transport properties and large exciton diffusion length found in single-crystals. An alternative way to photocurrent enhancement is also presented, by taking full advantage of excitons formed in the donor material.

References

[1] Brédas, J.L.; Norton, J. E.; Cornil, J.; Coropceanu, V. *Acc. Chem. Res.* **2009**, *42*, 1691-1699.
[2] Alves, H.; Pinto, R. M.; Maçôas, E. M. *Nat. Commun.* **2013**, *4*, 1842.
[3] Pinto, R. M. *J. Phys. Chem. C* **2013**, submitted.
[4] Pinto, R. M.; Maçôas, E. M. S.; Alves, H. *J. Mater. Chem. C* **2013**, submitted.

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OC8. Silicon Probes as Biosensors for Intra- and Extracellular Measurement of pH for Early Detection of Dysplasia

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Early detection of cancer is one of the most important steps for an effective treatment. Dysplasia is the medical term to describe an abnormality in cellular growth and can be considered a prelude to cancer. One of the possible markers that can be used to aid in the detection of dysplasia is the measurement of intra- and extracellular pH. Evidences show a relation between pH and the development stage of a malign tumour, denoted by an increase of fermentation as a result of a cellular metabolism increase [2].

In this work, pH potentiometric biosensors based on Silicon wet etching technology are developed. Silicon pyramidal structures with nanometric tips are envisioned to penetrate the cell membrane, thus being able to directly measure the intracellular pH through the selective layer (pH sensitive thin film). This process involves mask patterning through optical lithography to define the pyramid base on {100} Silicon wafers. The shape of the Si tip is determinant for the integrability, not only because it must be compatible with cell addressing (nanometric tip) but also because the subsequent microfabrication steps require structure profiles compatible with resist coating, and good step coverage for metal and insulation material deposition. Therefore, a systematic study of the conditions for the Si anisotropic etching was done, using aqueous solutions based on KOH and IPA, aiming a perfect control of the silicon pyramid edges. By controlling the etching time, temperature, and relative chemical concentrations during wet etch, the same pattern defined in resist can produce Si pyramids with various profiles, in well reproducible ways.

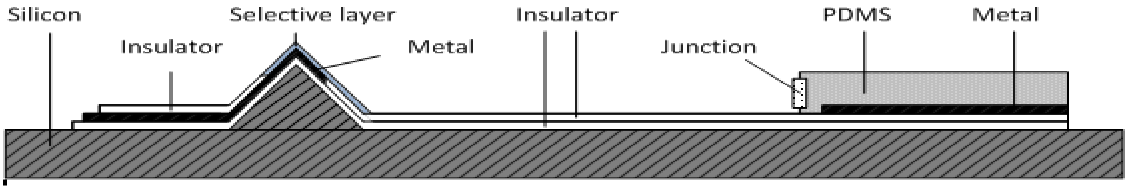

Figure 1. View of the schematic model for the pH microbiosensor.

References

[1] Zhang, X.; Lin, Y.; Gillies, R. J. *Journal of Nuclear Medicine* **2010,** *51*, 1167-1170.

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OC9. Bio-MOFs as Potential Drug Delivery Materials. A New Approach to Traditional MOFs

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Metal-organic frameworks (MOFs) have been attracting a great attention due to their versatility and wide range of applications. They are among the most exciting, high-profile developments in nanotechnology in the last ten years but only very recently their application across biology and medicine began to be studied.[1] The interplay between metal connectivity, and the denticity and geometry of the ligand determines the framework structure and tunes the pore size, making MOFs suitable candidates in applications of drug storage and delivery. The ability to engineer controlled localized delivery of drugs might both contribute to the efficiency of the treatment and reduce side effects, a major challenge in the new family of "bio-inspired" metal organic frameworks, BioMOFs.[1,2] We are particularly interested in BioMOFs for drug storage and delivery obtained by direct coupling of active pharmaceutical ingredients (linkers) to non-toxic (or low toxicity) metals.

Norfloxacin and pipemidic acid are antibacterial drugs that effectively inhibit DNA replication.[3] The activity of these quinolones can be improved by exploring their coordination to metals that can promote a synergetic effect. Several organometallic bismuth compounds are used in bactericidal and fungicidal applications and therefore Bi was chosen as a promising candidate for our studies with norfloxacin and pipemidic acid.[4,5] Mechanosynthesis yielded novel Bi compounds using norfloxacin and pipemidic acid as linkers, and also the introduction of pyridinic fragments as second linkers into these systems was successful. Also K, Cs and Rb reveal promising results.

References

[1] C. Janiak, J. K. Vieth, *New Journal of Chemistry* **2010**, *34*, 2366-2388.

[2] S. Keskin, S. Kizilel, *Industrial & Engineering Chemistry Research* **2011**, *50*, 1799-1812; P. Horcajada, R. Gref, T. Baati, P. K. Allan, G. Maurin, P. Couvreur, G. Ferey, R. E. Morris, C. Serre, *Chemical Reviews* **2012**, *112*, 1232-1268; A. C. McKinlay, R. E. Morris, P. Horcajada, G. Ferey, R. Gref, P. Couvreur, C. Serre, *Angewandte Chemie-International Edition* **2010**, *49*, 6260-6266.

[3] E. K. Efthimiadou, G. Psomas, Y. Sanakis, N. Katsaros, A. Karaliota, *Journal of Inorganic Biochemistry* **2007**, *101*, 525-535.

[4] P. Domenico, L. Baldassarri, P. E. Schoch, K. Kaehler, M. Sasatsu, B. A. Cunha, *Antimicrobial Agents and Chemotherapy* **2001**, *45*, 1417-1421.

[5] F. H. Allen, *Acta Cryst*. **2002**, B58, 380-388.

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OC10. Electrodeposition of Dendritic Transition Metal Films and their Application as Electrodes for Supercapacitors

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The development of electric energy storage devices with high energy density and fast charge-discharge ability has become one of the most challenging research areas in a wide range of applications such as electrical vehicles, back-up power sources and energy storage for renewable energy. In this context, electrochemical supercapacitors are attracting great attention due to their increased power density and lifetime span. However, these devices still lack energy density, a drawback that can be overcome by the development of new electrode materials with optimal properties. For the production of these electrodes, electrodeposition presents itself as a versatile process that allows fine-tuning of the film morphology and chemical composition.

In the present work, transition metal nanostructured films were produced via electrodeposition in order to form a porous dendritic structure with enhanced surface area. Their morphology and chemical composition was related to the electrolyte solution composition and electrodeposition parameters (deposition time and applied current density). Furthermore, the electrochemical behavior of the films was studied by cyclic voltammetry and chronopotentiometry in order to assess their application as electrodes for supercapacitors.

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OC11. Synthesis of cross-linkable P3HT Derivatives and Applications in Photovoltaic Cells

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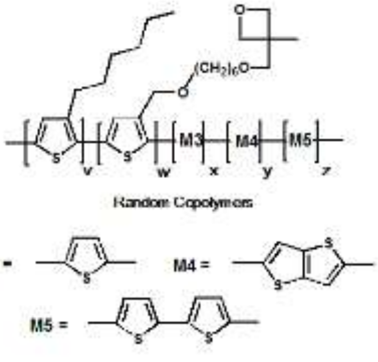
Poly(3-hexylthiophene) (P3HT) represents one of the most promising polymers for applications in efficient Organic Photovoltaic Cells (OPVs) - it was the first polymer where significant power-conversion efficiencies (PCE) were demonstrated for bulk heterojunction (BHJ) cells with [6,6]-phenyl-C61-butyric acid methyl ester (PC60BM) as electron-accepting material [1]. Since the «discovery» of OPV cells with reasonably high efficiencies, the progress in the field has been mainly due to modifications in polymer molecular design towards optimal optoelectronic properties, and control of morphological details of the active/organic layer. The cells efficiency, approaching 10 %, and device stability over time, are key issues for OPV cells entering the market.

Here, we present the synthesis, and thermal, optical, and electrochemical characterization and a series of new cross-linkable P3HT derivatives containing oxetane-functionalized lateral chains as the cross-linkable moieties (Scheme 1) [2].



Scheme 1. General formula of the new synthesised P3HT derivatives.

We investigate the applications of these copolymers, both in the soluble and in the cross-linked form, in BHJ photovoltaic devices. In particular, we demonstrate an overall improvement of cells stability upon cross-linking of the copolymers.

References

[1] Ma, W.; Yang, C.; Gong, X.; Lee, K.; Heeger, A. J. *Adv. Funct. Mater.* 2005 *15*, 1617.
[2] Brotas, G.; Farinhas, J.; Ferreira, Q.; Rodrigues, R.; Martins, I.N.; Morgado, J.; Charas, A. *J. Polym. Sci.: Polym. Chem.*, submitted.

Acknowledgements: This work was partially financed by FCT-Portugal (contracts no. PEst-OE/EEI/LA0008/2013 and PTDC/CTM/111263/2009. FCT is also acknowledged for the PhD grant of GB (SFRH/BD/62130/2009).

OC12. Current-Induced Magnetization Switching in a Single Ferromagnetic Element

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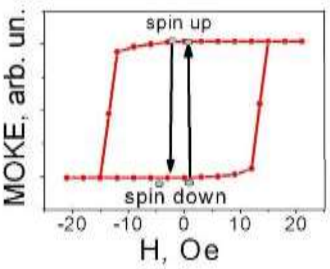

Current-induced magnetization switching (CIMS) is achieved generally – via spin transfer torques – either in engineered semiconductor materials doped by magnetic species [1] or in stacks of ultrathin magnetic and nonmagnetic layers patterned into the deep submicron regime [2]. The “spin-transfer” process opens up the possibility of new nanoscale devices for memory and other spin electronics applications.

We observe the CIMS in a single thick (up to 100 nm) Fe layer. The CIMS process is observable with magneto-optic Kerr effect (MOKE) (shown in the figure) *in situ* under current densities of j_e~±10^8 A/cm^2. We find that the dependence of the CIMS rate on j_e is an essentially nonmonotonous function – with, at least, two sharp maxima occurring at both polarities of the current. It is interesting that the CIMS rate can be improved (up to ~100 %) by irradiation of the films by femtosecond laser with a fluence of ~0.3 J/cm^2. To find a plausible explanation for the observed CIMS, we performed the Rutherford backscattering analysis of the film composition. These studies have revealed that the films are strongly oxidized through the whole film depth. Amongst various iron oxides, the noncentrosymmetric structures, e.g., γ-Fe_2O_3, are well known and the sizable spin-orbit effects are feasible in them. [3] The occurrence of such iron oxides phases in our samples is confirmed by their x-ray diffraction analysis. Due to spin-orbit coupling, inclusions of these phases generate spin-polarized electrons that are injected into grains of strong ferromagnets (α-Fe), and trigger the CIMS process via s-d exchange.

References

[1] Chernyshov, A.; et al.; *Nature Phys*. **2009**, *5*, 656–659.
[2] Miron, I. M.; et al.; *Nature* **2011**, *476*, 189-194.
[3] Dresselhaus G., *Phys. Rev*. **1955**, *100*, 580-586.

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OC13. X-ray MicroCT: Non-Destructive Tool for Material Characterization in Art and Science

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The X-ray microtomography has its roots in Computerized Axial Tomography (CAT) scans that have been used for medical imaging for several decades. CAT scans were an extension of conventional radiography projection, a technique that can produce a two-dimensional image of an object's internal structure. In these images, different compositional or microstructural features can be identified given that they have enough contrast in X-ray attenuation. The problem with the technique is that these features can only be located within the two-dimensional plane of the image. The position of any other features of interest cannot be located out of the image plane. Furthermore, a 2D radiograph image presents us only with average X-ray absorption through the object's out-of-plane dimension. A feature may be completely missed out because it may be overlapped with other competing features along the penetration path. (Micro)CT scans solve these problems by combining information from a series of radiographs recorded as the object is being rotated around a single axis (e.g. SkyScan 1172 model). Using mathematical algorithms, this series of images is reconstructed to produce a series of 2D "slices" (256 gray level image). Each voxel (volume element or 3D pixel) represents the X-ray attenuation, which is dependent on the material density. With recent software and hardware advances, 3D images can be easily obtained combining reconstructed gray images or segmented ones. Specialized analysis software also enables us to determine several 2D and 3D parameters. In this work we present several study cases that were conducted by our work team. We present some of the main advantages of this nondestructive methodology, as well some of its limitations.

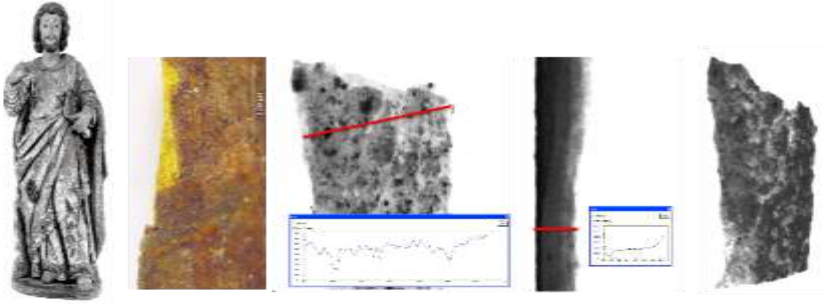

Figure 1. Sculpture of St. Joseph, XVI century, Museum of Aveiro. Gilded polychrome sample PT-SSJ-MA (Gilt Teller Project) bellonging to the lower part of the mantle. Microtomographic images (gray images): selected radiographs (red line attenuation profile) and 3D view (right).

References

[1] M. F.C. Pereira et al.; InArt2013, International Conference, Évora, 10-13th of July 2013

Acknowledgements: The authors acknowledge FCT financing for PEst-OE/CTE/UI0098/2011, PEst-C/EQB/LA0006/2011 and PTDC/EAT-EAT/116700/2010.

OC14. Raman Spectroscopy, XPS and XRD of Ferroelectric Domains in Pulsed Laser Deposited $Na_{0.5}K_{0.5}NbO_3$ Films

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Thin films of NKN ($Na_{0.5}K_{0.5}NbO_3$), produced by laser ablation of stoichiometric ceramic targets, have shown an increase of polycrystalline structure and increase in ferroelectric quality, when the substrate temperature is raised from room temperature up to 600 ºC. However, increasing loss of Na and K might occur. Alcali deficiency, a common problem in different deposition methods of NKN thin films, has been quantified by several methods. XPS analysis, using Mg Kα line, confirmed the loss of alcali atoms at deposition temperatures beyond 400 ºC. The analysis takes the intensities of the Na 1s peak at 1071.0 eV, the K 2p doublet with the -$2p_{3/2}$ peak at 293.4 eV, and the Nd 3d doublet with -$3d_{5/2}$ peak at 206.0 eV into account. Considering the charge states, suggests that excess of Nb and O might be present in the form of NbO_2.

Detailed information of the morphology and structure of the films was obtained from confocal Raman spectroscopy. The lateral resolution allowed us to scan domains with submicron precision. The change in film structure observed by SEM is accompanied by a shift of the Nb-O-octaeder stretching mode at an energy of 615 cm^{-1} , suggesting a change in internal stress of the films. Two further strong peaks [1] present in the ceramic NKN targets at 260 cm^{-1} and 852 cm^{-1}, are either low in intensity in the films or they do not change position. These results are correlated with XRD diffraction data to identify the possible content of non-stoichiometric NKN components.

[1] K. Kakimoto, K. Akao, Y. Guo and H. Ohsato, Raman Scattering Study of Piezoelectric $(Na_{0.5}K_{0.5})NbO_3$-$LiNbO_3$ Ceramics, Jpn. J. Appl. Phys. 44 (2005) pp. 7064-7067.

OC15. Sub-Micron Tailoring of Bi-Soft Segment Asymmetric Polyurethane Membrane Surfaces with Enhanced Hemocompatibility Properties

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Enhancement of membrane hemocompatibility is achieve through the control of the surface morphology. Bi-soft segment integrally skinned poly(estter urethane urea) (PEUU) membranes containing polycaprolactone (PCL) as a second soft segment are synthesized with PCL-diol ranging from 0% to 15% (w/w).

Scanning electron microscopy and atomic force microscopy characterized membrane asymmetry and sub-micron roughnessess, Ra, of top dense surfaces as major assets to the development of platelet/membrane surface interactions.

Here we show that the top dense surfaces of asymmetric PEUU membranes can be tailored with different morphologies when the ratio of the two soft segments PPO/PCL varies. A strong correlation between the top surface roughnesses, Ra, and platelet deposition is identified. The membrane with 15% (w/w) of PCL-diol, PEUU 85, shows the smoothest top dense layer with a Ra as low as 1 nm, which is 5 times below the characteristic value of the PEUU membrane with a single soft segment. The PEUU 85 asymmetric membrane displayed minimal platelet deposition and inhibition of extreme stages of platelet activation.

Poster Communications

P1. Magnetic Anisotropy in Py Thin Films Grown on Holographic Relief Gratings

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Magnonic crystals (MCs) are artificial ferromagnetic micro- or nanostructures with a periodic lateral contrast in the magnetization profile. Such metamaterials currently offer the perspective of magnetic field devices in which spin-wave phenomenon is controled to process information. Lithography is the group of techniques most commonly used to fabricate MCs [1]. These tools allow to tailor high-quality magnetic structures with precisely controlled nano-sized features. Despite the advantages of techniques such as electron beam lithography or focused ion beam, both process optimization and preparing large area samples are time consuming. Therefore alternative routes to produce MCs as template-assisted growth [1, 2] and direct laser patterning [3] have been explored during recent years.

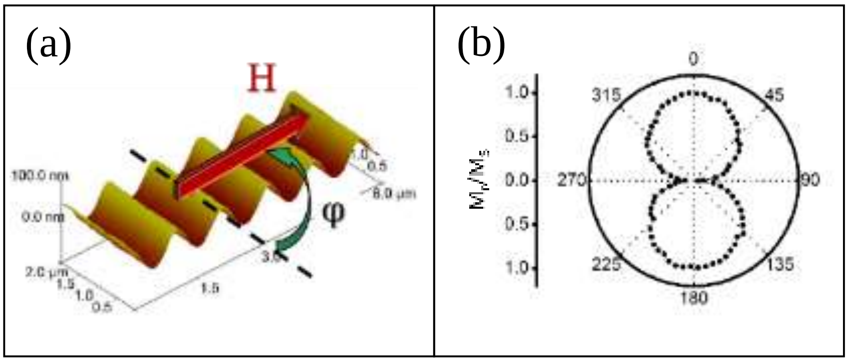

Figure:(a) 3D AFM image of a surface relief grating of a sample with sinusoidal profile (65 nm height and 1.2 μm periodicity) and (b) Polar plot showing normalized remanence magnetization.

The aim of the present work is to generate a simple method by combining conventional laser interferometry and standar thin film deposition technique to fabricate $Ni_{80}Fe_{20}$ (Py) magnetic layers with lateral periodicity, and to tailor the magnetic properties by varying geometrical parameters.

References

[1] Fassbender, J.; Strache, T.; Liedke, M. O.; Markó, D.; Wintz, S.; Lenz, K.; Keller, A.; Facsko, S.; Mönch, I.; McCord J.; New J. Phys. **2009**, *11*, 125002.

[2] Leitao, D. C.; Ventura, J.; Teixeira, J. M.; Sousa, C. T.; Pinto, S.; Sousa, J. B.; Michalik, J. M.; De Teresa, J. M.; Vazquez, M.; Araujo, J. P. *J. Phys.: Condens. Matter.* **2013**, *25*, 066007.

[3] Polushkin, N. I.; Oliveira, V.; Conde, O.; Vilar, R.; Drozdov, Y. N.; Apolinário, A.; García-García, A.; Teixeira, J. M.; Kakazei, G. N.; *Appl. Phys. Lett.* **2012**, *101*, 13240.

P2. Fabrication of a Nanosized Drug Delivery System

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Self-assembly is the autonomous organization of components into patterns or structures without human intervention. [1] It is a key tool in the development of new functional nanostructured materials fabricated by bottom up processes which has been applied in different areas, such as organic electronics [2], nanomedicine[3] and nanobiotechnology[4].

In this communication we report on the use of a layer-by-layer technique to produce self-assembled monolayers with drug delivery functionality. Our system combines three different components that are sequentially assembled on a mica substrate: i) a first layer made of poly(allylamine hydrochloride-PAH), a polyelectrolyte that at neutral pH deposits as flat chains [5]; ii) a second layer , made of heparin, a strong polyanion, and also a main anticoagulant and antihrombotic drug[6]; iii) on top of this biocompatible monolayer, a third layer of a β-blocker drug encapsulated on a cyclodextrin (nanocarrier) is deposited. Atomic force microscopy images of these monolayers show that the cyclodextrin monolayer has a good affinity towards heparine, since its surface has a very low roughness (root-mean-square, RMS, roughness is approximately 0.230 nm), suggesting that cyclodextrins are well-organized/dispersed on heparine-functionalized surface.

The study of the drug release process was monitored by UV-Vis spectroscopy. The film was immersed in a phosphate-buffered saline solution (PBS) at 37ºC, and at designated times the film was pulled out of the solution and UV-Vis spectra of the solution were recorded. Our preliminary results show that, in the presence of the buffer solution, the drug complex is gradually released from the film surface, being the majority of the drug released within the first few minutes.

References

[1] Whitesides, G.M.; Grzybowski, B. Science. **2002**, *295*, 2418-2421.
[2] Ferreira, Q., Alcácer, L.; Morgado, J. *Nanotechnology*. **2011**, *22*, 435604.
[3] Sahoo, S.K.; Parveen, S.; Panda, J.J. *Nanomedicine: Nanotechnology, Biology, and Medicine*. **2007**, *3*, 4 – 31.
[4] Xu, L.; Liu, Y.; Zhang, X. *Nanoscale*. **2011**, *3*, 4901 – 15.
[5] Kreke, M. R.; Badami, A. S.; Brady, J. B.; Akers, R. M.; Goldstein, A. S. *Biomaterials*. **2005**, *26*, 2975–81.
[6] Sasisekharan, R.; Raman, R.; Prabhakar, V. *Annu. Rev. Biomed. Eng.* **2006**, *8*, 181-231.

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P3. Anticorrosion Performance Of Composite Biodegradable Polymer Coating On Magnesium AZ31 Alloy

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High corrosion rate in aggressive media is the main drawback of magnesium based alloys for biomedical application. In this research we show that hydrofluoric acid pre-treatment followed by applying bilayer polymeric coating including polyetherimide(PEI) and polycaprolacton(PCL), greatly influence on delaying corrosion process in AZ31 magnesium alloys. Adding nano hydroxyapatite particles to the coating composition influences on coating properties and performance. In addition, the behavior of MG63 osteoblastic cells on coated samples was investigated through resazurin assay, Confocal Laser Scanning Microscopy (CLSM) and scanning electron microscopy (SEM).

Protective performance of the coating was studied through electrochemical impedance spectroscopy (EIS). Film structure and surface morphology of coating was investigated by Field emission scanning electron microscopy (FE-SEM).

The results demonstrate that remarkable improvement of the corrosion resistance of AZ31 magnesium alloys can be obtain by applying bilayer polymeric coating on AZ31 alloy.

P4. Detection of DNA with CBM-ZZ Fusions on Paper-based Microfluidic Devices Fabricated by Wax Printing

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Microfluidic paper-based analytical devices (µPADs) fabricated by wax printing are promising platforms for the development of simple and inexpensive molecular diagnostic assays, especially in low resource and remote settings, because paper is a ubiquitous material that is biodegradable and compatible with biological and chemical assays [1]. On the other hand, the wax-patterning method is a rapid, low-cost and environmentally friendly method for fabricating microfluidic devices in paper (no use of organic solvents throughout the fabrication process) [2].

Paper devices can be modified for biological assays by adding appropriate reagents to the test areas, and for this purpose, affinity immobilization strategies provide a good solution for bioactive paper fabrication [1]. Following this reasoning, we immobilized antibodies on paper through a fusion protein that combines a family 3 carbohydrate binding module (CBM) from *Clostridium thermocellum*, with high affinity to cellulose, and the ZZ fragment of the staphylococcal protein A, which recognizes IgG antibodies via their Fc portion [3, 4]. After rapid hybridization of DNA through capillary transport, antibodies anchored on paper via CBM-ZZ were able to capture labeled DNA strands and hybridized DNA using a DNA probe labeled with fluorescein. The ability of an anti-biotin IgG to discriminate complementary from non-complementary biotin-labeled target DNA was demonstrated in µPADs, in which hybridization was detected by fluorescence emission of the fluorescein-labeled DNA probe. The efficiency of the capture of labeled-DNA by antibodies immobilized on paper via CBM-ZZ construct was significantly higher when compared with a physical adsorption method where antibodies were simply spotted on paper without the intermediation of other molecules.

References

[1] Pelton, R. *Trends Anal Chem.* **2009**, *28*, 925-942.
[2] Carrilho, E.; Martinez, A. W.; Whitesides, G. M. *Anal Chem.* **2009**, *81*, 7091–7095.
[3] Tormo, J, et al. *EMBO J.* **1996**, *15*, 5739-5751.
[4] Nilsson, B., et al. *Protein Eng*. **1987**, *1*, 107–113.

P5. Nanofabrication of MgO magnetic tunnel junction pillars for spin transfer torque nano-oscilators

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Nanometric MgO-based magnetic tunnel junctions (MTJ) are expected to drive the next generation of spintronic devices such as magnetic random access memories (MRAM), spin-transfer torque MRAM cells (STT-MRAMs) or spin-transfer nano-oscillators (STNOs) [1]. The technological requirements of such devices are both challenging and heterogeneous in nature. For example, the capability to fabricate MTJs with resistance-area (R A) product lower than 5 Ωμm2 while exhibiting simultaneously a high tunnel magnetoresistance must to be combined with the aptitude to properly define pillars smaller 100 nm integrated into a device architecture [2]. The MTJ stacks consists of Si/SiO2(200)/Ta(5)/CuN(50)/Ta(3)/CuN(50)/Ta(3)/PtMn(15)/CoFe(2.3)/Ru(0.85) /CoFeB(2.5) /MgO /CoFeB(2.5)/Ta(10)/CuN(30)/Ru(7) (thickness in nm). The deposited stack was then annealed at 330ºC in vacuum for 2h under 1T. Unpatterned stacks revealed an average TMR 180% and RA ~5Ωμm2. The samples were then patterned into sub-micron circular (nominal diameters 200 to 500 nm) and elliptical (nominal sizes 150x300 to 200x650 nm2) pillars [3]. The switching field dependence on the size of nanometric MTJs revealead a squared transfer curve with a sharp transition between magnetic states [3]. Micromagnetic simulations [4] indicated a single-domain like state at remanence, also displaying a sharp transition between parallel/antiparallel free-layer configurations. Overall, the experimental switching fields were smaller than those obtained from simulations, consistent with the presence of a particular free layer profile, signature of the two angle etching step used for pillar definition. Further deviations between experimental and simulations were attributed to local defects and thermal activated processes.

References

[1] P.P. Freitas, R. Ferreira, S. Cardoso et al. J. Phys.:Cond. Matt. 19, 165221 (2007)
[2]R.J.Macedo,J.Borme,R.Ferreira,S.Cardoso,P.P.Freitas et al. J. Nanosci. Nanotech. 10 (2010)
[3] A. V. Silva, D. C. Leitao, Z. Huo, et al. IEEE Trans. Mag. 49, 4405 (2013)
[4] Z. Hou, A.V. Silva, D.C. Leitao, R. Ferreira, S. Cardoso, P.P. Freitas, Physica B http://dx.doi.org/10.1016/j.physb.2013.09.039

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P6. Synthesis of Carbon Nanoparticles Using Microwave Plasmas

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In the present work, the unique environment of microwave atmospheric plasmas driven by surface waves has been used to generate carbon nanoparticles. Vaporized benzene molecules are injected into a microwave argon plasma environment, where decomposition of benzene molecules takes place and carbon atoms and molecules are created. Partial benzene and total argon fluxes have been varied in the range 2-4 sccm and 250-500 sccm, respectively. The microwave power delivered to the plasma was kept constant at 500 W. The synthesized nanoparticles are collected by a filter system. In order to detect the active species of interest created during the decomposition processes the optical plasma emission in the 300 – 700 nm spectral range has been investigated. .The plasma radiation was collected by a quartz optical fiber coupled to a Jobin-Yvon Spex 1250 spectrometer equipped with a cryogenic, back illuminated, UV sensitive CCD camera. Strong plasma emissions of C_2 molecular bands, *i.e.*, the Swan system, with band heads at 473.7, 516.5 nm and 558,6 nm, and the carbon atomic line at 247,8 nm were detected. The gas temperature of the plasma, a key parameter for the benzene decomposition process, was determined by measuring the rotational temperature of the OH radical using the OH(A-X) (Q1 branch) emission band in the range 306 to 315 nm.

The analysis of the obtained samples demonstrates that nanoparticles have mainly been produced for the considered range of experimental conditions. The synthesized nanoparticles have a diameter of 23.63±5.44nm. This type of nanostructures is usually refered to in the literature as fulerene soot.

P7. Intrinsically Fluorescent Silica Nanocontainers: A Promising Theranostic Platform

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A large decrease in the side effects of a drug can be obtained if it is efficiently delivered in a timely manner and in the needed location only.[1] By combining therapeutic and diagnostic (theranostic) functionalities with targeting capabilities and large surface areas, nanoparticles provide an ideal vehicle for personalized medicine.

Mesoporous silica nanoparticles (MSNs) are characterized by an ordered pore system of 2-8nm diameter, pore volumes above 1mL/g and particle size from 40nm to several hundred nanometers. The preparation of fluorescent hybrid MSNs requires the presence of a fluorescent molecule during the synthesis, which becomes aligned with the pores, thus impervious to aggregation and self-quenching effects. The MSNs external surface can be selectively functionalized to immobilize polymers or (bio)molecules for possible targeting or sensing, and the pore is available for solvent diffusion, allowing the incorporation of different molecules.[2]

The main objective of our work was to develop hybrid MSNs with combined diagnostic and therapeutic functionalities, carrying fluorescent beacons for traceability and imaging, featuring a smart release control mechanism, and able to accommodate large drug loads and deliver their cargo on demand to a desired location. This communication is focused on the preparation of fluorescent MSNs incorporating a fluorescence perylediimide derivative (PDI) in the wall structure (MSN-PDI) and polymerized them with a temperature-responsive polymer shell (MSN-PDI-POLY). Laser scanning confocal microscopy of MSN-PDI and MSN-PDI-POLY after incubation in HEK293 cells shows the internalization of the nanoparticles. These new hybrid nanoparticles open up interesting possibilities for the development of a traceable drug delivery system.[3]

References

[1] Kelkar, S.S.; Reineke, T.M. *Bioconjugate Chem.* **2011**, *22*, 1879-1903.
[2] Soler-Illia, G.J.A.A; Azzaroni, O. *Chem. Soc. Rev.* **2011**, *40*, 1107-1150.
[3] Rodrigues, A.S; Ribeiro, T.; Fernandes, Fábio; Farinha, J.P.S; Baleizão, C. *Microsc. Microanal.* **2013**, *19*, 1216-1221.

Acknowledgements: *This work was partially supported by FCT-Portugal and COMPETE (FEDER), projects PTDC/CTM/115110/2009, PTDC/CTM- NAN/2354/2012, and PEst-OE/CTM/LA0024/2011. T.R., A.S., and F.F. also thank FCT for PhD (SFRH/BD/64702/ 2009; SFRH/BD/89615/2012) and Post-Doc (SFRH/BPD/ 64320/2009) grants.*

P8. Toward conducting fibres for intelligent textiles

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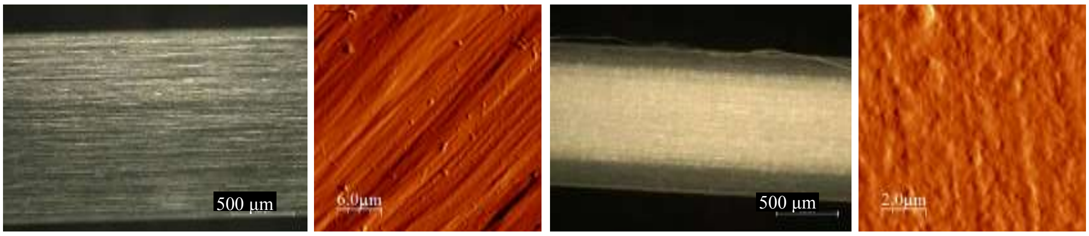
The development of electronic textiles is one of the hottest topics in organic electronics. There are already examples of smart textiles in garments for monitoring physiological and biomechanical signals.[1] However, the manufacturing schemes for current applications rely on the integration of off-the-shelf electronic components mounted on a textile substrate. Such components are silicon-based, thus unsuitable for applications where flexibility and fault-tolerance are required. Organic electronics is an alternative to conventional silicon technology and can overcome those limitations. In this sense, graphene, with high optical transparency and electrical conductivity, is a promising material. Furthermore it can be doped to increase the conductivity.[2]

In the pursuit of conducting fibres, our approach consisted in coating specially designed nanosmooth polypropylene fibres with graphene. Monolayer graphene was grown on copper foils by low pressure chemical vapour deposition using methane as a carbon source, and wet-transferred to the fibres after copper etching. Graphene adhesion to the fibres was found to be very sensitive to minute surface modifications. In that sense, several surface treatments were performed, such as UV light exposure, corona discharge and thermal pre-treatment. In particular, polymer coating was done using different polyimides and coating techniques. AFM microscopy was performed to evaluate the resulting changes in the surface of the fibres, and Raman spectroscopy was used to confirm the presence and quality of the graphene transferred onto the fibres.



(a) (b)

Figure 1. Polypropylene fibres used and corresponding AFM images taken at a 90º for:
(a) standard polypropylene; (b) biopolypropylene.

References

[1] Witt, J.; et al. *IEEE Sens. J.* **2012**, *12*, 246-254.

[2] Craciun, M. F.; et al. *Nano Today* **2011**, *6*, 42-60.

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P9. 9,10-Di(4-pyridyl)antracene Metal Organic Frameworks: Synthesis and Structure

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Metal organic frameworks (MOFs) have emerged as an important class of porous materials in the past decade. These crystalline hybrid materials are a product of the combination of metal ions or clusters with rigid organic ligands (bearing carboxylates and\or pyridines), allowing the design of an almost infinite number of architectures limited only by the imagination of chemists.[1,2]

The main objective of our work is the development of photoactive MOFs, and herein we report the preparation of a MOF containing an anthracene moiety. The reaction of 9,10-di(4-pyridyl)antracene and biphenyl.-4,4'-dicarboxilic acid and zinc nitrate under solvothermal conditions yields a microcrystalline powder (Figure 1A). The obtained DPyA-MOF was characterised by single crystal X-ray diffraction (Figure 1B).

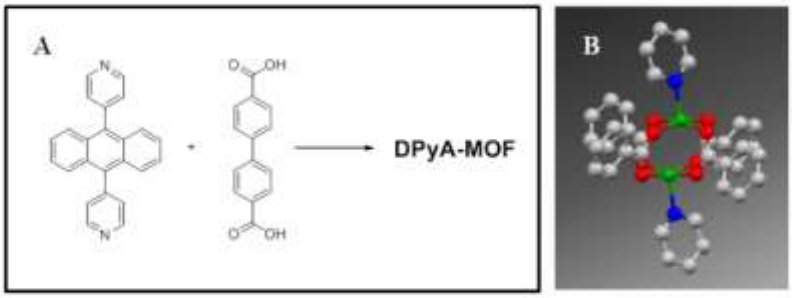

Figure 1. A) Scheme of the synthesis of DPyA-MOF. B) Zinc cluster in DPyA-MOF determined by X-ray diffraction, some atoms were omitted for clarity (C – gray; N – blue; O - red and Zn – green spheres).

References

[1] O. K. Farha, J. T. Hupp, *Acc. Chem. Res.* **2010**, *43*, 1166.

[2] D. Zhao, D. J. Timmons, D. Q. Yuan, H. C. Zhou, *Acc. Chem. Res.* **2011**, *44*, 123.

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P10. Wettabilty And Nanotribology of Fe^+ Implanted Si Surfaces

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Surface related phenomena such as adhesion, friction and wear still impose as one of the main limitations for contact-based operation micromechanical systems (MEMS) [1]. These phenomena are intrinsic of MEMS devices, since they arise from their small dimensions (1 mm to 100 nm) and tend to be aggravated from the silicon´s poor tribological properties, the most common material from which MEMS devices are fabricated. Several approaches to this problem have been attempted so far, mainly consisting on applying different types of coatings in Si such as DLC´s [2] and SAM´s [3] in order to change its surface properties.

In the present work ion implantation was used for the purpose of enhancing silicon´s tribological behaviour on micro-nanoscale. Si <100> p-type was implanted with Fe^+ ions with an energy 150 kev´s using a fluence of $\Phi = 2x10^{17}$ cm^{-2} at room temperature and normal incidence. Following the implantation, the samples were annealed at 800 and 1000 ºC in a tubular tube. The samples were characterized in SEM, XRD, ultramicro hardness, wettabilty measurements, RBS and in terms of nanowerar using an AFM.

The results show that the annealings promote the formation of two different silicides depending on the temperature. A significant increase of the water contact angle was observed for the as-implanted and 1000 ºC annealed sample. No significant difference was observed regarding both hardness and Young´s modulus. The better nanotribological properties were attained for the annealed samples, being the as implanted the sample which exhibit the highest wear rate and wear coefficient.

References

[1] Kim, S. H.; Asay, D. B.; Dugger, M. T. *Nano Today* **2007**, 2, 22-29.

[2] Luo, J. K.; Fu, Y. Q.; Le, H. H.; Williams, J. A.; Spearing, S. M.; Milne, W. I. *J. Micromech. Microeng.* **2007**, S147-S163.

[3] Patton, S. T.; Conwan, W. D.; Eapen, K. C.; Zabinski, j. S. *Tribol. Lett*. **2000**, 199-209.

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P11. Femtosecond laser ablation of bovine cortical bone

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Ultrafast lasers are extremely promising tools for minimally-invasive orthopedic surgery, but the influence of femtosecond laser ablation on the surface topography, structure and composition of bone was scarcely investigated up to now. The purpose of this work is to study this influence in vitro, using bovine cortical bone as a model. The ablation tests were performed in air and in dry conditions and under flowing water, with a 500 fs pulse duration laser (1030 nm wavelength) using fluences from 0.55 to 2.18 J/cm^2 and pulse frequencies between 50 and 3000 Hz. The results show that when processing is carried out in dry conditions and with pulse repetition rates up to 50 Hz, the structure of the remaining tissue is preserved and the only compositional changes detected are a slight reduction of the organic material content and a partial recrystallization of hydroxyapatite in the most superficial region of the samples. When the laser pulse frequency is increased to 2 kHz, the organic matter content at the samples' surface decreases further and slight surface carbonization occurs. On the contrary, no compositional alterations were observed when ablation was performed under flowing water. The results suggest that ablation occurred by a combination of thermal and electrostatic mechanisms, the first explaining the thermal effects observed. This work confirms that femtosecond lasers are a viable alternative to mechanical tools for delicate orthopaedic surgeries, where small amounts of bone must be cut or removed with negligible damage. Water cooling allows high pulse frequencies to be employed and, consequently, higher tissue removal rates to be achieved.

P12. Metal Ion Responsive Nonlinear Fluorescent Sensors Based on the 1,3,5-Triazine Core

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The design of a fluorescence molecular sensor combines a binding site and a fluorescent units (Fig.1). [1] In our studies, the sensor has a nonlinear response to excitation in the near-IR and the specific target consists in a metal ion, which has the capacity to change the fluorescence behaviour of the sensor. Due to the small size of a single cell, in situ detection of metal ions requires very sensitive microanalytical techniques with high spatial resolution. [2] Activation of the sensor by two-photon excitation allows an increased depth of penetration, reduced phototoxicity, and intrinsic 3D capabilities, which are key properties for ion mapping in biological systems using nonlinear optical imaging. Aiming at contributing to the progress in this field, the linear and nonlinear photophysics of 1,3,5-triazine derivatives substituted with two donor arms and a sensing unit have been studied. The effect of conjugation, nature of the donor arm and sensing units in the two photon absorption cross-section and emission quantum yields have been evaluated. A set of representative compounds were chosen for evaluation of the metal sensing ability in solution. All of them have proven to be turn off sensors, whose fluorescence is quenched by the metal, with a selective response to Cu^{2+} and Hg^{2+}.

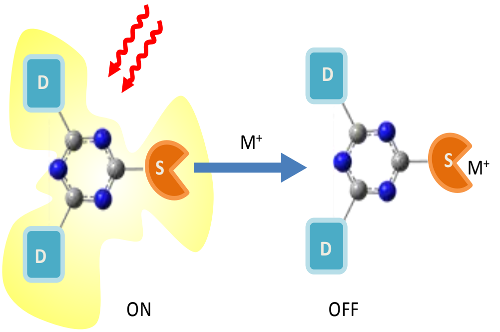

Figure 1- illustration of a nonlinear metal-ion-responsive fluorescent sensor build up on the basis of the 1,3,5-triazine electron accepting core with two electron donor arms and a sensing unit.

References

[1] A. Prasanna de Silva, PNAS, vol. 96, no. 15, 8336-8337. (1999).
[2] S. Sumalekshmy, Chem. Mater., 23, 483–500 (2011)

Acknowledgements: We acknowledge our colleagues Xingguo Chen and Jingui Qin of the Wuham University for providing the sensors and FCT for financial support (SFRH/BPD/75782/2011 and PTDC/QUI-QUI/117405).

P13. Simulating Changes in Physical Properties with Chain Length in [$C_n$mim] [NTf_2] Ionic Liquids

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The experimental measurement of vaporization enthalpies is extremely challenging namely because the vapor pressure of ILs at ambient temperature is low, while at high temperatures there can be thermal decomposition. Historically, the errors and differences between measurements by different groups and/or different techniques were considerable, even when the determinations where performed in the same laboratory, at different times [1]. Although recent determinations are more consistent, there are still room for controversy [2,3]. However, since enthalpies of vaporization in combination with densities are in the core of the data most used to obtain force field parameters for simulations of ILs, the quality of the predictions of the simulations depend strongly on the quality of the data available. Nevertheless, new force field refinements have been done with a higher accuracy [1].

With recent reports on high-accuracy thermophysical data for ILs, a trend-shift was detected at around n=6 for the [$C_n$mim] [NTf_2] series (n=3–12) [3]. In this communication, we report our most recent results on a study of this series by molecular dynamics simulations. A discussion will be made by comparing our findings with experimental results and by pinpointing challenges, successes and problems found.

References

[1] Köddermann, T.; Paschek, D. & Ludwig, R. *ChemPhysChem,* **2007**, *8,* 2464-2470.

[2] Verevkin, S. P.; Zaitsau, D. H.; Emel'yanenko, V. N.; Yermalayeu, A. V.; Schick, C.; Liu, H.; Maginn, E. J.; Bulut, S.; Krossing, I.; Kalb, R. *J. Phys. Chem. B,* **2013**, *117,* 6473-6486.

[3] Rocha, M. A. A.; Lima, C. F. R. A. C.; Gomes, L. R.; Schröder, B.; Coutinho, J. A. P.; Marrucho, I. M.; Esperança, J. M. S. S.; Rebelo, L. P. N.; Shimizu, K.; Lopes, J. N. C.; Santos, L. M. N. B. F. *J. Phys. Chem. B,* **2011**, *115,* 10919-10926.

P14. An electron microscopy and atomic force microscopy analysis on the self-lubricant behaviour of copper-carbon nanocomposites

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A microstructure refined to the nanometer scale improves mechanical strength. Furthermore, in the case of carbon dispersions in metals, possible reinforcing effects can be combined with specific properties of carbon phases, such as self-lubricating properties for nanodiamond and graphite [1,2]. High-energy milling is a powder metallurgy process extensively employed to produce nanostructured materials as well as fine particle dispersions in metallic matrices [3]. Nevertheless, continued milling is known to induce amorphization of graphite [4] and to some extent the same can be expected for other carbon allotropes, altering the intrinsic properties of these phases. Furthermore, combination of carbon phases with metallic matrices at the nanoscale represents a fundamental challenge: some metals, like copper, exhibit an intrinsically difficult bonding with carbon phases, which may result in weak interfacial boundaries. Furthermore, the consolidation techniques used must preserve the nanostructure in the composite materials. Suitable processing windows for the dispersion of nanodiamond (nD) and graphite (G) in nanostructured copper by ball milling have been previously established and consolidation has been achieved by either extrusion spark plasma sintering (SPS) or hot isostatic pressing (HIP). In the present work, the microstructure of the samples has been characterized by transmission electron microscopy. The friction coefficient of the materials has been determined with a CSM nanotribometer with a commercial steel ball counter body. Scanning electron microscopy and atomic force microscopy have been employed to characterize the wear tracks resulting from the previous measurements.

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References

[1] Nickchi T, Ghorbani M, Alfantazi A, Farhat Z, Mater Design 32 (2011) 3548

[2] Gubarevich AV, Usuba S, Kakudate Y, Tanaka A, Odawara O, Diam Relat Mater 14 (2005) 1549

[3] Suryanarayana C, Progress in Materials Science 46 (2001) 1

[4] Niwase K, Tanaka T, Kakimoto Y, Ishihara KN, Shingu PH, JIM 36 (1995) 282

P15. Microtribological behaviour of hydrogels in contact with simulated biological fluids

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The biotribological properties of hydrogel contact lenses (CLs), in particular their friction coefficient, play an important role in their performance, mainly in the users ocular comfort. Recent studies have shown that proteins, lipids and other biomolecules present in biological fluids can adsorb/interact differently with the CLs materials, but there is no information on their influence in the biotribological behaviour of the materials [1, 2]. In this work, the behaviour of two types of hydrogels, pHEMA/PVP (pHEMA based) and TRIS/NVP/pHEMA (silicon based), in the presence of two of the main components of the lachrymal fluid, cholesterol and albumin, was investigated in order to understand the role played by these biomolecules and to contribute to a better comprehension of the lubrication mechanisms of CLs materials. The variation of the friction coefficient was monitored using a nanotribometer. The materials surfaces were characterized by atomic force microscopy (AFM) due to the vital role surface roughness plays in microtribology [3]. Hydrophilicity was evaluated through contact angles measurement, while the hydrogels swelling behaviour was studied in detail. The Young´s moduli of the hydrogels were measured, and their structural properties were analyzed by nuclear magnetic resonance (NMR). The used techniques allow to ascribe an effect of the biomolecules not only on the variation of the friction coefficient but also at a structural level. Interestingly, it was observed that the lipid (cholesterol) as a tendency to influence the tribological response of the pHEMA based hydrogel, while the protein (albumin) affects the tribological response of the silicon based.

References

[1] Lee, S., G. Bourne, M. Sarntinoranant, Mechanical characterization of contact lenses by microindentation: Constant velocity and relaxation testing. Acta Biomaterialia, 2008. **4**: p. 1560-1568.

[2] Gong, J., Higa, M., Iwasaki, Y., Katsuyama, Y., Osada, Y., Friction of Gels. Journal of Physics and Chemistry B, 1997. **101**: p. 5487-5489.

[3] Bhushan, B., Handbook of Micro/Nano Tribology. CRC Press, 1999.

P16. Nano-domains in Bi-based lead-free ferroelectrics

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In our previous work we found diffuse streaks in the x-ray diffraction from the single crystal ferroelectric relaxor (BiNa)TiO_3-$BaTiO_3$ [1]. These streaks connect half-order reflections associated with octahedral tilts in the sample. The diffuse streaks and diffuse half-order peaks react upon the application of an external electric field.
Here we present results from simulations of the diffuse scattering pattern based on certain stacking faults in the R3c structure and show that the model can be applied to estimate the amount of stacking faults.
The stacking fault probability in turn can be used to calculate the size of the polar nano-domains in BNT-BT giving rise to the relaxor behavior.

References

[1] Daniels, J. et al. , *Appl. Phys. Lett.* **2011**, *98*, 252904.

Acknowledgements: *This work was carried out under the SFB 595 "Fatigue in functional electrical materials."*

P17. Retirado do programa

P18. Retirado do programa

P19. Retirado do programa

P20. Scavenging Genotoxins from Pharmaceuticals by Molecular Imprinting and Nanofiltration

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The manufacturing of pharmaceutical drug products often involves the use of highly reactive species for the formation of active pharmaceutical ingredients (APIs). Among them are genotoxins which are substances that can damage the DNA or cause errors in DNA replication and thus lead to tumor cells. Low levels of such reagents or by-products – called genotoxic impurities (GTIs) – being present in the final drug product has severe impact on product risk assessment. Recently GTIs have gained increased attention and pharmaceutical regulatory authorities carry on issuing guidelines that strict the limits of genotoxins in medicines. Removal of impurities generally involves multistep purification processes such as recrystallization, fractional distillation, resins, adsorbents, extraction and various chromatographic techniques. These purification processes have significant impacts on the total cost of the final API mainly related to the API loss. Preliminary study in our research group showed efficient API detoxification by means of molecular imprinting and organic solvent nanofiltration as one stage purification processes. Furthermore, a hybrid approach – exploiting nanofiltration and imprinting – has been developed for the efficient removal of a potentially genotoxic impurity from API post-reaction solutions. The presentation will give an overview on the recent advances in the implementation of organic solvent nanofiltration (OSN) and molecular imprinting (MIP) [1] in the downstream processing of pharmaceuticals. A case study on OSN and MIP synergic combination will be presented [2].

References

[1] Székely G.; Bandarra J.; Heggie W.; Sellergren B.; Ferreira F.C. **2011** *J. Membr Sci*, 381, 21-33.

[2] Székely G.; Bandarra J.; Heggie W.; Ferreira F.C.; Sellergren B. **2012** *Sep Purif Technol*, 86, 190–198.

[3] Székely G.; Bandarra J.; Heggie W., Sellergren B.; Ferreira F.C. **2012** *Sep Purif Technol*, 86, 79–87.

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P21. Polyhydroxyalkanoates Fibrous Scaffolds for Support Mesenchymal Stem Cells Culture

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Following a biorefinery approach, it was shown recently to be possible to use the crude glycerol generated during biodiesel production for the biological synthesis of polyhydroxyalkanoates (PHAs) [1, 2]. Human Mesenchymal Stem Cells (hMSC) provide an interesting model of regenerating cells, since they have the ability to differentiate into different cell lines, including the osteo-, chrondro-, adipo- and myogenic lineages. Additionally, these cells have modulatory properties which can be explored for cell therapies targeting immunologic diseases. Electrospun fiber meshes offer tunable mechanical and physical properties that can mimic the structure of the native extracellular matrix, the natural environment where cells inhabit. This integrated study shows that waste glycerol can be bio-valorized by the fabrication of electrospun cell biocompatible scaffolds, able to support hMSC ex-vivo cultivation, at acceptable proliferation levels, offering a considerable potential for use in regenerative medicine. The P(3HB-4HB-3HV) terpolymers, one containing 11.4 % 4HB and 3.5% 3HV and the other containing 35.6 % 4HB and 3.4 % 3HV, were electrospun into fibers of average diameters of 600 and 1400 nm, respectively. hMSC were cultured for 7 days in both fiber meshes, showing their ability to support stem cell growth. Comparative results clearly demonstrate that scaffold topology is critical, with electrospun PHA fibers succeeding on the support of significant cell adhesion and proliferation, where planar PHA films failed.

References

[1] Cavalheiro J. M. B. T.; de Almeida, M. C. M. D.; Grandfils, C.; da Fonseca, M. M. R.; *Process Biochem.* **2009**, 44, 509-515.

[2] Cavalheiro J. M. B. T.; Raposo R. S.; de Almeida, M. C. M. D.; Cesário M. T.; Sevrin C., Grandfils, C.; da Fonseca, M. M. R. *Bioresour Technol.*. **2012**, 111, 391-397.

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P22. Nanostructured Copper-Graphite-Alumina Powders Produced by High-Energy Milling

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Several graphite-fibber and graphite-particulate copper reinforced composites are commercially used in the thermal management and electromechanical industries. While copper presents high electrical and thermal conductivity, corrosion resistance and sufficiently high melting point, graphite toils through low coefficient of thermal expansion, high strength, high conductivity and self-lubricating ability. However, further application is hindered by the low thermal and electrical conductivity resulting from resistance at the copper/graphite interface.

In this work this issue is approached via high energy milling of copper-graphite mixtures in the presence of alumina. Alumina was chosen owing to its high melting point, high hardness, thermal stability and chemical inertness, aiming to promote microstructural grain refinement and uniform introduction of small incoherent strengthening phases. Furthermore, copper-alumina composites have almost the same electrical and thermal conductivities as pure copper [1]. The global aim is to achieve a uniform nanostructure resulting in improved composite strength and thermo-electrical performance, while keeping the graphite anti-sticking characteristics.

Tailored copper-graphite-alumina batches were planetary ball milled up to 16 h, using alumina jars and balls; copper-graphite batches were also prepared under the same conditions to evaluate the effect of contamination from the milling media. The microstructure of the produced materials was characterized by FEG-SEM/EDS and related to Raman, XRD and microhardness results.

Attained results show that alumina is present in resulting material from both systems, due to contamination from the milling media. However, size reduction is effective at shorter times in the copper-graphite-alumina. In both cases produced powders are nanostructured, containing graphite and alumina nanoparticles homogeneously distributed in copper, especially for longer milling times and in the presence of added alumina. Copper crystallite size and lattice parameter are only affected above 8 h milling time; nanographite amorphization and size decrease also result.

References

[1] Tian, B.; Liu, P.; Song, K.; Liu, Y.; Ren, F.; Su, J. Mater. Sci. Eng. A **2006**, 435, 705-710.

P23. Two-Photon Activated 3D Data Storage

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Computer technology needs high performance storage devices that must store, retrieve and process huge volumes of data at high speeds. Two-photon 3D data storage is one of the most promising techniques to meet these demands. The longer wavelengths used in a two-photon activated writing process allow for a longer penetration depth into the optical material and the nonlinearity of the process confines the writing to a nanometer volume. Using two-photon activated processes it is possible to store hundreds of layers within the volume of a 1 mm thick DVD-type [1].

In this work we demonstrate FRET assisted two-photon recording for a film containing a mixture of the photochromic molecule 1,2-bis(2-mehytylbenzo[b]thiophen-3-yl)hexafluorocyclopentene (PC) and a linear polymer based on the 2,4,6-tris(thiophen-2-yl)-1,3,5-triazine electron acceptor core in an inert matrix of ethyl cellulose. As depicted in the Figure 1, the polymer works as a two-photon absorption antenna (TPA) that transfers part of the excitation energy to the cyclic form of the PC inducing ring opening and becoming fluorescent.

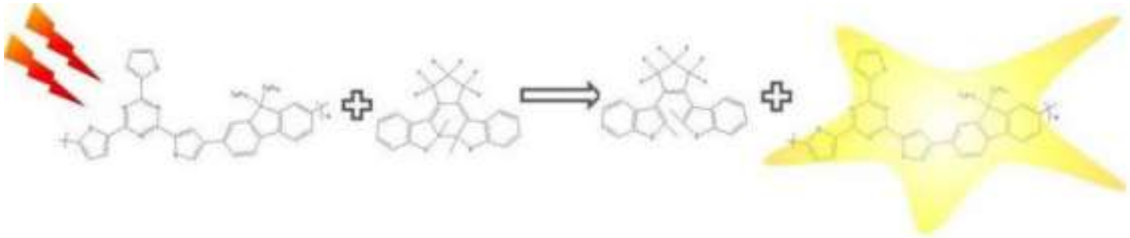

Figure 2. FRET assisted two-photon recording. Data was recorded with an irradiation time as short as 1 ms at 740 nm with a good S/N ratio, a performance that represents an improvement of the writing speed by 3 orders of magnitude when compared with photochromic polymer composites studied earlier [2].

References

[1] A. S. Dvornikov, E. P. Walker, P. M. Rentzepis, *J. Phys. Chem. A* **2009**, 113, 13633

[2] C. C. Corredor, L.-Z. Huang, K. D. Belfield, A. R. Morales, M. V. Bondar, *Chem. of Materials* **2007**, 19, 5165-5173.

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P24. Controlling the Morphologies on Solar Cells Based on Cross-linked Semiconducting Polymers at the Nanoscale

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Organic photovoltaic cells (OPVs), combining semiconducting polymers, as electron-donor materials, and fullerenes, as electron-accepting materials, are of high interest, both from the scientific and technological point of view. They combine low cost solution processability, fine-tuning of the optical and electrical properties upon modifications of the chemical structure of material and mechanical flexibility. However, the performance of OPVs is strongly depended of the organic active layer’s morphology: the excitons formed upon photon absorption have to reach the electron-donor/electron-acceptor interface for an efficient separation into charges (electrons and holes) before decaying and the generated charges have to reach the proper electrodes before they recombine. These constraints led to a proposed ‘ideal’ morphology for these cells consisting on an interdigitated-like structure of the donor-acceptor materials. To implement this approach, research has been focused on the patterning of the organic materials to form columns with ca. 20 nm in diameter.

In this communication, we report on a method to prepare insoluble cross-linked columnar films of a polyfluorene, upon phase separation in blends with polystyrene, used as assisting polymer [1]. The electron-donor nanostructured columnar films of these polymers were then coated with a soluble fullerene (PCBM), as the electron-acceptor, to form the active layer of OPVs [2]. The performance of these nanostructured solar cells is correlated with the column-like diameter of the patterned polymer, with the cells with the thinner columns showing the highest power conversion efficiencies (PCEs). Yet, the obtained PCEs still fall below that of the similar OPVs prepared upon blending of the two components. We will discuss on the origin of the PCE variation with column diameter and present the ongoing work to improve these OPVs performance.

References

[1] A. Charas, Q. Ferreira, J. Farinhas, M. Matos, S. M. Fonseca, H. Burrows, L. Alcacér, J. Morgado, *Macromolecules.* **2009**, *42,* 7903-79012.

[2] J. Farinhas, Q. Ferreira, R. Di Paolo, L. Alcacér, J. Morgado, A. Charas, *J. Mater. Chem.* **2011**, *21,* 12511-12519.

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P25. New Fluorescent Boron Sensors

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Boron is beneficial to human health and agriculture in trace quantities, but becomes toxic both to humans and crops in excessive quantities. Boron compounds are used in many industrial applications, including the fabrication of soaps and detergents, glass and ceramics, insecticides, fertilizers and pharmaceutical drugs, which increases the boron content in water duo to residual water discharges [1]. According to World Health Organization recommendations, boron concentrations in water for human consumption should be below 2.4 ppm [2].

Sensitive methods for the analysis of boron content in water, with a detection limit in the ppb range rely on large equipment, with relatively few examples of optical boron sensors described in the literature [3].

In the present work, we synthesize new fluorescent boron sensors with chelating ability, based on 2,3,6,7,10,11-hexahydroxytriphenylene (which features a high sensitivity and specificity for boron even at very low sensor concentration [4]), with a methacrylate motif (figure 1a), that will subsequently allow the polymerization of the sensor, incorporating it in smart polymer nanoparticles [5] in order to remove the boron content of aqueous systems (figure 1b).

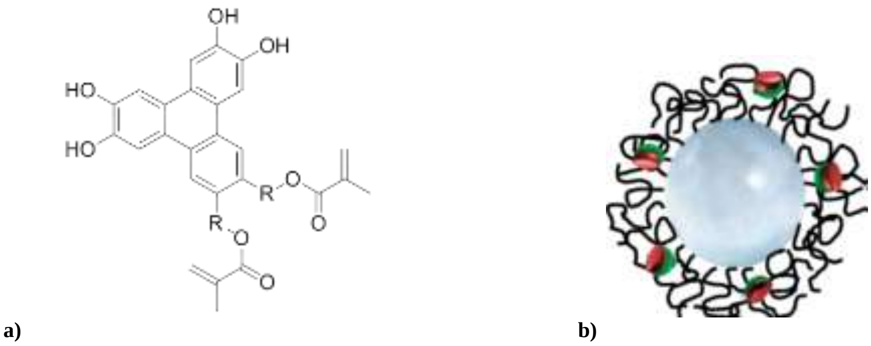

Figure 1. **a)** Structure of the synthesised optical boron sensor derived from hexahydroxytriphenylene; **b)** Schematic representation of the final nanomaterial (blue, nanoparticle core; black, polymeric shell; green, boron sensor; brown, chelated boron).

References

[1] Batayneh, A. T. *Int. J. Environ. Sci. Technol.* 2012, 9, 153-162. [2] World Health Organization. *Guidelines for drinking-water quality. 4th ed. World Health Organization,* 2011. [3] Takahashi, T, Yawata, S, Hoshino, H. *Anal. Bioanal. Chem.*, 2008, 391, 1101-1106. [4] Farinha, J. P. S., Baleizão, C. M. C., Alves, S. P. C. (Instituto Superior Técnico). PT106766. February 06 2013; [5] Borlido, L., Moura, L., Azevedo, A. M., Roque, A. C. A., Aires-Barros, M. R., Farinha, J. P.S. *Biotechnol. J.* 2013, 8, 709-717.

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P26. Nanoscale sensing devices based on magnetic tunnel junctions with soft pinned sensing layer

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Highly sensitive magnetoresistive nanosensors with high spatial resolution provide the necessary features for high accuracy magnetic imaging. MgO based magnetic tunnel junction (MTJ) stacks exhibiting large tunneling magnetoresistance (TMR) and low a resistance-area product (RxA) stand out as the best starting point for such nanometric sensing devices. State-of-the-art MgO-MTJs show large output voltages, large signal-to-noise ratios and can display TMR~200% with RxA~5 $\Omega\mu m^2$. Using such stacks, linear transfer curves are achieved by setting the magnetization of the sensing and reference layers perpendicular to each other [1]. The most common methods resort to shape anisotropy or biasing by permanent magnets [1]. Other routes employ out-of-plane magnetized sensing layers either of Pt(Co, Co-alloys), or thin CoFeB, but typically exhibit smaller TMR signals. Recently, MTJ stacks with two exchange-pinned electrodes have been introduced for the fabrication of micrometric sensors with controlled linearity and low aspect-ratio [2]. In this case, the linear range can be controlled by the multilayered stack, in particular by the exchange coupling strength in the sensing layer [2]. In this work we report the fabrication [3] and characterization of nanoscale MTJ sensors with two exchange-pinned electrodes. The perpendicular magnetization configuration for field sensing is set using a two-step annealing process, where the second annealing temperature was optimized to yield patterned sensors responses with improved linearity. The optimized circular nanosensors show sensitivities up to 0.1 %/Oe, larger than previously reported for nanometric sensors and comparable to micrometric spin-valves. These results are in accordance with micromagnetic and magneto transport simulations using Spin-flow3D [3-4].

References

[1] P.P. Freitas, R. Ferreira, S. Cardoso et al. J. Phys.:Cond. Matt. 19, 165221 (2007)
[2] R. Ferreira, E. Paz, P. P. Freitas et al., IEEE Trans. Magn. 48, 3719 (2012)
[3] A. V. Silva, D. C. Leitao, Z. Huo, et al. IEEE Trans. Mag. 49, 4405 (2013)
[4] Z. Hou, A.V. Silva, D.C. Leitao, R. Ferreira, S. Cardoso, P.P. Freitas, Physica B http://dx.doi.org/10.1016/j.physb.2013.09.039

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P27. Low Cost Silicon Junctions

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LoCoSil (Low Cost Silicon Junctions) summarizes the research carried on in the Semiconductor Materials and Energy Conversion Laboratory, within the project PTDC/EEA-ELC/108882/2008. The objective is the study of a low cost alternative process to the usual silicon crystalline doping through the diffusion furnace technique. The novelty is the use of highly doped hydrogenated amorphous silicon thin films, acting as dopant sources. These amorphous silicon thin films are deposited by PECVD technique on doped crystalline silicon substrates of opposite majority charge carriers, originating pn junctions [1].

Afterwards, these samples are placed in the diffusion furnace in order to induce firstly the dehydrogenation of amorphous silicon (350º - 550ºC), followed by the dopant diffusion into the crystalline silicon [2]. This diffusion process occurs at temperatures ranging from 900ºC to 1000ºC, for different dopant concentrations.

The p-n junctions characterization were made by I(V) curves; by four-point probe measurements and by SIMS analysis, in order to obtain the electrical PV parameters (short circuit current, I_{CC}, and open circuit voltage, V_{OC}), diffused layer sheet resistance, and doping profile, respectively. Typical PV values measured are $V_{OC} \approx 0.51$ V and $I_{CC} \approx 13$ mA/cm^2, obtained for a junction depth of 2.3 μm and sheet resistance of 50 Ω/sq. Although these results are promising they are not optimized yet and further work is needed, namely the study of the electric contacts behaviour of these junctions.

Finally, this study will give rise to the fabrication of multi-junction devices such as bipolar transistors and MOSFETs, followed by the integration of the latter in CMOS circuits.

As a spin-off result, the production of HIT heterojunctions will also be attempted.

References

[1] Lavareda G., Calheiros Velozo A., Nunes de Carvalho C., Amaral A., *Thin Solid Films* 543 (2013) 122-124.

[2] Calheiros Velozo A., Lavareda G., Nunes de Carvalho C., Amaral A, *Thin Solid Films* 543 (2013) 48-50.

P28. Synthesis Strategies Leading to Innovative Fluorinated Silica Nanocapsules

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The biomedical applications of silica nanoparticles have been a very active research field in the last ten years, owing to their biocompatibility, good water solubility, easy surface functionalization, and soft synthesis conditions capable to control their porous structure. Very recently, efforts have been made to develop methods for preparing hollow silica nanoparticles (nanocapsules) with multifunctional properties and improved loading capacity for a variety of therapeutic agents and diagnosis probes, in particular for those involved in the fight against cancer.[1]

In this work, we report different synthesis methodologies leading to the production of silica nanocapsules. Using the reverse emulsion technique, uniform spherical nanoparticles with diameters ranging from ~20 to 70 nm and variable cavity size were obtained.

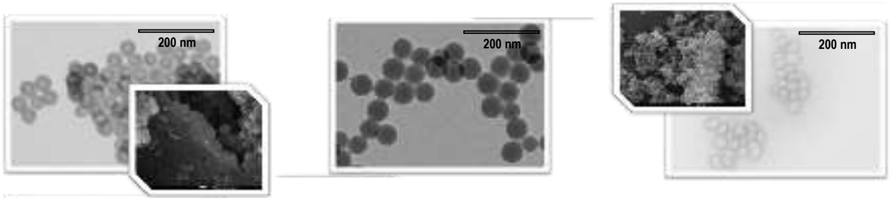

Figure 1: TEM and SEM (inset) images of different types of nanoparticles synthesized.

Some of these approaches employ fluorinating agents, such as hydrofluoric acid or silica precursors with short fluorinated alkyl chains, which rendered materials with additional features, namely enhanced cellular uptake and ability for tracking by ^{19}F NMR imaging.

References

[1] Wu, S.-H.; Mou, C.-Y.; Lin, H.-P. *Chem. Soc. Rev.* **2013**, *42*, 3862.

Acknowledgements: Luís Manuel Figueiredo Lopes acknowledges Fundação para a Ciência e a Tecnologia (FCT) for financial support (PhD grant BD/62616/2009).

P29. Hydrophobic Silica Based Aerogels Prepared at Atmospheric Pressure

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The unique properties of silica based aerogels are responsible for the continued interest in the development of these materials since Kistler's pioneering work. They are highly porous (densities in the range 3-500 kg.m^{-3}), excellent thermal insulators (thermal conductivity in the range 0.01–0.02 W.m^{-1}.K^{-1}) and non-flammable.[1]

The physical form (monolithic, powder, coating) and the physicochemical properties of silica based aerogels may be tailored in order to accomplish a specific application, thus determining the synthesis processes and parameters. Modifications towards hydrophobicity and lipophilicity are particularly appealing for applications in catalysis and protective coatings, when stability towards moisture is required.

In the present work, three approaches to the synthesis of hydrophobic silica-based aerogels are presented, with the common feature of being dried under subcritical conditions and avoiding hazardous post-synthesis hydrophobization reactions: *i*) hybrid aerogel powders prepared by a co-precursor method, using sodium silicate solution D40, from Solvay Portugal, and hexamethyldisilazane (HMDZ) for organic modification; *ii*) hybrid aerogel monoliths prepared from the co-precursors tetraethylorthosilicate (TEOS) and HMDZ, by optimization of the relative proportions; *iii*) aerogel monoliths prepared using TEOS as the only precursor, and an ageing solution containing an optimized proportion of HMDZ.

The hydrophobic aerogels were analyzed by scanning electron microscopy, contact angle measurements, N_2 adsorption-desorption isotherms at 77 K, envelope density measurements, and diffuse reflectance infrared (DRIFT) spectroscopy.

References

[1] Aegerter, M. A.; Leventis, N.; Koebel, M. M. (Eds), Aerogels Handbook, Springer Science+Business Media, New York, 2011.

Acknowledgements: The authors acknowledge Fundação para a Ciência e a Tecnologia (FTC) for financial support (Project PTDC/ECM/118262/2010, NANORENDER) and Solvay Portugal for kindly providing the sodium silicate solution.

P30. Stimuli-Responsive Fiber Scaffolds for Stem Cell Cultivation

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In vivo, some stem cells are found in specific microenvironments, composed by cells, solute factors and the extracellular matrix (ECM). Important ECM components are fibrous proteins that confer specific mechanical properties and structure. The electrospinning technique can be used to produce nanofibers that mimic different ECM environments (diameters of ca. 200-500 nm, and through the use of different materials to tailored rigidity). Nanofibers can also be produced aligned or randomly oriented, offering interesting scaffold properties to study the alterations in stem cell behavior induced by polymeric supports. The use of stimuli-responsive polymers to coat nanofibers is particularly interesting, offering the possibility of controlling the polymer-expanded/collapsed state in water by using an external stimulus, such as temperature. Copolymers of ethylene glycol methacrylates are water soluble, biocompatible, and exhibit a lower critical solution temperature that can be accurately tuned from 28 to 90ºC by adjusting the ratio of the monomers. If grown from nanofibers, these scaffolds can be used in the gentle release of adherent steam cells.

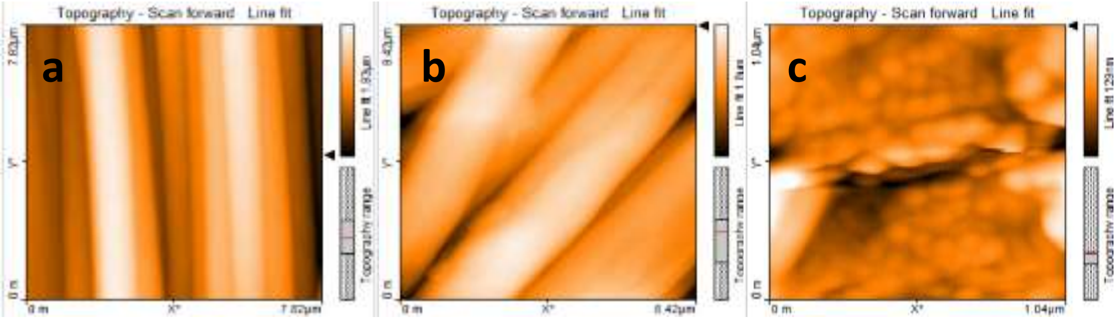

Figure 1. AFM image of the bare fibers (a) and fibers coated with thermoresponsive polymer, after treatment at 10ºC (b) and 50ºC (c).

References

[1] Paneva D.; Bougard F.; Manolova N.; Dubois P.; Rashkov I. *European Polymer Journal*, **2008**, 44, 3, 566-578.

[2] Roy, D.; Brooks, W. L. A.; Sumerlin, B. S. *Chem. Soc. Rev.* **2013**, 42, 7214-7243.

Acknowledgements: M.M. *S. A. acknowledges a postdoctoral grant from FCT, Portugal (SFRH/BPD/90720/2012).*

P31. Dynamics of magnetic moments coupled to electrons and lattice oscillations

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Inspired by the models of A. Rebei and G. J. Parker [1] and A. Rebei *et al.* [2], we studied a physical model which describes the behaviour of magnetic moments in a ferromagnet. The magnetic moments are associated to *3d* electrons which interact with conduction band electrons and with phonons. Each of the interactions were studied individually and then the results were collected assuming that the electron-phonon interaction can be neglected. The dynamics of the magnetic moments can be described, effectively, by an equation of motion of the Landau-Lifshitz [3] type, supplemented with friction and noise which are related by a fluctuation-dissipation theorem. We obtained, from first principles and under a nonperturbative approach, the two-point noise correlation functions. The physical interpretation of the conduction electron contribution to the noise correlation functions is of high interest as it is related to the shifts of the energy levels and the rates of nonconservative phenomena due to the interaction. These correlation functions exhibit properties which are characteristic of the ferromagnetic material in study.

References

[1] A. Rebei and G. J. Parker, Phys. Rev. B **67**, 104434 (2003).

[2] A. Rebei, W. N. G. Hitchon and G. J. Parker, Phys. Rev. B **72**, 064408 (2005).

[3] L. D. Landau and E. M. Lifshitz, Phys. Z. Sowiet **8**, 153 (1935).

Acknowledgements: B.M. thanks the support from project IT-PQuantum, as well as from Fundação para a Ciência e a Tecnologia (Portugal), namely through programme POC\-TI/PO\-CI/PT\-DC and projects PEst-OE/EGE/UI0491/2013,and DP-PMI and PEst-OE/EEI/LA0008/2013 and PTDC/EEA-TEL/103402/2008 QuantPrivTel, partially funded by FEDER (EU), and from the EU FP7 projects LANDAUER (GA 318287) and PAPETS (GA 323901). This work is also supported by the National Science Center in Poland as a research project in years 2011-2014.

P32. Novel nanostructured UCx materials for radioactive ion beam production

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An online isotope separator facility, as ISOLDE-CERN, produces ionic beams of rare isotopes with short lifetime (RIBs) for studies in nuclear and atomic physics, materials science, biology and medicine. These beams result from the bombardment of a target material by an accelerated proton beam, which creates nuclides that diffuse from the target and are ionized, accelerated and separated by mass before delivered at the experimental stations. In this process, the target is a key component. Micrometric uranium carbide-based targets have been widely used and are currently a reference material at ISOLDE. However, new and more intense RIBs are expected if submicron/nanostructured targets are achieved. Therefore, the aim of the present study is the preparation of nanostructured U-based carbides to be tested as target materials.

To reach this goal, two different approaches were tried. The first path was solid-gas reaction between metallic U and methane via UH_3 intermediate. In this way, a very fine and reactive UC powder was formed with crystallite size below 30 nm.

In the second approach, solutions of U acetate and acetylacetonate were prepared and processed by electrospinning. The solutions have different spinnability, resulting in nanometric fibers only in the case of the acetylacetonate precursor. Subsequent heat-treatments lead to the formation highly porous UC_x samples, with high surface area and crystallite sizes of 28 and 66 nm at 800ºC and 1550ºC, respectively.

These results show that nanostructured UC_x materials can be successfully produced by solid-gas reaction and electrospinning, the last technique being a very versatile method to tune the desired surface-interface features. Batches of some of these materials are now under preparation for in-situ proton irradiation.

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P33. Insulating Coatings for Electrical Conductors

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Electrical conductors need to be isolated from the environment and from other conductors, in order to prevent short circuits. Most wire and cable insulators are polymeric, either thermoplastic (can be softened and re-softened by repeated heating, but remain solid when operated within the rated temperature limits) or thermoset (undergo vulcanization, cross-linking or curing by heating, thus setting the physical properties to avoid melting or flow by repeated heating). These insulators are usually extruded onto the cables during the manufacturing process [1].

The present work presents the preliminary results on an insulating coating being developed for direct application onto naked aluminium cables or other conductors. It consists in a hybrid inorganic-organic nanocomposite of alumina within a polyurea-polyurethane binder. The synthesis process is environmental friendly, performed at room temperature and free of toxic by-products. The rheological properties of the precursor mixture are adequate to an easy polymerization *in situ*, and the coating curing may occur at the working temperature of the medium-voltage cable.

References

[1] P. Król, B. Król, *Colloid Polym Sci* **2012**, *290*, 879-893.

Acknowledgements: The authors acknowledge Fundação para a Ciência e a Tecnologia (FCT) and EDP-Distribuição for financial support. The authors are grateful to Prof. João Carlos Bordado and his group for kindly providing some of the pre-polymers and catalysts.

P34. Polymeric Core-Shell Nanoparticles Functionalized with 1,2-Propanediol Amino Functions for Wastewater Treatment

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Resin based methacrylates functionalized with 1,2-propanediol amino functions have shown to be efficient chelants of boron from wastewater [1]. Here, is presented an alternative process for boron chelation through the co-polymerization of modified methacrylates in thermosensitive core-shell nanoparticles (Figure 1).

A methyl methacrylate (MMA) core and a shell composed by a copolymer of the thermosensitive monomer N-isopropylacrylamide (NiPAAM), with the positively charged monomer 2-aminoethyl methacrylate hydrochloride AEMH and a methacrylate modified with one, two or three diol groups [2], were prepared through emulsion polymerization. The aforementioned modified methacrylates were synthesized to test different boron chelating efficiencies. Mono diol methacrylate was obtained by acidification of glycidyl methacrylate. The methacrylate with two diol functions – di-(1,2-propanediol)aminoethyl methacrylate (HPAEM) – was synthesized through basic catalysis using AEMH and glycidol. Optimization of three diol methacrylate synthesis is still going on.

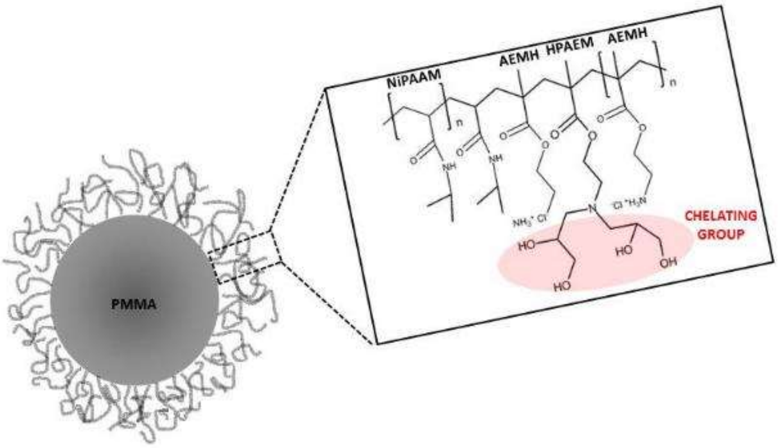

Figure 3- Polymer nanoparticles with a PMMA core and a co-monomer polymer shell of NiPAAM, AEMH and methacrylate bearing two 1,2-propanediol amino functions.

References

[1] Senkal, B. F.; Bicak, N. *Reactive & Functional Polymers.* **2003**, 55, 27–33.

[2] Moura, L. M.; Martinho, J. M. G.; Farinha, J. P. S. *Chem. Phys. Chem.* **2010,** 11, 1749 – 1756.

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P35. Retirado do programa

P36. Ultrastructure of Sialoliths

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This study evaluates the internal architecture and growth patterns of 30 sialoliths characterized at different scales by computed microtomography and electron microscopy. Radiographs were acquired using a µCT SkyScan 1172 instrument with a 1.3 Megapixel camera operated at 10W. Microscopy observations were carried out with backscattered electron (BSE) signal using a JEOL JSM 7001F operated at 15 kV and a Hitachi H8100 instrument operated at 200 kV.

Tomography reconstructions show cores in most of the sialoliths, these were surrounded by concentric or irregular patterns with variable degrees of mineralization (Figure 1 (a)). At finer scales the sialoliths consisted of banded and globular structures ((Figure 1 (b) and (c)). The banded structures are compatible with the Liesegang–Ostwald precipitation phenomenon, whereas the globular ones appear to develop self-similar features as a result of a viscous fingering process (Figure 1 (b)). Electron diffraction patterns demonstrated that Ca- and P-based electrolytes crystallize in a structure close to that of hydroxyapatite (Figure 1 (c)).

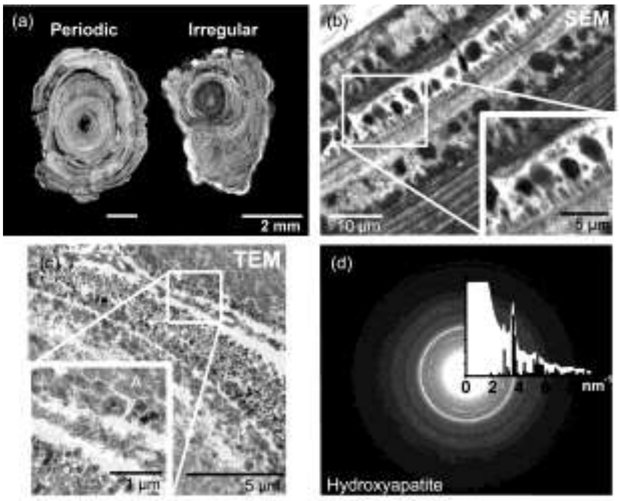

Figure 4. (a) Coronal tomography reconstructions of two evaluated specimens. (b) Globular structures presenting self-similar morphology. (c) Banded structures. (d) Diffraction pattern obtained in the region A

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P37. Effect of Ag nanoparticles and casting solution composition on structure and properties of asymmetric cellulose acetate membranes prepared via phase inversion method

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Asymmetric cellulose acetate (CA) and cellulose acetate–silver nanocomposite membranes were prepared via the wet phase inversion method by dispersing polyvinylpirrolydone-protected Ag nanoparticles in the CA casting solutions of different compositions. Gelling was induced by immersion precipitation in a cold water bath. Silver nanoparticles were synthesized ex situ and added to the casting solution as a concentrated aqueous colloidal dispersion.

The effects of the casting solution composition on the structure, pure water flux (PWF) and separation properties of the membranes were studied by comparing the nanocomposites with the silver-free materials. The membrane composition played an important role in the location of the silver nanoparticles, the larger nanoparticles were mostly observed by scanning electron microscopy in the bottom of the membranes. Incorporation of nanoscale silver resulted in structural changes and in an increase in hydraulic permeability. Increasing Ag concentration in the casting solution film resulted also in increasing pure water flux.

P38. In Vitro Controlled Drug Release From Contact Lens Materials Under Physiological Ocular Tear Flow

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Nowadays, over 90% of current ophthalmic drugs are administered topically through eye drops, but the residence time of the drug in the eye is short, and only 1% to 7% of the administered drug is absorbed by the eye, leading to a final poor drug bioavailability and, in some instances, to undesirable side effects [1].

In the last few years, efforts have been made to develop more efficient drug delivery systems. Therapeutic soft contact lenses have demonstrated to be an ideal platform for the controlled delivery of numerous drugs as well as comfort molecules [2].

Typically, drug release experiments are conducted at infinite sink conditions, but, under normal physiological conditions, the human eye has a reduced tear volume and a tear turnover rate that varies between 1 and 4 µL/min Thus, infinite sink conditions are not the most appropriate to study the drug release kinetics in the eye.

The present work involves the development of a novel microfluidic device which simulates the physiological conditions (temperature, tear volume and flow rate) and the test of contact lens materials as controlled drug release vehicles. The microfluidic device was produced from Poly(methyl methacrylate) (PMMA) and engineered to possess an inner chamber with a volume of 45 µL. Isotonic saline solution was allowed to flow directly over the therapeutic contact lens with a volumetric flow rate of approximately 3µL/min, similar to that of the human eye. Two types of hydrogels were prepared as contact lens materials: a poly-hydroxyethylmethacrylate (pHEMA) based hydrogel and a silicone hydrogel. Both hydrogels were loaded with an antibiotic (levofloxacin) and an antiseptic (chlorhexidine) by soaking in the drug solutions. Extended drug release for 2-3 days was observed, while the experiments performed in infinite sink conditions, showed a release time of 10 hours. This demonstrates that the hydrodynamic conditions significantly affect the drug release kinetics of therapeutic contact lenses and that extrapolation to in vivo behavior should be done with care.

References

[1] Lang, J.C., *Adv. Drug Deliv. Rev.* **1995**, 16 (1), 39–43.
[2] A. Urtti, *Adv. Drug Deliv. Rev*. **2006**, 58 (11), 1131–1135.

P39. Biomimetic Replicas - Transfer of Complex Architectures from Plant Surfaces onto Polymeric Materials

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The manipulation of the topography at the micro and nano-level is a way to enhance the surfaces with which we interact. The surfaces in the natural world present characteristics well adjusted to their underlying biological functions, which generally results from the existence of a hierarchical pattern of micro- and nanostructures. Plant surfaces are particularly rich in topographies that influence properties such as adhesion and wettability, providing inspiration for the improvement of existing artificial surfaces [1]. The replication of natural patterns to polymeric materials constitutes a simple way to identify the micro-architectures responsible for such properties. However, plant micro-architectures are challenging to replicate, due to their complexity and high aspect ratio features [2]. A soft lithography technique, based on a two step casting, was developed by Koch *et al* [3] for the replication of plant micro-features. The application of Koch's molding technique enabled the accurate transference of the microstructures from a set of leaves (*Oxalis pes-caprae*, *Gladiolus communis*) and petals (*Rosa*, *Osteospermum 'Nairobi Purple'*) to an epoxy resin. The replicas were characterized according to their structure (profilometry, optical microscopy, SEM), wettability (static, dynamic) and ability to adhere particles, microorganisms and animal cells. Replicated surfaces had nano-features with roughness between 0.4 and 12.3 μm, which conferred a hydrophobicity slightly under the one observed in the natural samples. Drop impact studies demonstrated that the replicas' micro-topography do not reproduce completely the spread and rebound behavior characteristic of the original samples, a fact consistent with the high contact angle hysteresis (>22°). The replicas of the *Oxalis pes-caprae* manifested a capacity to avoid microorganism adhesion significantly higher (~6 times) than a control surface.

References

[1] - Bhushan, B. *Phil. Trans. R. Soc. A.* **2009**, *367*, 1445-1486

[2] - Koch, K.; Schulte, A. J.; Fischer, A.; Gorb, S. N.; Barthlott, W. *Bioinspir. Biomim*. **2008**, *3*, 1-10

[3] - Koch, K.; Dommisse, A.; Barthlott, W.; Gorb, S. N. *Acta Biomater.* **2007**, *3*, 905-909

P40. Local quantum critical systems - Response functions and transport in and out of equilibrium

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In the first part of the talk I will introduce a set of Kondo-like systems, featuring magnetic impurities in contact with a bath, whose equilibrium phase diagram comprises several stable phases separated by quantum critical lines. I will mention some of the consequences of such critical points on the equilibrium physical properties.

In the second part of the talk I will address the non-equilibrium properties of such systems when in contact with baths at different thermodynamic potentials. I will describe some of the steady state properties, in particular a surprising emergence of an effective temperature for the impurity.

Finally, I will describe some ongoing work on real-time dynamics after a quench.

P41. A Novel Substrate Based on Graphene Oxide and Silver Nanoparticles for Detection of Nucleic Acids by SERS

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Surface-enhanced Raman scattering (SERS) is a powerful and reliable analytical technique for the ultra-sensitive detection of analytes[1]. Substrates used in SERS are typically composed by metallic nanoparticles, in particular silver (Ag) and gold (Au), due to the strong enhancement that may be induced in the Raman signal of surface adsorbed molecules. Recently, the SERS studies of graphene based substrates has become an important theme of research which include the research on graphene/metal composites and the interaction of graphene with metals[2].

Herein, Ag NPs decorated graphene sheets (Ag/GO) were prepared for use as good SERS substrate for biomolecules detection. Ag NPs were synthesized in situ at the surface of graphene oxide (GO) sheets according to a method previous described by us[3]. GO was selected to prepare these nanocomposites since the oxygen functional groups present at its surface function as nucleation sites for the metallic NPs[3]. The final aqueous suspension was used to identify adenine, cytosine, guanine, thymine, ssDNA, and dsDNA.

The SERS results summarized in Fig.1 show that Ag/GO can act as SERS substrate for adenine, cytosine, and dsDNA at 10^{-5} M concentration, with $EF_{analytical}$ between 10^3 and 10^4. The other analytes were not identified with this substrate. Detailed studies are in progress to elucidate these results that are promising for the selective detection of nucleic acids.

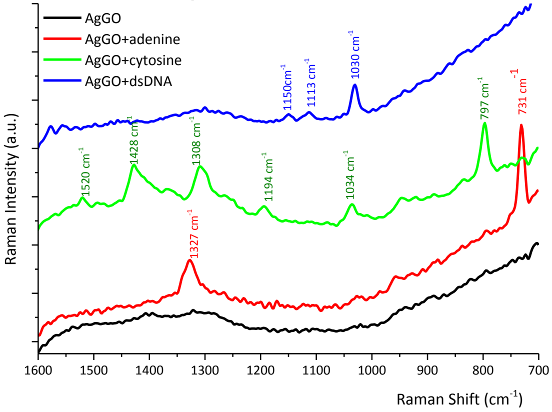

Figure1 – SERS spectra of adenine, cytosine, and dsDNA using AgGO as substrate.

References

[1] J. Ando, K. Fujita, *Current Pharmaceutical Biotechnology* **2013**, *14*, 141.
[2] S. T. Sun, P. Y. Wu, *Physical Chemistry Chemical Physics* **2011**, *13*, 21116.
[3] G. Goncalves, P. A. A. P. Marques, C. M. Granadeiro, H. I. S. Nogueira, M. K. Singh, J. Gracio, *Chemistry of Materials* **2009**, *21*, 4796.

P42. Particles Decorated by an Ionisable Thermoresponsive Polymer Brush in Water: Experiments and Self-Consistent Field Modelling

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Responsive polymer nanoparticles with well controlled size distributions are not only of academic interest, but are also considered for a wide range of applications, such as sensors, medical diagnostics or environmental remediation.

We have synthesized anionic multi-stimuli responsive core-shell polymer nanoparticles with low size dispersity, composed of glassy poly(methyl methacrylate) cores of ca. 40 nm radius and poly(N-isopropyl acrylamide) (PNIPAM) anionic brush-like shells with methacrylic acid comonomers.[1] We observed a volume phase transition upon an increase in temperature and this response was pH and ionic strength dependent.[1] We modeled the multi-responsive behavior of the hydrophobic polyelectrolyte brush using the Scheutjens-Fleer Self-Consistent Field (SF-SCF) approach,[2,3] confronted the predicted change in the brush height with the observed change of the hydrodynamic radius and degree of dissociation and obtained estimates for the average chain lengths of the corona chains, the grafting density and charge density distributions.

References

[1] Pinheiro, J. P.; Moura, L.; Fokkink, R.; Farinha, J. P. S. *Langmuir* **2012**, *28*, 5802-5809.

[2] Rud, O. V.; Mercurieva, A. A.; Leermakers, F. A. M.; Birshtein, T. M. *Macromolecules* **2012**, *45*, 2145-2160.

[3] Alves, S. P. C.; Pinheiro, J. P.; Farinha, J. P. S.; Leermakers, F. A. M. submitted.

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P43. New Routes for Bio-Inspired Materials: APIs as Spacers And Guest

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API coordination complexes present a new pathway for the development of improved precursors to new bio-inspired materials. In this study we report the first coordination complexes of gabapentin, a neuroleptic drug, with several lanthanide chlorides (LnCl3), (Ln= La^{3+}, Ce^{3+}, Nd^{3+}, Er^{3+}), Mn^{2+} and Y^{3+}, obtained by mechanochemistry, a "green" and environment-friendly synthetic technique. Gabapentin is a well-known drug that has been used in our group mainly in polymorphism[1] and co-crystallization studies.[2]

The networks obtained are based on monomers, dimers, trimers, hexamers and infinite 1D chains. In most cases, gabapentin coordinates to the metal/lanthanide using at least one of the following coordination modes: the bidentate coordination –chelation, mode I; the "bridge" coordination, mode II; and the "bidentate-bridge", mode III.[3]

Coordination complexes of an active principal ingredient (API) may open up a new route for the delivery of drugs: as the release of the API would be achieved by material degradation, these networks could act as drug carriers and deliverers avoiding side effects due to the release of the linker.[4] Making use of the paramagnetic behaviour of the metal/lanthanide we can go a step further and explore the possibility of using them as contrast agents in imaging for magnetic resonance imaging (MRI).[4,5]

References

[1] Braga, D.; Grepioni, F.; Maini, L.; Rubini, K.; Polito, M.; Brescello, R.; Cotarca, L.; Duarte, M. T.; Andre, V.; Piedade, M. F. M. *New J. Chem.* **2008**, *32*, 1788-1795; Reece, H. A.; Levendis, D. C. *Acta Crystallogr. Section C-Cryst. Struct. Commun.* **2008**, *64*, O105-O108.

[2] Andre, V.; Fernandes, A.;. Santos, P. P.; Duarte, M. T. *Cryst. Growth Des.* **2011**, *11*, 2325 2334.

[3] Quaresma, S.; André, V.; Antunes, A. M. M.; Cunha-Silva, L.; Duarte, M.T. *Cryst. Growth Des.* **2013**, *13,* 5007-5017.

[4] McKinlay, A. C.; Morris, R. E.; Horcajada, P.; Ferey, G.; Gref, R.; Couvreur, P.; Serre, C. *Angew. Chem. Int. Ed.* **2010**, *49*, 6260-6266.

[5] Keskin, S.; Kizilel, S. *Ind. Eng. Chem. Res.* **2011**, *50*, 1799-1812.

Acknowledgements: Authors acknowledge funding to Fundação para a Ciência e a Tecnologia (PTDC/CTM-BPC/122447/2010, Projeto Estratégico - PEST-OE/QUI/UI0100/2013, RECI/QEQ-QIN70189/2012 and SFRH/BPD/78854/2011).

P44. Improving protective coatings for AA2024 alloys with pH-sensitive active containers

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This work contributes to the development of new feed-back active anticorrosion systems. Corrosion protection of aluminium alloys often relies on the application of a coating on the metallic surface. The coating provides a barrier that restricts the ingress of corrosive species. Novel feedback-active coating can be composed of a passive matrix and active compounds- healing agents- for extra corrosion protection. The coatings have to provide release of the healing agent to stop local corrosion rapidly after changes in coating integrity.

The aim of this work is to study the anti-corrosion properties of water-based epoxy coatings loaded with pH sensitive particles, acting as feedback active containers for healing agents and applied to aluminium alloy AA2024-T3. These pH sensitive particles start to dissolve at acidic pH, releasing the healing agent, which then suppresses the corrosion activity of the alloy. Thus, pH sensitive particles were loaded with different healing agents. Electrochemical Impedance Spectroscopy (EIS) was used to estimate the electrochemical parameters related to the barrier properties of the coatings and corrosion protection ability provided when loaded with pH sensitive containers. Study of barrier properties were accomplished by SEM/EDX analyses. The corrosion inhibition ability was also corroborated by localised electrochemical measurements – scanning vibrating electrode technique (SVET) and localised impedance spectroscopy (LEIS).

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P45. Biocompatible fluorescence based temperature sensor

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Optical sensors exploiting the fluorescence temperature dependence of either intensity or lifetime have been widely explored.[1] The use of temperature fluorescence based sensors in real applications is very simple because they can work with cheap excitation sources such as LEDs, and the signal can be collected in intensity, time or phase modes. Additionally, they exhibit a very fast response and reversibility.

Stimuli-responsive polymers are particularly interesting materials, giving the possibility to control the polymer expanded/collapsed state in water by using an external stimuli, such as temperature.[2] Water-soluble biocompatible copolymers of 2-(2-methoxyethoxy)ethyl methacrylate and oligo(ethylene oxide)methacrylate exhibit a lower critical solution temperature (LCST) that can be accurately tuned by adjusting the ratio of the two monomers.[3]

Herein we present the preparation of these themoresponsive co-polymers labeled with different pyrene derivatives using atom transfer radical polymerization (ATRP), and the LCST tuned to ca. around 37ºC. The collapse/expansion of the polymer chains changes the pyrene excimer-to-monomer intensity ratio, providing a very sensitive remote temperature sensing platform. Additionally, the intensity of the monomer is temperature independent, allowing the internal calibration of the sensor system.

References

[1] McDonagh, C.; Burke, C. S.; MacCraith, B. D. *Chem. Rev.* **2008**, *108*, 400-422.

[2] Roy, D.; Cambre, J. N.; Sumerlin, B. S. *Progress in Polymer Science* **2010**, *35*, 278-301.

[3] Lutz, J.-F. *J. Polym. Sci: Part A: Polym. Chem.* **2008**, *46*, 3459-3470.

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P46. Morphology Of Organic Memories Based On A Ferroelectric/Semiconductor Phase-Separated Blend

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Recently non-volatile organic memories based on ferroelectric phase-separated blends have been reported. These memories are programmed making use of the two stable polarization states of the ferroelectric [1, 2]. The proposed mechanism is based on the creation of a stray field: when the ferroelectric is polarized an electric field is generated between the polarization charges and the respective opposite image charges at the electrode [3]. The field lines, which cross the semiconductor phase, modulate the charge injection at the electrode-semiconductor interface inducing a resistive switching.

In order for this mechanism to work a lateral phase separation has been proposed to occur [1-6] between the ferroelectric and the semiconductor. In this work we aim to clarify the structure of the blend by using as a cross-linkable polyfluorene the F8T2Ox1 (an oxetane-functionalized derivative of poly(9,9-dioctylfluorene-*alt*-bithiophene) [7, 8] as a semiconductor and the random copolymer poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)) as the ferroelectric.

To achieve this goal, memory devices are prepared by blending P(VDF-TrFE) and F8T2Ox1. After the F8T2Ox1 cross-linking, the P(VDF-TrFE) is removed by immersing the blend in a selected solvent. The obtained morphology is observed by non-contact AFM before and after P(VDF-TrFE) removal.

References

[1] Asadi, K.; de Leeuw, D. M.; de Boer, B; Blom, P. W. M. *Nature Materials* **2008**, *7*, 547-550.
[2] Khan, M. A.; Bhansali, U. S.; Cha, D.; Alshareef, H. N. *Adv. Funct. Mater.* **2013**, *23*, 2145-2152.
[3] Kemerink, M.; Asadi, K.; Blom, P. W.M.; de Leeuw, D. M. *Organic Electronics* **2012**, *13*, 147-152.
[4] McNeill, C. R.; Asadi, K.; Watts, B.; Blom, P. W. M.; de Leeuw, D. M. *Small* **2010**, *6*, 508-512.
[5] Asadi, K.; Wondergem, H. J.; Moghaddam, R. S.; McNeill, C. R.; Stingelin, N.; Noheda, B.; Blom, P. W. M.; de Leeuw, D. M. *Adv. Funct. Mater.* **2011**, *21*, 1887-1894.
[6] Li, M.; Stingelin, N.; Michels, J. J.; Spijkman, M.-J.; Asadi, K.; Beerends, R.; Biscarini, F.; Blom, P. W. M.; de Leeuw, D. M. *Adv. Funct. Mater.* **2012**, *22*, 2750-2757.
[7] Charas, A.; Ferreira, Q.; Farinhas, J.; Matos, M.; Alcácer, L.; Morgado, J. *Macromolecules* **2009**, *42*, 7903-7912.
[8] Farinhas, J.; Ferreira, Q.; di Paolo, R. E.; Alcácer, L.; Morgado, J.; Charas, A. *J. Mater. Chem.* **2011**, *21*, 12511-12519.

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P47. Synthesis of Carbon Nanostructures Using Plasmas

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A microwave, atmospheric argon plasma driven by surface waves has been used for synthesizing carbon nanostructures. The method is based on sending vaporized ethanol molecules through a microwave (2.45 GHz) argon plasma environment, where decomposition of ethanol molecules takes place and carbon atoms are created. These carbon atoms nucleate subsequently in the outlet plasma stream to form nanostructures that are collected by nylon membrane filters. A surfatron-based setup is used to create the surface wave induced microwave plasmas. External, forced cooling/heating has been applied using a cryostatic system to fix the temperature in the nucleation zone of the plasma reactor. To this end, a tubular heat exchanger concentrically aligned with the discharge quartz tube has been placed immediately after the end of the active plasma zone. The synthesized carbon nanostructures were analyzed by Transmission Electron Microscopy (TEM), and micro-Raman spectroscopy. Carbon nanostructures with different morphologies have been selectively synthesized through the control of the outlet plasma stream temperature.

P48. Silica Based Superhydrophobic Coatings

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Meteorologists distinguish between three basic types of ice forming on vertical and horizontal surfaces by deposition of supercooled water droplets: soft rime, which is a fragile white ice, feathery and light, that forms under calm or light wind; hard rime, which is also a white ice, but denser and less milky, with a comb-like appearance, that forms under high wind velocities; and clear ice, which is transparent and homogeneous, denser than both rimes, and that clings tenaciously to the surfaces on which it forms. Depending on the atmospheric conditions, the three types of ice may form on tree branches, houses, cables or aircraft surfaces, sometimes with dangerous consequences.

One of the most promising approaches to the creation of icephobic surfaces involves the development and preparation of superhydrophobic coatings.[1] There are different strategies to address this problem, but in general authors agree that decreasing the surface energy of the material, increasing the local contact angle of a textured surface and forming a texture with multimodal roughness on the surface are essential. The lotus leaf (Figure 1) is a good example of how nano roughness is responsible for increasing the contact angle of water.

Figure 1. Water droplets on a lotus leaf.

In the present work, a superhydrophobic coating to be applied on aluminium surfaces was developed, based on silica nanoparticles prepared by the Stöber process and embedded in a fluorinated acrylic copolymer.

References

[1] L. B. Boinovich, A. M. Emelyanenko, *Mendeleev Commun*. **2013**, *23*, 3-10.

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P49. Characterization of Friction Stir Channels

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Friction stir channelling (FSC) is an innovative solid-state manufacturing technology able to produce continuous internal channels, open or closed, in a monolithic plate in a single step. During FSC a controlled amount of workpiece material flow-out from the processed zone producing the internal channel. The heat energy that softens the workpiece material is generated from dissipation during plastic deformation, internal viscous dissipation during the material flow and dissipation from frictional work between the tool and the workpiece.

The high level of adaptability of FSC makes it possible to apply to many different technical field domains and can bring significant advantages for already existent and new industrial applications.

This research work is based on a detail metallographic, geometric, roughness and hardness analysis of integral and continuous FS channels produced in a monolithic plate of the non-heat treatable aluminium alloy strain hardened AA5083-H111 with 15mm of thickness. In this study channels produced with different technological parameters were carefully characterized. The metallography of the region that surrounds the channel is presented and a relationship between it and the processing parameters is pointed out. The hardness distribution in the processing zone, especially in the nugget zone, is presented and discussed. Channel's geometric characterization is also presented and discussed as well as the roughness of the interior of the channels. The channel microstructure and geometry were obtained using optical microscopy and the roughness features were obtained, measured and analysed via laser microscopy and SEM.

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P50. How to improve the antimicrobial activity on biomaterials?

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Transition metal carbonitrides (MeCN, Me= Ti and Zr) coatings doped with silver nanoparticles are being tested to determine the viability of their application in head femoral hip prosthesis, as a surface modification to prevent implant rejection due to infection, one of the major causes of revision surgeries [1,2]. In a previous study, the biological results of these coatings revealed no sufficient antibacterial activity to prevent bacteria colonization and biofilm formation, probably due to the low or even no ionization of silver [3]. Thus our first aim was to evaluate the effect of the complex medium used in biological assays tryptic soy broth (TSB), the surface properties of the samples were assessed after immersion on that medium by comparison with immersion in a salt solution (SS), NaCl (0.9 %) - that can promote the ionization of silver. Surfaces morphological changes were observed by scanning electron microscopy (SEM) and silver nanoclusters were found after contact with SS depending on the silver content of the films. However, coatings with low content of silver (Ag < 11 at. %), did not show significant formation of Ag on the surface, and hence, low silver activity is foreseen. In addition, in order to achieve the silver ionization, an oxidative procedure, named silver activation, was performed. Significant morphological changes were observed, with silver based masses on surface. These activated samples showed antimicrobial activity, assessed by Halo test, showing promising results after silver activation. As a result, electrochemical tests have been carried out in order to understand the silver inactivity before activation and to propose a model for the silver activation mechanism.

[1] Bernard, L.; Hoffmeyer, P.; Assal, M.; Vaudaux, P.; Schrenzel, J.; Lew, D. *The Journal of antimicrobial chemotherapy* **2004**, *53*, 127–129.

[2] Hetrick, E. M.; Schoenfisch, M. H. *Chemical Society reviews* **2006**, *35*, 780–789.

[3] Carvalho, I.; Henriques, M.; Oliveira, J. C.; Almeida Alves, C. F.; Piedade, A. P.; Carvalho, S. *Science and Technology of Advanced Materials* **2013**, *14*, 035009.

P51. Drug Release from pHEMA Based Hydrogels Used for Therapeutic Contact Lenses

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Most ophthalmic formulations are administered topically, leading to significant drug loss and may cause undesirable side effects, as a result of the drug absorption into the blood stream. Ophthalmic drug delivery by contact lenses is expected to be more efficient than eye drops due to the continuous extended release of drug and increased residence time in the tear film.

In this work we demonstrate the successful in vitro extended release – along 10 hours – from a poly-2-hydroxyethylmethacrylate (p-HEMA) based hydrogel and a silicone hydrogel of two drug molecules: the broad spectrum antibiotic levofloxacin and the antiseptic chlorhexidine. The silicone hydrogel resulted from the addition of TRIS, a hydrophobic monomer containing silicon (3-tris(trimethylsilyloxy)silylpropyl 2-methylprop-2-enoate), to pHEMA.

The samples were characterized with respect to their transmittance, wettability, swelling behavior, friction coefficient, ionic permeability and mechanical properties. The surface topography/morphology was accessed by atomic force microscopy and scanning electron microscopy.

The hydrogels were loaded with the drug by soaking in the respective solution. In vitro drug release was followed through drug quantification by high performance liquid chromatography and by spectrophotometry UV-Vis.

Several models of drug release kinetics were evaluated. Peppas-Korsmeyer model yielded the best fitting to the experimental data, demonstrating a classical Fickian diffusion.

Both hydrogels maintained levofloxacin concentration in the release medium above the minimum inhibitory concentrations (MICs) of two different bacteria: *Staphylococcus aureus* and *Pseudomonas aeruginosa*, for about 9 hours. The concentration of chlorhexidine, when compared to commercially available products, was suitable and below toxic levels for an identical period.

P52. Copper Thin Films Electrodeposited from EMIM-Based Ionic Liquids

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Technological development of functional metal and alloy coatings has been driven by the increase use of exotic metals in the electronic and energy industry, strict requirement for a greener manufacturing process and the need for higher quality films with better controlled properties. One proposed method is an electrodeposition process using an ionic liquid as solvents. Research in ionic liquids has increased exponentially in the last 15 years due to their superior properties compare to aqueous solutions. Ionic liquids can be used to deposit many non-reactive metals due to their large potential window, does not suffer from hydrogen embrittlement due to their zero vapour pressure and does not require a toxic bath as they are non-flammable, non-volatile and recyclable [1].

Although a large body of work has been carried out on ionic liquids, the electrodeposition process from ionic liquid solutions is still not fully understood [1]. This work seeks to relate the morphology and properties of the metal coatings with its nucleation and growth mechanism and kinetics; the atomic processes occurring during electrodeposition; the structure and properties of the ionic liquids and ionic liquid solutions in the bulk solution as well as near the interface; electrode surface characteristics and environmental conditions.

The results shown will be for the electrodeposition of copper from Cu-salt solutions in 1-ethyl-3-methylimidazolium ethyl sulfate (EMIM $EtSO_4$) and 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM TFSI) ionic liquids. This will include the change in microstructure and morphology of the copper films at varying concentrations of copper salt, types of copper salt, deposition temperature and deposition. The structure of the EMIM $EtSO_4$ ionic liquid and the solution (EMIM $EtSO_4$ – $CuCl_2$) will also be shown. This was done by identifying the vibration modes of EMIM $EtSO_4$ using Raman and IR spectroscopy in conjunction with density functional theory (DFT) calculations. Changes in Raman and IR spectra due to the $CuCl_2$ salt are also studied in order to see the changes in structure, identify the metal complex in the solutions and determine if any intermediate compound/structure are formed.

References

[1] Endres, F.; Abbott, A.; MacFarlane, D. *Wiley VCH.* Weinheim 2008

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