I RGC

I REUNIÃO DO GRUPO DO CARBONO

I MEETING OF THE CARBON GROUP

12-13 / junho / 2017 PORTO

Sociedade Portuguesa de Química

Grupo do Carbono

Livro de Resumos

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O presente livro foi produzido a partir dos trabalhos submetidos directamente pelos autores. Foram apenas introduzidas pequenas alterações de edição que de modo algum modificaram os conteúdos científicos. O modelo final de impressão foi estabelecido para a I Reunião do Grupo do Carbono de acordo com as normas divulgadas publicamente nos anúncios do evento. A responsabilidade dos conteúdos científicos é dos respectivos autores.

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PREFÁCIO

O Grupo do Carbono foi criado no âmbito da Sociedade Portuguesa de Química em setembro de 2015, por solicitação de um conjunto de associados que desenvolvem actividade nesta área científica nas Universidades de Aveiro, Coimbra, Évora, Lisboa, Nova de Lisboa e Porto, e também no IPB. Em 2016, o Grupo do Carbono foi admitido como membro da European Carbon Association.

O Grupo do Carbono pretende congregar os interesses de quem trabalha com o carbono nas suas diversas vertentes e alotropias, incluindo investigadores na área da química, da física e dos materiais, e ainda todos os que utilizam materiais de carbono em qualquer das suas múltiplas aplicações industriais.

O evento que agora celebramos (I RGC) marca o início das actividades do Grupo do Carbono. Este evento pretende privilegiar a divulgação de trabalhos que envolvam fundamentos, desenvolvimentos e aplicações dos materiais de carbono nas mais variadas áreas do conhecimento científico. A I RGC pretende ainda ser um fórum de discussão sobre os mais recentes avanços na ciência dos materiais de carbono, estimulando novas colaborações entre grupos de investigação multidisciplinares, e apelando à participação activa de estudantes e jovens investigadores que desenvolvam trabalhos neste domínio.

O programa do encontro integra sessões plenárias e comunicações convidadas sobre temas actuais, proferidas por investigadores de renome internacional, incluindo ainda comunicações orais e em painel, no sentido de proporcionar um evento de elevada qualidade científica. Durante o encontro realizar-se-á também uma Assembleia Geral dos associados, na qual será eleita a Direcção do Grupo do Carbono para o próximo biénio.

A Comissão Organizadora agradece a todas as empresas e instituições que apoiaram a realização deste evento, assim como a todos os participantes, cuja adesão a este projecto constitui um incentivo para futuras actividades e realizações do Grupo do Carbono.

Porto, 12 de junho de 2017

José Luís Figueiredo

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PROGRAMA CIENTÍFICO

12 de junho de 2017

10:00-11:00	Registo e entrega de documentação
11:00-11:30	Sessão de Abertura
11:30-12:15	**CPL1** “Plasmonic effects in graphene” N.M.R. Peres (U. Minho)
12:15-12:45	**CC1** “Doped graphene and composite carbon materials as electrocatalysts towards Pt-free fuel cells” M.J. Lázaro (Instituto de Carboquímica, CSIC), D. Sebastián, G. Lemes, J.M. Luque, M.V. Martínez-Huerta, E. Pastor
12:45-14:30	Pausa para almoço
14:30-15:00	**CC2** “Nanocarbon hybrids grown by Microwave plasma CVD and their applications” N. Santos, A. Carvalho, A. Fernandes, F.M. Costa (U. Aveiro)
15:00-15:15	**CO1** “Label-free detection of DNA hybridization with graphene field-effect transistors” R. Campos (INL, Braga), J. Borme, G. Machado Jr., M.F. Cerqueira, P. Alpuim
15:15-15:30	**CO2** “Preparation of carbon nanotubes-based heterostructures by atomic layer deposition” R. Silva (CICECO, U. Aveiro), A.V. Girão, N. Pinna, R.F. Silva
15:30-16:30	Comunicações Flash
16:30-17:30	Apresentações em Painel e Cocktail (patrocinado pela Paralab)
17:30-18:30	Assembleia geral do Grupo do Carbono
20:30	Jantar do Evento Restaurante Casa da Música Casa da Música - Piso 7 Avenida da Boavista, 604-610 4149-071 Porto

13 de junho de 2017

09:30-10:15	**CPL2** “The unique versatility of carbon materials” F. Rodríguez-Reinoso (Universidad de Alicante)
10:15-10:45	**CC3** “Activation with carbon dioxide or air: Which is better?” P. Carrott (U. Évora)
10:45-11:15	Pausa para café
11:15-11:45	**CC4** “Carbon based materials: applications in chemical catalysis and electrocatalysis” C. Freire (Fac. Ciências, U. Porto)
11:45-12:00	**CO3** “Mechanochemical preparation of Pd and Pt composites for Suzuki-Miyaura reactions” M. Soliman (CQE, IST/UTL), A.P.C. Ribeiro, M.S. Saraiva, E.C.B.A. Alegria, A.J.L. Pombeiro
12:00-10:15	**CO4** “Modulation of carbon dot fluorescence by heteroatom-doping and microwave-synthesis” P. Ferreira (CIQ, U. Porto), D.M.A. Crista, L.P. Silva, J.C.G.E. Silva
12:15-12:30	**CO5** “Upconverting phosphors/carbon dots nanostructures for glucose sensing” A. Kumar (CIQ, U. Porto), L.P. Silva, D.M.A. Crista, P.J.O. Ferreira, J.C.G.E. Silva, K. Kumar
12:30-12:45	**CO6** “Aminated fluorescent carbon dots: Synthesis and characterization” I. Martins (CQM, U. Madeira), H. Tomás, J.Rodrigues
12:45-14:30	Pausa para almoço
14:30-15:00	**CC5** “Properties of carbon materials for catalytic wet peroxide oxidation” H.T. Gomes (Instituto Politécnico de Bragança)
15:00-15:15	**CO7** “CNTs growth geometry and CNFs chirality: Role of solid-state routes and faceting” L.S. Lobo (LAQV/REQUIMTE, FCT/UNL)

15:15-15:30 **CO8** “Carbon nanotubes as efficient catalysts - A computer modeling approach”
A. Magalhães (UCIBIO/REQUIMTE, Fac. Ciências - U. Porto), I.S. Tavares, C.F.B.R. Figueiredo

15:30-15:45 **CO9** “Challenges in the organic functionalization of carbon nanotubes”
M. Proença (Centro de Química, U. Minho), R. Araújo, R.M. Novais, E. Cunha, M. Melle-Franco, P.E. Lopes, M.C. Paiva

15:45-16:15 Pausa para café

16:15-16:30 **CO10** “Recovery of rare earth elements using a magnetic graphene-based nanocomposite”
C. Lopes (CICECO, U. Aveiro), E. Afonso, E. Pereira, C. Vale, T.Trindade, C.M. Silva

16:30-16:45 **CO11** “Layer-by-layer films of graphene and natural polymers”
M. Silva (IPC/i3N, U. Minho), S.G. Caridade, A.C. Vale, E.P. Cunha, M.P. Sousa, J.F. Mano, N.M. Alves, M.C. Paiva

16:45-17:00 **CO12** “Enhancement of thermal properties of fluids using nanocarbons”
C. Castro (CQE/IST), F.E.B. Bioucas, J.M.P. França, S.I.C. Vieira, X. Paredes, S.M.S. Murshed, M.J.V. Lourenço, F.J.V. Santos, A.A.H. Pádua

17:00-17:15 **CO13** “An innovative method of graphite exfoliation in an aqueous-organic medium”
B. Figueiredo (GRAPHENEST), R.P. Silva, V.E. Abrantes

17:15-17:45 Sessão de Encerramento

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PLASMONIC EFFECTS IN GRAPHENE

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Graphene is a two-dimensional form of pristine carbon. It can be doped both electrostatically and chemically. When doped graphene behaves as conductor with the charge carriers having high speed, $c/300$, where c is the speed of light. Doped graphene can support surface plasmon-polaritons, a hybrid form of radiation and collective charge oscillations. These surface plasmons exist in the THz and mid-IR spectral range and can propagate long distances. This property makes them suitable to sensing and electro-optical applications. When near a metal graphene exhibits a novel form of surface plasmons, termed acoustic plasmons, which can be squeezed down to the nm-scale. When placed in a magnetic field, graphene exhibits large Faraday rotation angles, which can be tuned by electrostatic gating. Using a metallic grating it is possible to explore the magneto-optical surface plasmons introducing an extra degree of freedom related to the magnetic field. This coupling allows the enhancement of the Faraday rotation is certain spectral regions. All these topics will be addressed in this communication.

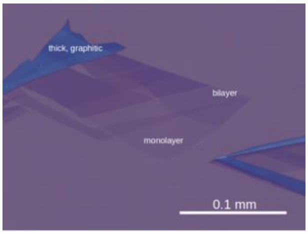

Figura 1. Graphene Flake on a glass.

Acknowledgements. N.M.R. Peres would like to acknowledge the collaboration of Eduardo Dias and Yuliy Bludov who did most of the calculations shown in this presentation, and financial support from the Graphene Flagship Project.

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THE UNIQUE VERSATILITY OF CARBON MATERIALS

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The uniqueness of the versatility of carbon materials will be discussed using a series of examples taken from some of the materials studied by our research group along the last more than fifty years. Thus, carbon adsorbents constitute a good example of this versatility, not only for the variety of precursors/activation methods that can be used in their manufacture, but also for the flexibility in their physical form or porous and chemical structure, that are the base for the very large number of industrial applications. Such materials include activated carbon in its many forms, carbon molecular sieves, mesoporous carbons, etc. and their application in adsorption, gas separation, gas storage, carbon dioxide capture, methane or carbon dioxide hydrate synthesis, energy storage, controlled delivery of drugs, etc.

The versatility is also notorious in the use of carbon materials in catalysis, either with the carbon being the catalyst by itself or the carbon being the support for the catalyst. Although carbon is used as catalyst in important industrial processes such as the manufacture of phosgene, thionyl chloride or gliphosate, the versatility is more clearly shown in the use of carbon (mainly porous carbon) as support of heterogeneous catalysts due to the variety in the porous structure and surface chemistry.

In the above materials, the porosity is the main parameter responsible for the versatility, but this versatility is also clear in the so-called structural carbons, including carbon foams, carbon mesophase, isotropic graphite and carbon-metal composites, with important applications in the manufacture of automotive components, internal wall in the future nuclear fusion reactors or in the aerospace industry.

Finally, some examples will be shown relative to research devoted to the study and applications of graphene and carbon nanotubes, with special emphasis in biomedical applications.

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CONFERÊNCIAS CONVIDADAS (CC)

DOPED GRAPHENE AND COMPOSITE CARBON MATERIALS AS ELECTROCATALYSTS TOWARDS PT-FREE FUEL CELLS

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The use of electrochemical devices like fuel cells for electrical energy production is considered to be a promising option to solve energy and environmental related problems. Graphene based materials have been recently proposed as electrocatalyst in alkaline membrane fuel cells (AMFCs) because of their excellent properties confering promising activity toward the oxygen reduction reaction (ORR). Doping procedures allow the introduction of heteroatoms in the carbonaceous matrix of graphene, leading to novel properties. In particular, some nitrogen-carbon functionalities are highly active in the electrochemical reduction of oxygen, of interest of fuel cells towards Pt-free electrodes. On the other hand, titanium-based materials including nitrides, carbides and carbonitrides have exhibited good properties as Pt support to decrease the noble metal loading while increasing the stability of the catalysts in acidic media. Composites. formed by introducing carbon nanomaterials with different dimensions and even heteroatom dopants into transition metal carbides or nitrides nanoparticles, can result in materials having unique physico-chemical and electrochemical properties for AMFCs.

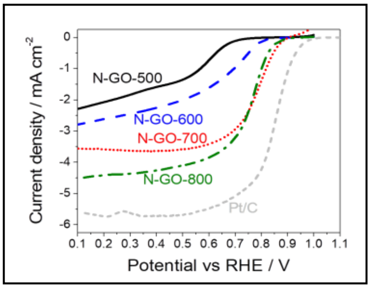

Figure 1. ORR activity (alkaline medium) of nitrogen-doped graphene (N-GO) as a function of treatment temperature.

In the present communication, the effects of graphene doping with nitrogen (Figure 1) and composites with titanium and cobaltwill be explored to be applied at the cathode low temperature fuel cells, aimed to cost-effective Pt-free electrodes.

Acknowledgements

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NANOCARBON HYBRIDS GROWN BY MICROWAVE PLASMA CVD AND THEIR APPLICATIONS

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Carbon, the structural element in organic compounds, is known to exist in many allotropic forms, such as diamond, carbon nanotubes and graphene. Nowadays, due to their unique properties, these allotropes are among the most promising materials with huge potential for high-tech applications in a wide range of fields. Moreover, the combination of different carbon allotropes in the same material can provide it with intrinsic properties exceeding the mere sum of their components, thus boosting the applications performance. In fact, hybrid nano-carbon structures are particularly interesting materials due to their synergistic combination of sp^2 and sp^3 bonded forms at the nanoscale.

Supported by a background experience in diamond/nanodiamond synthesis and applications, our group has been producing and studying the properties of multi-phased carbon forms grown by Microwave Plasma Chemical Vapour Deposition (MPCVD). Using this approach, our latest focus has been put on graphene-diamond hybrids (GDH) and diamond-graphite nanoplatelets (DNPs).

For the first time, graphene diamond hybrids were simultaneously synthesized by our group in a single step. These hybrids consisted in graphene few-layer sheets sprinkled by nanocrystalline diamond hemispherical clusters. The fundamental structural properties of this material were studied showing a strong covalent bond between both phases, enabling electron field emission, for cold cathode devices. Alongside, suspended graphene-based membrane transducers are being explored, capable of both detecting and produce vibrating signals, taking advantage of the outstanding properties of graphene for acoustic and thermo-acoustic applications.

Diamond-graphite nanoplatelets consist on vertically aligned diamond nanoplatelets (~ 5-10 nm) encapsulated by a layer of nanographite, in a maze-like configuration. The high aspect ratio of the DNPs showed to enhance convective heat dissipation when compared to standard flat nanocrystalline diamond coatings, known for its high performance. Effective heat transfer at low production cost, weight, and thickness are crucial characteristics that DNPs can meet when developing thermal management solutions for the increasingly miniaturized, yet powerful, new generations of a wide variety of devices.

Diamond-graphite nanoplatelets substrates have also proved to constitute desirable substrates for the development of biocompatible materials for electrically assisted tissue regeneration purposes. An optimization of the synthesis procedure improves the sp^2 phase purity, reduces the electrical resistivity and promotes vertical growth, resulting in rougher morphologies, with better defined nanoplatelet structures featuring an enhanced surface area. DNPs were demonstrated to promote the osteoblastic maturation by up-regulating local cellular processes in response to cell−material interaction. Additionally, the applied electrical direct current stimulates the cell growth and metabolism of preosteoblasts.

ACTIVATION WITH CARBON DIOXIDE OR AIR: WHICH IS BETTER?

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Porous carbon adsorbents can be produced from a wide variety of natural or synthetic organic materials. Adsorbents with narrow microporosity are frequently obtained by a solid-gas process, referred to as physical activation, using carbon dioxide or water vapour as the reactive activating gas. Air is not generally used due to its much higher reactivity and which can lead to preferential surface oxidation and inhomogeneous activation of the solid precursor particles.

However, certain precursor materials, including pure lignin [1] and some synthetic polymers [2], have very low reactivity and require activation times of 12 hours or more. In these cases, air activation could be a useful option which would allow activation times to be reduced to a few hours thereby resulting in considerable savings in the cost of process gas and energy usage [3]. Inhomogeneity, from the outside to the centre of the particles, is minimized due to the low reactivity and also by using low diameter particles, namely, powders or fibres.

In the presentation, the pore structure of materials made by carbon dioxide or air activation will be considered and compared. The performance of the adsorbents for some specific applications will also be addressed.

Acknowledgements. FISIPE SA (Portugal, Member of SGL Group - The Carbon Company) is thanked for the preparation of precursor fibres. The work was partially financed by the Fundação para a Ciência e Tecnologia (FCT, Portugal) with National (OE) funds (project UID/QUI/0619/2016).

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CARBON BASED MATERIALS: APPLICATIONS IN CHEMICAL CATALYSIS AND ELECTROCATALYSIS

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The current global energy crisis, reflected in the depletion of fossil fuels and growing of environmental pollution, has stimulated a great effort in the development of eco-sustainable chemical methods for biofuels and bio-products production as alternatives to petro-based derivatives, as well as new renewable energy conversion and storage chemical/electrochemical technologies. [1] All these new methods and technologies needs new materials and carbon materials appear as a key choice, due to their intrinsic catalytic properties, as well as their excellent properties to act as supports for several other materials with catalytic properties, specifically metal and metal oxides.

In this talk, several examples of carbon-based materials will be presented as catalysts/electrocatalysts in several chemical/electrochemical energy-related reactions. Functionalization of carbon nanotubes with sulfonic acid moieties has been shown as a versatile strategy to introduce acid properties to enhance catalytic activity of these materials as solid acid catalysts in the transformation of biomass resources into biodiesel (ex: esterification of free fatty acids) and bioproducts (ex: alkylation of furan derivatives). Heteroatom-doped carbon nanomaterials were also studied in the selective reduction of nitro- into amine-arenes, with high catalytic activity and stability/reusability. Furthermore, several carbon materials (pristine and doped-carbon nanotubes, graphene flakes derivatives) nanocomposites with metals oxides: mixed valence cobalt oxide, phosphomolybdates and phosphotungstates have been successfully applied in energy-related electrochemical reactions involving hydrogen and oxygen evolution reactions (HER and OER, respectively), as well as oxygen reduction.

Acknowledgments. The work has been funded by Fundação para a Ciência e a Tecnologia (FCT), FEDER under Programme PT2020, Project UID/QUI/50006/2013-POCI/01/0145/FEDER/007265 and project “UniRCell”, with the reference POCI-01-0145-FEDER-016422 and Programme FCT–UT Austin, Emerging Technologies, Project UTAP-ICDT/CTM-NAN/0025/2014.

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PROPERTIES OF CARBON MATERIALS FOR CATALYTIC WET PEROXIDE OXIDATION

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Catalytic wet peroxide oxidation (CWPO) is a water treatment technology normally regarded as a tertiary treatment for the elimination of organic compounds present in waste waters at low concentrations. The classical example of such technology is the Fenton process, where hydrogen peroxide is decomposed by iron sulphate, used as homogeneous catalyst, to yield hydroxyl radicals ($HO^\bullet$). By making use of these very reactive and non-selective oxidizing species, the elimination of organic compounds can be accomplished by CWPO under mild conditions of temperature and pressure.

On the other hand, carbon materials, well known catalysts for the decomposition of hydrogen peroxide into $HO^\bullet$, have been particularly studied in recent years as alternatives to the homogenous Fenton catalyst and to heterogeneous metal supported catalysts for CWPO. The application of these metal-free materials represents a major advance in CWPO due to the avoidance of metallic species in the treated waste water and due to their versatility, simplicity of use and ease of recovery. It has been observed that the process efficiency is influenced by several characteristics of the carbon materials, such as surface chemistry, structural features and adsorptive interactions.

This keynote lecture aims to present the main findings obtained in recent works by our research group on the application of carbon materials in CWPO. While the presence of acidic O-containing functionalities inhibits CWPO performance, the presence of S-containing surface groups and basic active sites, have a positive influence. In addition, when complemented by suitable surface chemistry, the presence of structural defects, stable metal impurities, high surface area and porous structure are also found to be key parameters. The cumulative knowledge acquired allows the proper tuning of the carbon materials properties in order to develop highly active, stable and efficient catalysts for CWPO. This enables the exploration of new treatment capabilities, including the application of CWPO in secondary treatment, through process intensification approaches, for the elimination of pollutants present in waste waters at high concentrations.

Acknowledgments. This work was financially supported by projects: POCI-01-0145-FEDER-006984 – Associate Laboratory LSRE-LCM funded by FEDER through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) – and by national funds through FCT; AIProcMat@N2020 - Advanced Industrial Processes and Materials for a Sustainable Northern Region of Portugal 2020", with the reference NORTE-01-0145-FEDER-000006, supported by NORTE 2020, under the Portugal 2020 Partnership Agreement, through FEDER. HTG acknowledges all co-authors that contributed to the results presented in the communication.

COMUNICAÇÕES ORAIS (CO)

LABEL-FREE DETECTION OF DNA HYBRIDIZATION WITH GRAPHENE FIELD-EFFECT TRANSISTORS

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DNA detection is of high importance since it can provide information in a variety of fields, including research on molecular biology, genetic disease diagnosis, biological informatics, forensics and environmental monitoring. Field-effect transistors (FETs) allow to achieve high sensitivity, specificity and rapid measurement without the need of labelling.

Graphene has exceptional properties, including high 2D electrical conductivity, large surface area, high chemical stability and low cost. The fact that it provides an exposed, natural 2D surface populated with high-mobility electrons or holes, whose concentration can be set by applying a gate potential to the graphene, allows for the design of novel types of chemical sensors based on FET architectures. However, graphene high sensitivity and chemical stability comes at the cost of a poor analyte selectivity, which implies that biorecognition with graphene requires surface functionalization.

Here we develop a FET based on a single graphene layer for label-free detection of target DNA hybridization with probe DNA. The probe immobilization is achieved with the help of a pyrene linker, attached to the graphene surface via π-π interaction. The FET is designed with an in-plane receded gate, with source and drain contacts, prepared to support a liquid-gate dielectric that closes the high-impedance gate-source circuit. Transducing is based on local gating whenever a biorecognition event, i.e. DNA hybridization, takes place at the transistor channel surface. By consecutive monitoring of the FET transfer curve, the Dirac point movement is tracked, showing a shift towards more positive gate potentials with increasing target DNA concentrations between 1 aM until it reaches a plateau at 100 fM, while keeping sensitivity to single nucleotide polymorphism. The detection of aM levels of DNA hybridization using a FET is a 3 order of magnitude improvement on previous detection levels [1] and is among the best from all detection strategies [2].

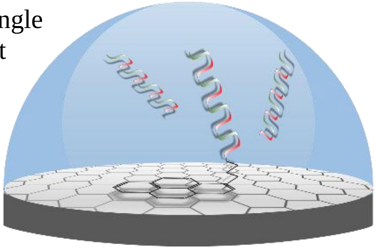

Figure 1 – Schematic representation of the EGFET.

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PREPARATION OF CARBON NANOTUBES-BASED HETEROSTRUCTURES BY ATOMIC LAYER DEPOSITION

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The controlled deposition of thin films on high surface area supports are prerequisites for a rational design of interfaces and the production of novel multifunctional materials. Carbon nanotubes (CNTs) present a high surface area and exceptional physical properties. As matter of fact, they are ideally suited as support for a secondary material that can be deposited onto their surface either as particles or as a thin film. Atomic layer deposition (ALD) technique emerges as a powerful and versatile technique for the coating or decoration of the CNTs with metal oxides. It permits a precise deposition of conformal and homogenous thin films, based on a reaction between precursor materials, which are separated into successive surface reactions. Accordingly, the reactants are kept separated reacting with surface species in a self-limiting process, i.e. without the presence of gas phase reactions. The conformal growth of the ALD film is a direct consequence of self-limited surface reaction and the film thickness is determined by the number of cycles. ALD technique is widely used for metal oxide thin films deposition, which formation involves the reaction between a metal precursor and an oxygen source [1]. ALD is, therefore, specifically suited for the preparation of heterostructures. Here, we will present an ALD approach for the deposition of metal oxides for coating 3D arrays of CNTs without damaging the substrate geometry. The obtained heterostructures are definitely suitable for a variety of applications in different fields ranging from energy storage to catalysis.

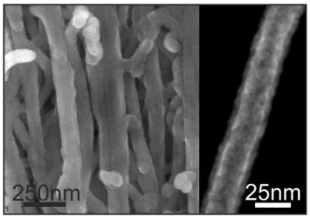

Figure 1. Coated CNTs.

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MECHANOCHEMICAL PREPARATION OF Pd AND Pt COMPOSITES FOR SUZUKI-MIYAURA REACTIONS

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The application of green, simple, time- and energy-saving mechanochemical ball-milling procedures for the dispersion of palladium and platinum salts or oxides over MWCNTs (multi-walled carbon nanotubes) and activated carbon is reported.

Carbon nanotubes have exceptional properties (*e.g.* high mechanical strength and surface areas) which make them promising materials for various applications. In this respect, we apply dispersed palladium and platinum composites [1-2] as catalysts in the Suzuki-Miyaura reactions. Both the preparation of the dispersed materials and the catalytic Suzuki-Miyaura reactions were performed by ball-milling and the results are discussed (Fig. 1).

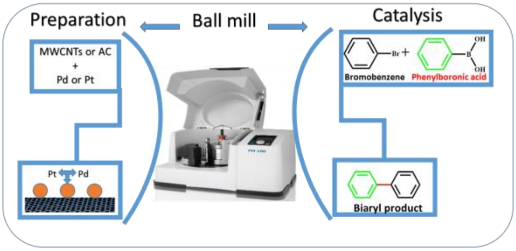

Figure 1. Carbon catalysts preparation and catalytic reaction in ball mill

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MODULATION OF CARBON DOT FLUORESCENCE BY HETEROATOM-DOPING AND MICROWAVE-SYNTHESIS

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Carbon dots are fluorescent carbonaceous nanoparticles usually with dimensions less than 10 nm [1-3]. They possess very attractive properties, such as water-solubility, high stability, high fluorescence quantum yield, biocompatibility, low toxicity and are easy to functionalize [1-3]. These unique properties of carbon dots have led to promising applications in bio-sensing, optical imaging and catalysis, among others [1-4].

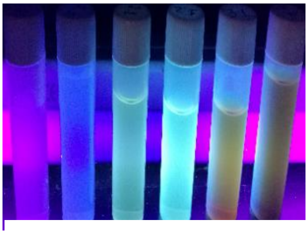

Figure 1. Fluorescence of synthesized Carbon Dots.

Inspired by their usage, there is a growing interest in the design of a well-defined, green and quick methodology for carbon dot synthesis, with controlled tuning fluorescent properties. In an ongoing project, carbon dots were obtained following a green synthesis approach from citric acid/heteroatom under microwave irradiation. With this approach, we obtained doped carbon dots in a very wide range of the visible spectrum (with varying fluorescence intensities), ranging from the violet (390 nm) to the red (620 nm) region (Figure 1).

The use of a microwave-based approach, combined with a synergistic effect of the various heteroatom-dopants, allowed for the quick and well-defined synthesis of carbon dots with controlled and diverse characteristics that can have various applications.

Acknowledgments. This work was made in the framework of projects PTDC/QEQ-QAN/5955/2014 (funded by FCT/MEC and COMPETE-POFC), NORTE-01-00145-FEDER-000028 (funded by NORTE2020) and POCI-01-0145-FEDER-006980 (funded by COMPETE2020).

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UPCONVERTING PHOSPHORS/CARBON DOTS NANOSTRUCTURES FOR GLUCOSE SENSING

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The presence of high glucose level in human plasma create lot of health complications and affect the normal function of body organs. Nowadays diabetes has become an epidemic and very common disease within mid age population. At present about 422 million peoples are affected with this problem through out the world. Feasible blood glucose monitoring biosensor with higher accuracy is still desirable.

In the present work we developed a biosensor based on fluorescence resonance energy transfer (FRET) between up conversion nanoparticles (UCNPs) and carbon dot nanoparticles (CDs). These UCNPs-CDs nanostructures were used as a donor/acceptor pair to construct FRET-based biosensors, which utilized both the photo physical merits of UCPs and the quenching ability of CDs and thus afforded favourable analytical performances.

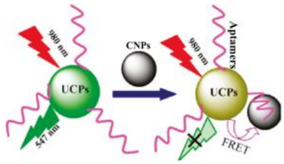

Figure 1. FRET from UCNPs to CDs.

The high quantum yielded colloidal dispersed NaGdF$_4$:Ho^{3+}/Yb^{3+} UCNPs were synthesized via thermal decomposition method and CDs were developed through microwave assisted synthesis process. Both particles were attached to each other using surface aptamers based on poly ethylene glycol (PEG) (figure 1). The effect of different concentrations of glucose solution and human plasma collected from different diabetic patients on the luminescence efficiency of this system were studied using 980 and 350 nm excitation in order to examine the effect of glucose concentration on the luminescence intensity of these particles. The sensor performance was examined comparatively.

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AMINATED FLUORESCENT CARBON DOTS: SYNTHESIS AND CHARACTERIZATION

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Carbon dots (CDs) are a class of zero-dimensional nanomaterials that were first discovered by Xu *et al.* [1] in 2004, and described as carbon quantum dots in 2006 by Sun *et al*. [2] Carbon dots have a quasi-spherical shape and a size range between 1-10 nm. They present very interesting properties, *e.g.* excellent photostability, low cytotoxicity, the possibility of surface functionalization, water solubility and high quantum yields when compared to other fluorescent molecules. [3] These properties are related to the composition, structure, and organization of CDs. Carbon nanodots (CNDs) and carbon quantum dots (CQDs) are two distinct types of carbon dots that are organized differently; CNDs have an amorphous carbon core while CQDs present a crystalline structure with sp^2 hybridization, both have surface functional groups such as carboxyl (-COOH), hydroxyl (-OH) and amino ($-NH_2$) groups. [4]

The aim of this work was to prepare new carbon dots with enhanced optical properties to be used in biomedical applications. The CDs were synthesized by using the hydrothermal process and starting materials rich in carbon, oxygen, and nitrogen content, *e.g.* citric acid, ascorbic acid and 1,6-hexanediamine.

Our results revealed that the CDs obtained have good fluorescence, dependent on the excitation wavelength; the formation of the black dots was confirmed by TEM, and the ATR spectra showed that the particles are amide terminated. The obtained CDs were characterized also using: DLS, NMR, UV-Vis and Fluorescence Spectroscopy.

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CNTs GROWTH GEOMETRY AND CNFs CHIRALITY: ROLE OF SOLID-STATE ROUTES AND FACETING

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"*The central problem in nanotube science is still the mechanism*" [1]. Isothermal kinetics and in-situ TEM or SEM are good approaches to understand the mechanism at phenomenological level [2-5]. The kinetic approach has been recognized to be the best root to understand the mechanism [2,4]. Solid-state chemistry at the nanoscale enables to understand this type of catalysis. The proposed mechanism includes two novelties in relation to this branch of science [8]: a) The use of 1st Fick's Law, not the 2nd; b) A sustained driving force between two phases with two complementary roles. One phase promotes gas decomposition (S_1-external) and the other phase (S_2-internal) is the basis for nucleation and growth of the carbon structure. Steady-state C atoms diffusion operates during growth from S_1 to S_2 and the thicknesses of S_1 and S_2 are inversely proportional to the C diffusivities [4]. The *ratio* of the carbon atom covalent diameter to the transition and noble metals one predicts interstitial carbon diffusion operating (*ratio* < 0.60). The novelty of using solid-state chemistry science has to do with: a) Initial phase changes; b) 1st Fick's Law operating (under steady-state); c) Relatively fast bulk diffusion rates compared to macro-scale rates. The mechanism explains octopus and spiral growth in CNTs and chirality. A recent study has shown that carbon structures can grow at very low temperatures (120ºC) under low C_2H_2 pressure [7]. This behavior can be understood combining kinetics and thermo-dynamics.

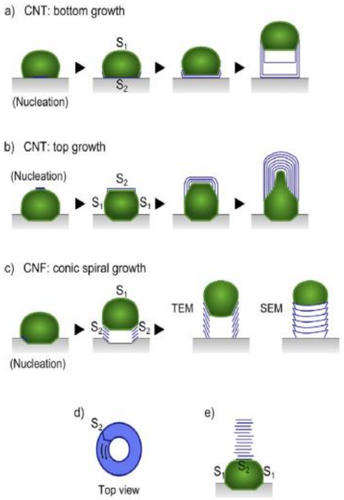

Fig 1. Alternative nucleation and subsequent growth mechanisms.

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CARBON NANOTUBES AS EFFICIENT CATALYSTS – A COMPUTER MODELING APPROACH

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The properties of chemical reactions might alter dramatically when bulk conditions are changed. For example, theoretical studies have shown that some S_N2 reactions suffer a significant increase in their rates when they occur inside single-walled carbon nanotubes (SWNTs) as compared to gas-phase medium.[1,2] To date, no systematic investigation has considered the effect of SWNT structure on the kinetics of reacting systems.

The present work is a quantum mechanical study that sheds some light on this issue by comparing the impact of different types of SWNTs, namely armchair(n,n), zigzag(n,0) and chiral(n,m), on the particular Menshutkin S_N2 reaction between ammonia and chloromethane. The calculations have been performed at the Density Functional Theory (DFT) level, using the functional M06-2X and double-zeta basis sets of atomic functions.

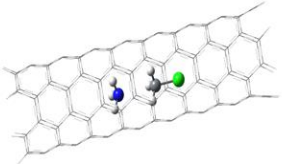

Figure 1. Reactants (NH_3 e CH_3Cl) of a Menshutk in type of reaction inside a SWNT.

In general, all SWNTs considered in this work are able to reduce significantly the activation energy and the endothermicity of the reaction when compared to the values in gas-phase. For large diameters, all types of SWNTs converge to the limit values of these two energetic parameters, respectively, 28 kcal.mol^{-1} and 21 kcal.mol^{-1}, which correspond to the reaction over a graphene surface. However, as the diameters decrease, each type of SWNT shows a different potential well, with chiral (6,4) SWNT (diameter 6.8 Å) exhibiting the lowest energy barrier of 17.9 kcal.mol^{-1}.

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CHALLENGES IN THE ORGANIC FUNCTIONALIZATION OF CARBON NANOTUBES

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The diverse applications of carbon nanotubes (CNT), intimately associated to their unique properties, is limited by the strong π–π inter-tube interactions. This is the major reason for their aggregation in bundles and the subsequent poor interaction with other materials. Surface chemical modification by grafting different functional groups has been used to improve and manipulate their properties.

This work will summarize the research carried out by our group, exploring the CNT functionalization through different cycloaddition reactions. The challenges faced in the 1,3-dipolar cycloaddition of azomethyne ylides [1] and in the Diels-Alder reaction with butadiene [2] and with maleic anhydride [3] will be discussed, considering that the conditions used for these reactions can partially influence the chemical nature of the product.

The non-covalent interaction between the CNT surface and conjugated aromatic systems in order to reduce their entanglement will also be referred. The use of suitably derivatized pyrene [4] and perylene [5] compounds, allowed the efficient dispersion of CNT in aqueous media.

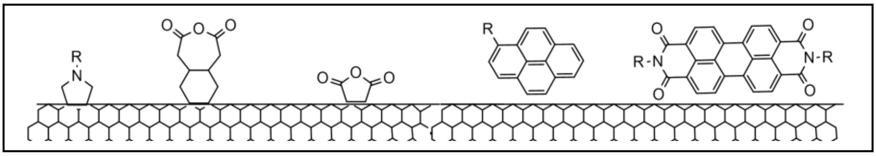

Figure 1. The covalent and non-covalent functionalization of CNT

Acknowledgments. We gratefully acknowledge FCT for the grant awarded to R.F. Araújo (SFRH/BPD/88920/2012) and to E. Cunha (SFRH/BD/87214/2012).

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RECOVERY OF RARE EARTH ELEMENTS USING A MAGNETIC GRAPHENE BASED NANOCOMPOSITE

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Rare earth elements (REEs) are defined by the IUPAC nomenclature, as the 15 lanthanides together with yttrium and scandium. Because of their properties, REEs can be widely used in many areas including catalysts, metal alloys, electronics, glass, magnets, ceramics, new materials and some other high-technology fields. For this reason, the demand for REEs is continually growing. The conventional REEs extraction consists in grinding large volumes of hard rock and removing REEs through acid extraction. This process is very energy intensive, disturbs large areas of pristine land, and generates large volumes of toxic tailing. Although still little explored, a friendly alternative to this process is the recovery of REEs from effluents using adsorption, since this technique is very versatile, efficient, has simple design and wide adaptability.

Figure 1. Image of a solution containing the magnetic graphene-based nanocomposite.

In our study, we evaluate the adsorption capability of a Fe_3O_4/graphene based nanocomposite, prepared by electrostatic self-assembly, to recover of Lanthanum (La), Europium (Eu) and Terbium (Tb), three of the most important REEs.

Before their practical application, the magnetic nanocomposite was fully characterized by appropriate techniques, and then batch experiments were carried out to evaluate its efficiency toward La, Eu and Tb. Preliminary results show that the recovery of La, Eu and Tb by the nanocomposite is strongly dependent of the solution pH. For alkaline pH values the removal efficiency of La, Eu and Tb from water was superior to 90%, which highlights the potential of using this material to recovery some REEs. More, the magnetic property of the nanocomposite allows its rapid separation from the matrix by application of an external magnetic field.

Acknowledgements. This work was developed in the scope of the projects CICECO-Aveiro Institute of Materials (POCI-01-0145-FEDER-007679 | Ref. FCT UID/CTM/50011/2013) and CIIMAR (Ref. FCT UID/Multi/04423/2013) financed by national funds through the FCT/MEC and co-financed by FEDER under the PT2020 Partnership Agreement. Cláudia Batista Lopes also acknowledge the post-doctoral grant SFRH/BPD/99453/2014.

LAYER-BY-LAYER FILMS OF GRAPHENE AND NATURAL POLYMERS

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Graphene and its derivatives are promising reinforcement for polymer nanocomposites. In this work freestanding films (FS) based on chitosan (CHI), alginate (ALG) and functionalized graphene were developed using layer-by-layer assembly. Suspensions of functionalized graphene nanoflakes (f-GF) and nanoribbons (f-GNR) were prepared from expanded graphite (EG) and multi-walled carbon nanotubes (MWNTs), respectively. The EG and MWNTs were covalently functionalized using a 1,3-dipolar cycloaddition reaction of an azomethine ylide, allowing the exfoliation of the nanoparticles. [1] Characterization of the f-GNR and f-GF suspensions confirmed the exfoliation process. The layer-by-layer deposition of functionalized graphene and CHI/ALG was investigated and FS films were produced. A total incorporation of 1.7 wt.% of f-GF and 2.5 wt.% of f-GNR was estimated. Graphene increased the storage modulus and dynamic mechanical response at 1Hz and 37ºC, and decreased the electrical resistivity. Biological assays revealed cytocompatibility towards L929 cells. In conclusion, these new f-GF and f-GNR reinforced FS films present potential for biomedical applications.

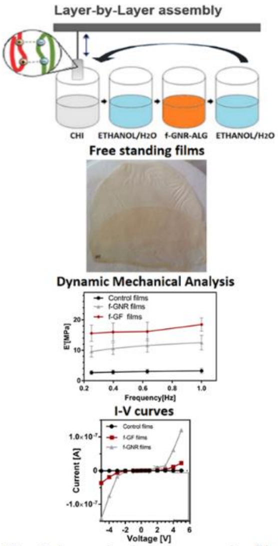

Fig. 1. Layer-by-layer composite film fabrication and their mechanical and electrical characteristics.

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ENHANCEMENT OF THERMAL PROPERTIES OF FLUIDS USING NANOCARBONS

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The development of nanofluids in the last 20 years led to many attempts to apply efficiently the discovered enhancements in thermal conductivity caused by the presence of nanoparticles in the common heat transfer liquids, from low to moderate temperatures. Problems about the characterization of nanomaterials used, preparation and short/long term stability of the prepared dispersions, and the adequacy of the experimental techniques used namely for thermal conductivity, due to the scatter of published data, are evident. These problems are aggravated with IoNanofluids, because the structure of the base ionic liquids is by far more complex than the common molecular solvents, and because their interactions with nanomaterials are more challenging (interactions between the ions and the nanoparticles) [1].

In this paper we will focus on some results obtained with MWCNT's and graphene as heat transfer enhancers in ionic liquids, from the characterizations of the nanomaterials, the preparation of the dispersions, the measurement of thermal conductivity and the molecular modelling.

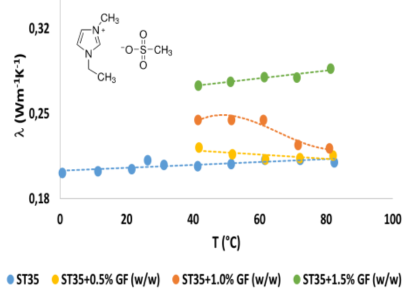

Figure 1. Thermal conductivity enhancement of ST35 IoNanofluid as a function of the concentration of the graphene (2-3 layers)

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AN INNOVATIVE METHOD OF GRAPHITE EXFOLIATION IN AN AQUEOUS-ORGANIC MEDIUM

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Graphene is an extremely promising material with unique properties and unlimited potential, capable of disrupting several markets [2] – due to its thermal/electrical conductive properties, flexibility and strength, graphene has been hailed as the future of nanomaterials, and can be used in energy storage, in composites, medical diagnostics and drug delivery systems, or even in such concepts as folding smartphones. The present work is related with an innovative process for producing high quality graphene, affordably and efficiently, and on a scale capable of meeting the potential market demand for graphene, using a proprietary system. This system is based on a thermochemical-mechanical process, which achieves liquid exfoliation of graphite using ultrasonic waves to form cavitation bubbles in a non-contaminant chemical solution, which impact the graphite and break it into graphene particles (see Figure 1). Figure 2 presents several Raman spectra from different sources where two (green and magenta) were obtained with the previously described system, and the remaining blue [3], red [1] and black [4] spectra are from literature for 4- and 5-layer graphene particles.

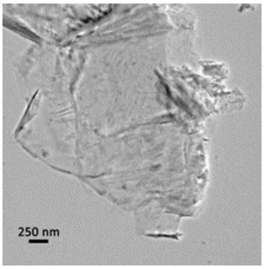

Figure 1. Transmission electron microscopy bright-field image of a GRAPHENEST's sample.

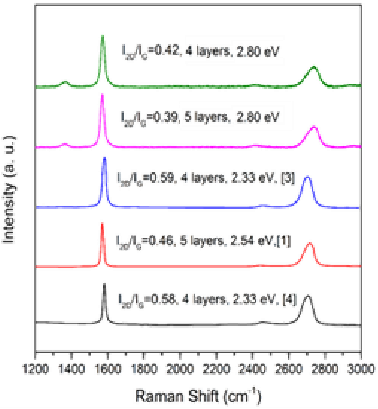

Figure 2. Normalized Raman spectra of few-layer graphene (FLG) particles from different sources. Green and magenta spectra were obtained during the present work, while blue [3], red [1] and black [4] spectra are from literature for 4- and 5-layer graphene particles.

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COMUNICAÇÕES EM PAINEL (CP)

CARBON NANODOTS FROM OLIVE MILL WASTEWATER: A SUSTAINABLE ROUTE

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Olive oils are obtained from the fruit of the olive tree (*Olea europaea* L.) by combined mechanical and physical operations. Portugal has a significant production of olive oil (76 k tonnes/year over the last 5 years, 2010-2015) [1]. Olive oil is typically obtained by two main processes: batch press and continuous centrifugation. Depending on the particular process used, 200-1600 L of olive mill wastewater (OMWW) is produced per tonne of processed olives. Taken the lowest of these values, an estimate points to around 15 million L of OMWW may be produced each year in Portugal. The OMWW exhibits very low biodegradability parameters which pose serious issues for its treatment. Sustainable production of high-valued carbon materials from industrial low-valued and problematic wastes is particularly appealing and highly desirable.

In this communication, we show for the first time that highly luminescent carbon nanodots (CNDs) can be obtained directly from a two-stage OMWW in excellent yields following expedite and sustainable processes with minimum post-processing. The morphology, surface functionality, microanalysis and photophysical properties of the as-synthetized nanostructured materials will be presented and discussed in regard to several operation variables (viz. reaction temperature, dwell time and additives).

The as-prepared CNDs present a tunable photoluminescence (excitation-dependent) spanning over the entire visible spectra which can be modulated by synthesis. Under specific synthetic conditions, the as-synthesized CNDs are deep blue emitters ($\lambda_{\text{em max}}$ ~ 410 nm; λ_{exc} = 340 nm) displaying a notable quantum efficiency (Φ_{F} ~ 0.4), an extremely high photostability ($\sigma_{\text{em var}}$ = 0.008 upon 5h of continuous irradiation at 340 nm), and a pH-responsive luminescence (pH 1-12). Such luminescent properties of CNDs, allied to their easy synthesis, carbon source affordability and excellent dispersion in aqueous solutions and polar protic and non-protic organic solvents, render them with unique capabilities to be used in several current and emerging applications in the fields of cellular imaging, chemo/biosensing, (photo)catalysis and optoelectronics.

Acknowledgments. We thank IPL (Project Nanolive/IDI&CA/2016) and FCT/MCTES (UID/QUI/00616/2013) for financial support.

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ON THE NATURE OF CARBON NANODOTS PHOTOLUMINESCENCE FROM OLIVE WASTES

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A great structural diversity of carbon nanodots (CNDs) have been obtained in the last ten years by a variety of methods, carbon sources, additives and/or passivating agents, and operation parameters. Not unexpectedly, many properties diverge owing to disparate structural features. The photoluminescence (PL) is one of them. A vast literature is already available on this topic, with findings that are somehow apparently contradictory. At least three possible origins of PL in CNDs have been identified: i) quantum confinement effects associated with the sp^2 domains of the carbon core; ii) surface states lying in the edges of sp^2 carbogenic core; iii) molecular states originating from molecular species embedded or covalently linked to the carbon matrix.

We have investigated the temperature-dependent PL of CNDs derived from olive mill wastewater. The highly emissive ($\Phi_F \sim 0.4$) nanodots exhibit a main (slightly asymmetric) emission band peaking at ~ 410 nm ($\lambda_{exc} = 340$ nm) which decreases linearly as the temperature raises from 0ºC to 80ºC, owing to an increased population of non-radiative channel traps activated on temperature rising. The PL spectra, fitted by two Gaussian functions at each evaluated temperature, reveal the presence of two main emitting components in line with the PL excitation spectra (two bands centred at 242 nm and 336 nm, monitored at the emission maximum) which do not change their position upon an increase in temperature. The high energy PL band (H) at 400 nm with an fwhm of 50.1 nm may be ascribed to π-π^* core transitions while the broader (fwhm = 75.3 nm) lower energy band (L) found at 434 nm may be a result of mixed n-π^* and π-π^* transitions (ratio L/H = 1.38). Both bands show a very slight (*ca.* 2-3 nm) increase of bandwidth and only a small red shift gap of the bands (14 and 15 meV, respectively) upon heating, an effect that is similar to that observed in metallic quantum dots (QD) and divergent from that in semiconductor QD. Under conditions where the formation of larger regions of carbogenic cores are favoured (*e.g.* 300ºC), the ratio of bands above assigned to core and surface states increased (L/H = 0.83), and a concomitant reduction of quantum efficiency is observed, further pointing to the origins of PL in these CNDs. Emission from molecular states may be ruled out given the PL excitation-dependency of CNDs.

Acknowledgments. We thank IPL (Project Nanolive/IDI&CA/2016) and FCT/MCTES (UID/QUI/00616/2013) for financial support.

CARBON DOTS: WHO IS THE BRIGHTEST OF THEM ALL

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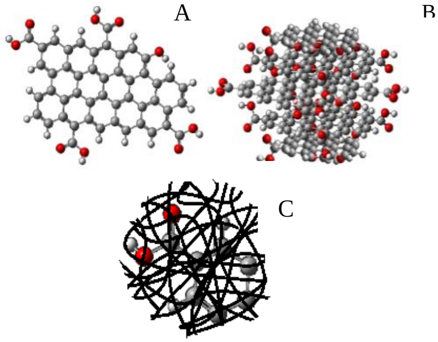

Figure 1: Different types of dots produced, A) sheet like graphene quantum dots, B) crystalline carbon quantum dots and C) amorphous polymer dots.

The origin of photoluminescence in carbon dots is under intense debate. Understanding the photoluminescence mechanism of carbon dots is one of the most important issues to be solved in adapting this material to novel applications. Our interest is in using carbon dots as near-infrared antenna in functional materials, taking advantage of their exceptional nonlinear absorption and emission properties. Nitrogen doped, crystalline carbon dots have been reported with high Two-Photon Absorption (TPA) values (on the 10^4 GM range).[1] In contrast, very modest values (<100 GM) have been reported for undoped amorphous carbon dots.[2] At the moment, the limited number of studies where the TPA properties have been address in a systematic and quantitative way preclude a conclusive analysis about the critical factors for an effective two-photon brightness. In this paper we discuss the TPA properties of carbon dots produced by either top-down methods, involving the conversion of a graphite based material to graphite oxide sheets, or bottom-up methods, involving the synthesis of quantum dots from the pyrolysis of organic compounds. The material that is produced using different methods can be quite different in terms of structure, crystallinity and types of oxygen containing functional groups decorating the edges or the surface of the carbonaceous core. (Figure1) In this poster we discuss the TPA properties in connection with the structure of the different types of dots investigated.

Acknowledgments. Financial support from FCT is acknowledged (SFRH/BPD/75782/2011, SFRH/BPD/105478/2014, IF/00759/2013, UID/NAN/50024/2013 and PD/BD/127805/2016).

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HYDROPHILIC CARBON NANOMATERIALS GENERATED AT THE CATHODE AND ANODE OF GRAPHITE: A COMPARATIVE STUDY

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Hydrophilic carbon-based nanomaterials comprising carbon clusters, often referred as carbonaceous fragments or oxidation debris, have emerged in the literature in the last years [1,2]. Although these materials are often regarded as an undesired by-product of the synthesis of graphene-base materials, they are extremely attractive for engineering novel delivery systems and novel therapeutic strategies in biomedicine because of their outstanding solubility in water.

Recently, a simple methodology to produce amorphous hydro-soluble carbon nanomaterials in one single step was developed by our group based on an electrochemical approach [3]. Interestingly, it has been demonstrated that the hydrophilic carbon nanomaterials generated at the graphite anode have a dual behaviour: the ability to behave as an electrolyte and to be used as an electrode material with meaningful capacitive properties. Following the initial development work we further pursued investigations on the physical and chemical properties of the electrochemically generated hydrophilic carbon nanomaterial aiming to understand if these species could be also generated at the cathodic side of the electrochemical cell. To address this issue, the solutions generated upon one hour of galvanostatic polarization, using graphite as both anode and cathode electrodes, were collected from both compartments, analyzed and compared in a systematic way.

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RAW AND BLEACHED PAPER PULP AS RAW MATERIALS FOR ACTIVATED CARBON PRODUCTION

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The production of activated carbons from alternative raw materials fits within the concept of a sustainable economy, where value-added materials are produced from cheap substrates. In this work, two types of pulps, derived from the paper production process, were used as precursors to produce activated carbons. For this purpose, raw and bleached pulp were impregnated with two chemical activation agents (K_2CO_3 or H_3PO_4) and then pyrolyzed under controlled atmosphere and washed with hydrochloric acid. The materials were physically and chemically characterized by proximate and elemental analyses, Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), Boehm's titration for functional group analysis and determination of total organic carbon (TOC), inorganic carbon (IC), specific surface area (S_{BET}) and point of zero charge (PZC). The physico-chemical characterization showed that both raw materials and activated agents resulted in activated carbons with an acidic surface (PZC from 2.3 to 4.6) with a high prevalence of carboxylic acids as surface functional groups. The carbons presented TOC contents between 59 and 72% and a well-developed microporosity with S_{BET} between approximately 770 and 970 $m^2\ g^{-1}$. The verified physico-chemical properties, comparable to several brands of commercial activated carbons, indicate the potential of these materials to be applied, for instance, as alternative adsorbents in water remediation solutions.

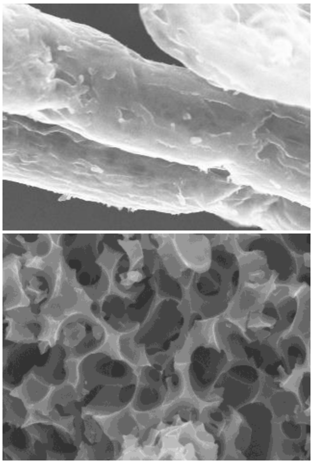

Figure 1. SEM micrograph of raw pulp (top) and pyrolyzed raw pulp activated with K_2CO_3 (bottom) at 10 000×

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ACTIVATED CARBONS FROM MDF AND PB WOOD COMPOSITES - POWDER AND MONOLITH FORMS

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Activated carbons (ACs) have been one of the most important materials used all over the world for centuries and they are nowadays, in the adsorption field, one of the most relevant. These adsorbent materials have multiple applications, from the food and beverage fields, to the health and industrial areas, and they play a crucial role in our society. In particular, academic and industrial communities keep their attention in the valorization of different types of wastes, such as lignocellulosic and syntethic polymers, to produce ACs, an added value material [1,2].

The focus of this work is to compare the structural and chemical characteristics of powder and monolith forms of ACs produced, Figure 1, by physical activation with CO_2, using medium density fibreboard (MDF) and particleboard (PB) engineered wood composites wastes as precursors. The information obtained allows us to predict the best application type for each of the forms of the final AC. All the samples and respective precursors were characterised by thermogravimetric analysis, lignocellulose content, nitrogen adsorption at 77K, FTIR, CHNS-O elemental analysis and determination of pH of point of zero charge.

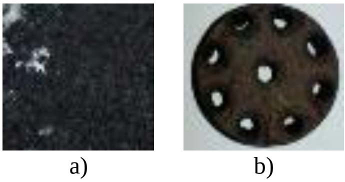

Figure 1. Typical appearance of ACs prepared from MDF precursor in different physical forms (a) powder b) monolith).

With this work, we expect to give a positive contribution to the discussion around the thematic of the optimal size of the precursor and, in particular, to the production of ACs of large size, namely monolith perforated AC structures.

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ACTIVATED CARBONS FROM ANGOLAN WOODS FOR THE ADSORTION OF MCPA AND DIURON

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Carbon materials, and in particular activated carbon (ACs), are currently one of the most relevant and fundamental adsorbent materials in many areas of human activity, such as medical applications, gas separation and storage, removal of pollutants and odours and catalysis [1,2]. Angola is experiencing a considerable amount of wood wastes, which is the consequence of cutting down the trees for the implantation of residential areas and industrial facilities, like mining, oil and gas, and also for their use in the production of domestic coal. This huge amount of biomass wastes is abandoned and suffers a slow degradation process. In this work we report the preparation of ACs by activation with CO_2 from wood wastes collected in Angola and its use for the adsorption from liquid-phase of pesticides of interest by their availability and toxicity, MCPA and Diuron [3]. The ACs samples were characterised by nitrogen adsorption at 77K, FTIR, CHNS-O elemental analysis and determination of pH of point of zero charge (pzc). The liquid phase adsorption studies were done at 25ºC using a batch method and a shaking thermostatic bath. The ACs produced are primordially microporous with BET apparent surface area and pore volume up to $2130 m^2g^{-1}$ and $0.99 cm^3g^{-1}$, respectively. Regarding the surface chemistry, ACs are of basic nature as indicated by the pzc, FTIR and elemental analysis. The MCPA and Diuron adsorption studies shown that the ACs tested show interesting results for the removal of pesticides. This can be particularly interesting and an asset in countries like Angola where the pesticides has been vastly and carelessly used with soil and water contamination as a consequence. The maximum adsorption capacities were 295 and 400mg/g for MCPA and Diuron, respectively.

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GLUCOSE DERIVED CARBON/CARBON NANOTUBE HYBRIDS FOR SUPERCAPACITOR APPLICATIONS

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Interest in hydrothermal conversion of biomass has increased sharply in recent years due to its low cost and mild synthesis conditions, making the process more affordable and environmentally friendly than conventional methods. However, one of the main limiting factors hindering the applicability of the as-prepared hydrothermal carbons is that they usually exhibit limited porosity. Some strategies are thus needed to overcome this drawback and to tailor the properties of hydrothermal biomass derived carbons.

In the present study, glucose-derived carbon/carbon nanotube hybrids were prepared by hydrothermal carbonization (HTC) of glucose in the presence of different amounts of carbon nanotubes (CNT): 0, 2, 4 and 8 % wt. The as-prepared hybrids were subjected to chemical activation with KOH 50 w/w. % at 700ºC under N_2 flow. The applied thermal post-treatment and the incorporation of CNT promote modifications in the porous and chemical properties of the synthesized materials. The potential of the hybrid carbon materials towards their use in electrochemical applications was studied by several techniques in a three-electrode cell. Chemical activation increases the specific capacitance of the glucose-derived carbon from 12 to 178 F/g, due to the higher microporosity. The capacitance decreases when a high concentration of CNT is added to the precursor solution. However, CNT offer higher molecular diffusion due to the presence of mesoporosity and higher electrical conductivity. The combination of these two properties will lead to advanced electrodes yielding lower electronic/molecular resistance and, therefore, higher operation rates. In conclusion, this work highlights the importance of tailoring the properties of the electrode materials to achieve enhanced energy storage in supercapacitor devices.

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GLYCEROL BASED ACTIVATED CARBONS FOR IOHEXOL REMOVAL

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Recently we have been developing a study aiming the valorization of residues from biodiesel production [1]. In the present work, glycerol-based activated carbons were prepared by a two-step procedure: carbonization with sulfuric acid, adapting the procedure described in ref. 2, followed by activation with K_2CO_3 (char: K_2CO_3 ratio 1:3, 700 °C for 1 h), or thermal activation (500 °C, 600 °C and 700 °C, for 1h). The activated carbons were characterized by: N_2 adsorption, FTIR spectroscopy, Elemental Analysis, SEM and pH_{PZC}. The acid carbonized sample is a non-porous material with A_{BET} of 10 m^2g^{-1}. The thermal activation step allowed to obtain materials with around 450 m^2g^{-1}, while the sample chemically activated has A_{BET} of 980 m^2g^{-1}. All the carbons are microporous materials (Fig.1a). Two glycerol based activated carbons and one commercial sample were tested as adsorbents of iohexol, an iodinated X-ray contrast media (ICM), from aqueous solution. The performance of the glycerol-derived carbons is comparable to that of the commercial sample, both in the kinetic (Fig. 1b) and equilibrium assays.

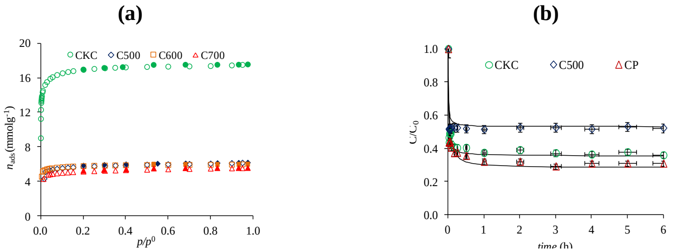

Figure 1. (a) N_2 adsorption isotherms at -196 °C (closed symbols represent desorption points; **(b)** Iohexol adsorption kinetic results (30 ºC; 6 mg; 9 cm^3 of 180 ppm solution). Samples - thermal activated: C500, C600 and C700; chemically activated- CKC.

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PRODUÇÃO DE CARVÕES ATIVADOS A PARTIR DE CARBONIZADOS OBTIDOS POR HTC

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Os carvões ativados (CA) têm sido exaustivamente estudados durante o último século. A razão deste interesse deve-se à alargada gama de aplicabilidade destes materiais, desde a indústria ou tratamento de águas até à biomédica. Atualmente tem-se assistido a uma maior diversificação de técnicas de produção com a finalidade de especialização de cada material. Uma desses técnicas é a utilização da carbonização hidrotérmica (HTC) no passo prévio à ativação dos materiais, utilizando como precursores materiais puros e derivados lenhocelulósicos. Este processo mimetiza o processo natural de produção de carvão, fazendo uso de condições específicas de pressão e temperatura. Como resultado estes carvões apresentam morfologias regulares e química superficial rica, prevalecendo a presença de grupos ácido, hidroxilo e grupos aromáticos. No presente trabalho foram preparados carvões ativados a partir de quitosano utilizando HTC no passo de carbonização seguido de ativação por CO_2. Verificou-se que o processo de HTC, dependendo da temperatura de carbonização, promoveu o aumento do teor em carbono e de nitrogénio até um máximo de 40 e 10%, respectivamente. Este elevado teor de nitrogénio, sem que se tivesse realizado qualquer pré ou pós-tratamento, é umas das vantagens do método usado neste trabalho.

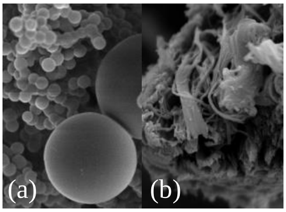

Figura 1. Imagem SEM (a)HTC quitosano; (b)CA produzido a partir do HTC de quitosano.

Como se verifica na figura 1(b), os carvões ativados perderam quase a totalidade das estruturas esféricas criadas durante o processo de HTC alterando significativamente a morfologia dos CA produzidos. Estes apresentam uma morfologia filamentosa resultante do processo de formação da estrutura porosa no processo de ativação. Nas condições testadas, os CA produzidos apresentam características microporosas com áreas superficiais aparentes entre $400m^2g^{-1}$ e $2130m^2g^{-1}$ e volumes microporosos entre 0.17 e $0.92cm^3g^{-1}$.

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IONOTHERMAL SYNTHESIS OF ACTIVATED CARBONS

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Activated carbon (AC) materials have a key role in numerous applications (adsorption, catalysis, energy conversion/storage) mainly due to their high surface areas, tunable pore size distribution and surface chemistry [1]. The industrial production of AC is a well-established process but the scientific community continues to search for novel synthetic approaches to obtain more specialized AC.

In the present study glucose, cellulose and pine sawdust were used as carbon source and eutectic salt mixtures ($LiCl/ZnCl_2$, $NaCl/ZnCl_2$, $KCl/ZnCl_2$) were tested as porogen (Fig. 1). The thermal treatment was made under N_2 flow (10ºC/min up to 240 ºC (2h) heating up to 800ºC or 1000 ºC (2 h)). Regardless the carbon source the BET area values of the materials synthetized decrease as the radius of the alkaline metal in the eutectic mixture increases. The use of $LiCl/ZnCl_2$ mixture originates materials with BET area values around 2000 m^2/g, and when glucose was used as precursor the total pore volume attained 1.54 cm^3/g. Samples prepared with mixtures containing Na and K have 50 to 80 % of mesopores. This synthesis allows tuning the pore size distributions since by controlling the eutectic mixture and the carbon precursor, being possible to develop pores in the micro to mesopore range. The potential of these materials for water decontamination technologies was assessed by preliminary adsorption studies of pharmaceutical compounds.

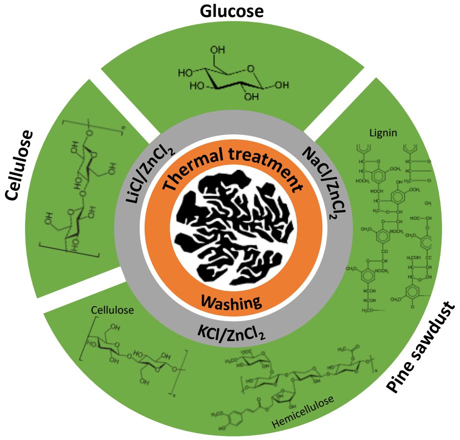

Figure 1. Scheme of the ionothermal synthesis.

Acknowledgements. This study was funded by projects PEst-OE/QUI/UI0612/2013 (CQB) and UID/QUI/50006/2013 - POCI/01/0145/FERDER/007265 (REQUIMTE) from FCT/MEC through national funds and co-financed by FEDER, under the Partnership Agreement PT2020. ASM thanks FCT for a Post-doc grant (SFRH/BPD/86693/2012).

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NANO-GRAPHENE OXIDE - GLYCOL PORPHYRINS: SYNTHESIS AND EFFECTS

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Nano-graphene oxide (NanoGO) and its functionalized derivatives have attracted great interest in nanomedicine due to its own intrinsic properties, all the dimensions lower than 100 nm and a singular chemical structure, which allows interesting possible biomedical applications such as drug delivery, tissue engineering, hyperthermia cancer therapy and photodynamic therapy.[1] However, the toxicity of NanoGO nanosheets is not yet well-known and it is necessary to understand its entry mechanisms into mammalian cells in order to avoid cell damage and human toxicity. Concerning NanoGO administration, although NanoGO colloids are soluble in water, they need further functionalization with molecules which improves the material dispersion and stability in aqueous solutions.

In the present study, NanoGO has been covalently functionalized with glycol porphyrins through esterification reactions. The resultant hybrid materials are characterized by scanning electron microscopy, atomic force microscopy, X-ray photoelectron spectroscopy, Fourier transform infrared, ultraviolet-visible absorption and fluorescence spectroscopy.

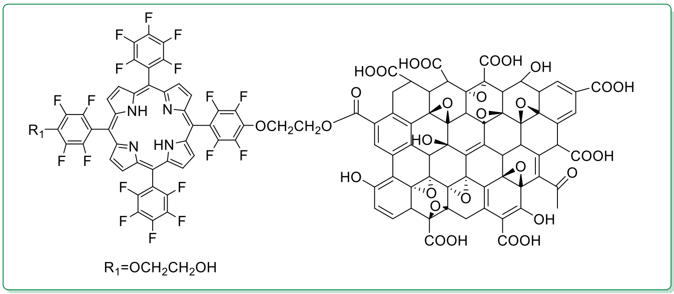

Figure 2: Glycol Porphyrin-NanoGO hybrid material

Preliminary studies on the behavior of hybrid materials after being in contact with different cell types were developed. The effects of materials on cell proliferation, cell morphology and cytokine release were analyzed. Moreover, the production of reactive oxygen species (ROS) was also measured.

Acknowledgments. Financial support from FCT (SFRH/BPD/75782/2011, SFRH/BPD/105478/2014, IF/00759/2013 and PD/BD/127805/2016).

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N-DOPED GRAPHENE IN THE CATALYTIC REDUCTION OF 4-NITROPHENOL

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Graphene emerged as one of the most prominent carbon nano-materials, with great versatility towards different applications. Its properties such as high surface area, chemical inertness and easy surface modification, in addition to its reusability and eco-compatibility, make of graphene a perfect material for application as a metal-free catalyst[1]. The reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) is of great value for the production of anilines and paracetamol, and its catalytic reduction with sodium borohydride ($NaBH_4$) requires a basic catalyst. Lately, this reaction became popular as a model reaction for the study of the catalytic properties of nano-materials[2]. In this work, metal-free N-doped graphene was obtained using a cost-effective solvent-free method and used as catalyst on the basic reduction of 4-NP.

The nano-materials were prepared by ball milling commercial graphene with different N-precursors, with further thermal treatments. Its structure and composition were studied and correlated to its catalytic performance. The surface properties of the graphene as well as the quantity and quality of N atoms were analyzed by N_2 adsorption at 77 K, elemental analysis and XPS spectroscopy.

The catalytic tests were monitored by UV-Vis spectroscopy, from which the conversions and yields were calculated. A great variation on the adsorption and desorption of the product was observed depending on the reductant/catalyst ratio. In addition, it was verified that the volume of solvent, hence the concentration of the reactants, played an important role on the efficiency of the reaction. A great yield was obtained for a small water volume and a high reductant/catalyst ratio.

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FLG/CNT HYBRIDS PRODUCED USING OXIDE SPINELS

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Graphene is an extremely versatile 2D material for nanotechnology applications due to its excellent physical and chemical properties. Hybrids based on graphene take advantage of these properties to create functional 3D materials by anchoring other nanomaterials on graphene. Among the different additives, carbon nanotubes (CNTs) are among the most studied. The high aspect ratio in combination with their electrical conductivity and mechanical properties can lead to 3D nanostructures with improved functional properties. Indeed, a synergistic behavior has already been reported between CNTs and graphene or few-layered graphene (FLG) for application in energy, catalysis, and electronics [1]. Catalytic chemical vapor deposition (CVD) preparation of CNT-FLG hybrids is commonly achieved by mixing catalysts that separately produce FLG or CNTs [2]. Here, we report a single step preparation of CNT/FLG hybrid materials by a fluidized bed CVD process using a single catalyst.

Different $Al_xCo_{1-x}Fe_2O_4$ (x = 0.025–0.10) catalysts were prepared using the citrate-nitrate gel combustion method. CVD synthesis was carried out at 650°C in a horizontal fixed bed reactor using ethylene as the carbon precursor. The samples were characterized by TEM, XRD, Raman spectroscopy, TGA, and N_2 adsorption-desorption measurements.

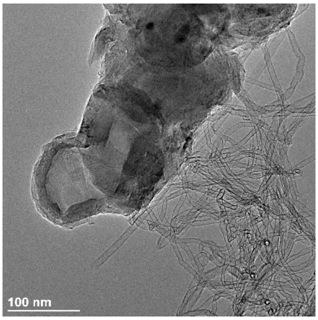

Figura 1. TEM micrograph of the hybrid material obtained with $Al_{0.025}Co_{0.975}Fe_2O_4$.

Al doping of cobalt ferrite in the 0.01–0.025 mol range led to the formation of a uniform hybrid, where the FLG thickness and CNT diameter could be controlled by changing the reaction conditions. Only FLG was obtained when $CoFe_2O_4$ was used as catalyst. However, the introduction of small amounts of Al induced the production of CNTs. For catalysts with higher Al content (e.g., $AlCoFeO_4$), CNTs were selectively produced. Hence, there is a small window (x < 0.05), where CNTs and FLG can be obtained. These materials could be a useful steppingstone for the single catalyst-based preparation of CNT/FLG hybrid materials.

Acknowledgements. B.F. Machado acknowledges the FCT Investigator Program (IF/00301/2015), with financing from the European Social Fund and the Human Potential Operational Program.

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GRAPHENE-BASED NANOCOMPOSITES FOR ENVIRONMENTAL APPLICATIONS

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In recent years, two-dimensional graphene, the newest type of carbon nanostructures has been extensively explored in a wide range of fields. However, its usage in environmental applications has been less investigated. On the other hand, magnetic materials are of considerable interests in material chemistry because of their unique physical properties and outstanding surface chemistry properties. Taking advantage of the combined benefits of graphene and magnetic nanoparticles, here we report a simple strategy for preparing magnetic graphene-based nanocomposites, based on the deposition of magnetite nanoparticles on graphene sheets, for application in multiple environmental uses. As a proof of concept, the nanocomposites produced will be tested as sorbents to remove toxic elements and compounds from water, as well as to recovery scarce trace elements used as key components for the development of new technologies (the so-called technology-critical elements).

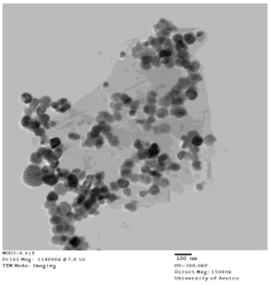

Figura 1. TEM image of the magnetic graphene-based nanocomposite

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MICROWAVE PLASMA PRODUCTION OF FREE-STANDING GRAPHENE/N-GRAPHENE SHEETS: AN XPS STUDY

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Graphene and its derivative N-graphene have attracted an exceptional research interest due to their unique chemical and physical properties. Nanosheets in the form of free-standing graphene flakes with just a few atomic monolayers find applications where an alternative to horizontal graphene supported by solid surfaces is needed. While in supported-graphene only one surface is available, free-standing graphene has the advantage of a quite unique structural feature characterized by both free surfaces and at least three open edges that can effectively be utilized.

Lately, it was shown that self-standing graphene sheets can be produced using plasmas at atmospheric pressure conditions [1, 2]. The current challenge is to find an industrially scalable process to produce a high quality material on a large scale at low cost and in a reproducible manner.

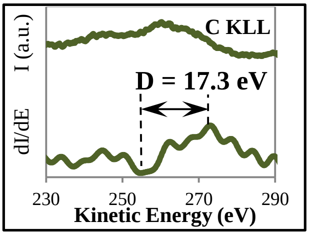

Figure 1. C KLL and 1st derivative of graphene.

Among the battery of analytical techniques, the X-ray photoelectron spectroscopy (XPS), can help to evaluate the quality of the as-synthesized graphene, namely by quantifying the sp^2/sp^3 carbon ratio and/or the doping efficiency. Another useful parameter is the one obtained from the 1st derivative of the C KLL Auger structure, called the D parameter, which is the energy difference between absolute maximum and minimum.

Table 1. D parameters reported for different carbon structures [3]

Graphite	Diamond	SWCNT	DLC	Carbonized Wood	Carbon-black pellets
21.2	13.7	17.5	14.7	14.3	14

Acknowledgements. A. M. Ferraria acknowledges Fundação para a Ciência e a Tecnologia (FCT) for grant SFRH/BPD/108338/2015 and project UID/NAN/50024/2013.

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S-DOPED GRAPHENE FLAKES@SEMICONDUCTORS HYBRID FOR THE PHOTOCATALYTIC DEGRADATION OF ORGANIC DYE

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Heterogeneous photocatalysis has received much research interest because of its powerful potential applications in undertaking many important global energy and environmental challenges in a cost-effective sustainable manner. Due to their unique properties, graphene nanosheets-supported semiconductor composite photocatalysts have been widely prepared and applied in different photocatalytic fields: pollutant degradation, H_2 production, and CO_2 reduction.[1]Very recently, the heteroatom doping of graphene has been increasing as a synthetic methodology to enhance the performance of graphene-based materials for a wide range of applications, namely in photocatalysis.[2]

In this work, the synthesis and characterization of sulphur-doped graphene flakes decorated with CuS and manganese ferrite (MnF_2O_4) semiconductors nanoparticles are described. The S-doping of graphene flakes was performed by ball milling followed by heat treatment at 600ºC. The CuS and MnF_2O_4 were sequentially immobilized into the as-prepared S-doped graphene flakes by *in situ* growth methods. The nanomaterials were characterized by FTIR, XPS, TEM and XRD, which confirmed the successful incorporation of sulphur on the graphene structure, as well as the grafting of CuS and MnF_2O_4 nanoparticles.

For the photocatalytic proof-of-concept, the hybrid nanomaterial was tested in the degradation of rhodamine B (RhB) using UV-vis spectroscopy to monitor the reaction evolution; RhB-P-25 system (P-25, commercial TiO_2)[3] was used to benchmark the prepared photocatalyst. The control reaction without photocatalyst was also performed.

Acknowledgements. This work was supported by Fundação para a Ciência e a Tecnologia (FCT)/MEC and FEDER under Program PT2020 (project UID/QUI/50006/2013-POCI/01/0145/FEDER/007265) and through project UTAP-ICDT/CTM-NAN/0025/2014 in the framework of UT Austin|Portugal Program. IKB and MA (SFRH/BD/89156/2012) thank FCT for their grants. CP thanks FCT for Investigator contract IF/01080/2015. Ana C. Estrada also thanks FCT for a post-doctoral grant (SFRH/BPD/86780/2012).

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ENCAPSULATION OF NUCLEIC ACIDS IN CARBON NANOTUBES: THERMODYNAMICS AND KINETICS

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Selective and controlled delivery of genetic cargo to a living cell, using encapsulation into nanoporous solids, involves a three-step kinetics: *i)* confinement of the biomolecule, followed by *ii*) diffusion along the endohedral volume, and finallly *iii)* ejection of the biological material towards the cellular interior. In order to study the thermodynamical [1, 2] and kinetical properties associated with the process [3], we employ atomically detailed computer experiments to probe the encapsulation of double-stranded canonical B-DNA, into hydrophobic and hydrophilic carbon nanotubes with diameters in the range $D = 3 - 4$ nm (Figure 1). It is found that nucleic acid confinement is thermodynamically favourable leading to DNA@SWCNT hybrids with lower free-energies (– 40 kJ/mol) than the bulk DNA. Furthermore, the larger topology induces an anisotropic translation preferentially along the nanotube main axis, which is annihilated when diameter decreases to 3 nm and diffusion occurs approximately symmetrical along any direction in space; there is an initial time window (≤ 2 ns) where DNA diffusion obeys Fick's law ($\propto t$), beyond which it transitions to a single-file type regime ($\propto t^{1/2}$).

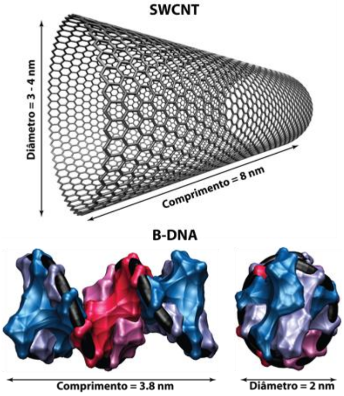

Figure 1. *Top)* Single-walled carbon nanotube *Bottom)* Dickerson B-DNA.

Physiological conditions employed (310 K, [NaCl] = 134 mM) allow the extrapolation of results to *in vivo* systems, constituting a landmark for biomolecular encapsulation in the context of cellular delivery.

Acknowledgments. This work was supported by the Associate Laboratory for Green Chemistry LAQV, which is financed by national funds from FCT/MEC (UID/QUI/50006/2013) and co-financed by the ERDF under the PT2020 Partnership Agreement (POCI-01-0145-FEDER - 007265). F.J.A.L. Cruz gratefully acknowledges financial support from FCT/MCTES (Portugal) through grant REQUIMTE/BPD/004/2016.

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COMPETITIVE BINDING OF POLYMER AND PROTEIN ON CARBON NANOTUBES

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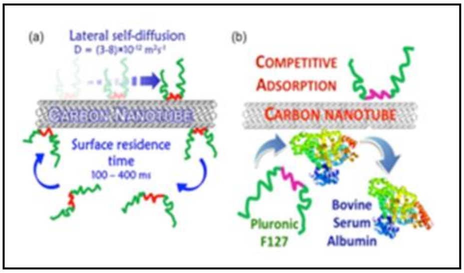

Figure 1. Main findings: (a) lateral diffusion of polymer along the nanotube and surface residence times; (b) competitive adsorption of polymer and protein onto the nanotube surface.

Since carbon nanotubes are hydrophobic in character and thus do not disperse in water, covalent surface modification or addition of dispersing agents are usually needed [1,2]. Gauging the binding strength of dispersants, such as surfactants and polymers, onto the CNT surface is extremely valuable *inter alia* for optimizing dispersion efficiency or developing separation processes [1,2]. However, this problem is difficult to assess experimentally and thus available data are scarce. Herein, we present results from self-diffusion NMR in aqueous dispersions of SWNTs prepared with either the block copolymer F127 or the protein bovine serum albumin, BSA [3,4]. The experiments detect the amount of F127 molecules adsorbed onto the SWNT surface. This quantity is recorded (i) in F127-SWNT dispersions to which BSA is added and (ii) in BSA-SWNT dispersions to which F127 is added. Interestingly, the data show that F127 molecules replace BSA ones adsorbed at the SWNT surface, while BSA leaves the adsorbed F127 coverage practically intact [4]. Consequently, F127 is found to bind more strongly than BSA. Hence, we provide an unambiguous method to evaluate dispersants by their adsorption strength onto carbon nanotubes.

Acknowledgments. FCT is acknowledged for financial support through PEst-C/QUI/UI0081/2013; FEDER and FCT/MES through NORTE-01-0145-FEDER-000028.

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AMPHIPHILIC CARBON NANOTUBES AS STABILIZERS FOR PICKERING EMULSIONS

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Stable Pickering emulsions were prepared using different amphiphilic carbon nanotubes (ACNTs) synthesized as described elsewhere [1], i.e. using ethylene (E) and acetonitrile (A). These ACNTs were used to stabilize Pickering emulsions (Fig. 1A). The way as the emulsion properties are affected by the ACNT load, pH, sonication time, presence of lipophilic compounds and H_2O_2, addition order of the oil and water phases onto the ACNT, was studied. Optical micrographs were taken 72 h after the Pickering emulsion preparation under different conditions (Fig. 1B) in order to measure the average droplet diameter. ACNTs synthesized with both acetonitrile and ethylene (amphiphilic A20E20, E10A20 and A20E10) formed perfectly stable emulsions. ACNTs prepared with only acetonitrile (hydrophilic A30) or ethylene (lipophilic E30) did not form stable emulsions. The presence of H_2O_2 had such a strong effect over the emulsion properties that it was possible to stabilize emulsions with a low ACNT load only by adding H_2O_2.

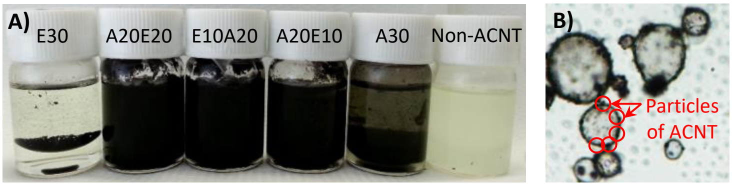

Figure 1. (A) Photographs of oil/water mixtures with different ACNTs and (B) optical micrograph of the mixture stabilized with E10A20.

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NANOTUBOS DE CARBONO DOPADOS COM AZOTO NA OXIDAÇÃO HÚMIDA DE COMPOSTOS ORGÂNICOS

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A incorporação de diferentes heteroátomos (O, N, S, B, P) na superfície dos materiais de carbono e a descoberta das suas propriedades catalíticas veio abrir uma janela de novas oportunidades a esta classe de materiais que, até então, eram maioritariamente explorados pela comunidade científica como suportes [1].

Neste trabalho é apresentada uma nova metodologia de incorporação de grupos azotados, reconhecidos por melhorarem o desempenho catalítico de materiais de carbono em reações de oxidação [2]. Este novo método permite a incorporação de grupos piridínicos, pirrólicos e azoto quaternário na rede sp2 de nanotubos de carbono comerciais. Trata-se de um método sem solvente envolvendo um tratamento mecânico num moinho de bolas seguido de um tratamento térmico em atmosfera inerte ou de amónia. Os materiais dopados com azoto revelaram-se promissores na oxidação do ácido oxálico pelo processo de oxidação húmida (Figura 1), com excelente desempenho catalítico comparado tanto com o material comercial (NTC-O) como com o material apenas tratado mecanicamente (NTC-MB), o que é explicável com base na natureza dos grupos superficiais.

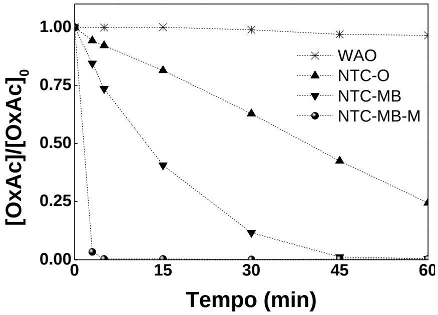

Figura 1. Evolução da concentração de ácido oxálico por oxidação catalítica húmida (WAO – oxidação não catalítica).

Agradecimentos. Este trabalho foi desenvolvido no âmbito do projeto "AIProcMat@N2020 - Advanced Industrial Processes and Materials for a Sustainable Northern Region of Portugal 2020", com referência NORTE-01-0145-FEDER-000006, cofinanciado pelo Programa Operacional Regional do Norte (NORTE 2020), através do Portugal 2020 e do Fundo Europeu de Desenvolvimento Regional (FEDER) e do Projeto POCI-01-0145-FEDER-006984 - Laboratório Associado LSRE-LCM - financiado FEDER, através do COMPETE2020 – Programa Operacional Competitividade e Internacionalização (POCI) e por fundos nacionais através da Fundação para a Ciência e a Tecnologia I.P. R.P. Rocha agradece a bolsa FCT SFRH/BD/95411/2013.

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CFRP BIOINSPIRADOS PARA MELHORIA DA RESISTÊNCIA AO IMPACTO E AUTOSSENSORIZAÇÃO

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Os compósitos reforçados com fibras de carbono (CFRP) são cada vez mais usados em aplicações de elevado desempenho devido às excelentes propriedades mecânicas e baixo peso que apresentam. A resistência interlaminar continua, no entanto, a ser uma das maiores limitações do seu desempenho mecânico [1-3].

Recentemente, tem-se vindo a tentar superar o problema, aplicando nos CFRP mecanismos semelhantes aos que garantem um elevado desempenho ao impacto em organismos vivos, p.e., o exosqueleto dos artrópodes que apresenta uma estrutura fibrosa laminada helicoidal (Bouligand) à escala micrométrica [4-6]. Sistemas sensoriais estudados em seres vivos também têm inspirado o desenvolvimento de compósitos multifuncionais [7], sendo ainda um desafio a criação de tecnologias de fabrico capazes de replicar estas estruturas/sistemas.

Neste trabalho fabricaram-se CFRPs com desempenho mecânico melhorado, usando laminados bioinspirados com fibras orientadas helicoidalmente (tipo Bouligand) e nanotubos de carbono (CNT) como sensores capazes de lhes conferiram multifuncionalidade (monitorização de dano). Produziram-se por infusão por vácuo, usando uma resina epóxída reforçada com fibras contínuas de carbono, placas CFRP (100x40x4 mm) com empilhamentos helicoidal e standard que, para comparação de propriedades, foram sujeitas a ensaios de impacto e de compressão após-impacto. Para garantir a multifuncionalidade, transferiram-se florestas de CNT verticalmente alinhados (VA-CNT) obtidas por deposição química a vapor (CVD) para o laminado. Usaram-se ainda técnicas não-destrutivas (NDT) de ultrassons (C-Scan) na análise da microestrutura e avaliação dos danos produzidos após impacto. Os resultados evidenciam as dificuldades encontradas em fabricar as placas e as melhorias que a integração de estruturas bioinspiradas conferem às características e multifuncionalidade dos compósitos.

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GOLD ON SURFACE MODIFIED CARBON MATERIALS FOR CYCLOHEXANE HYDROCARBOXYLATION

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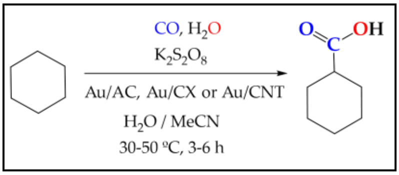
Gold nanoparticles (Au NPs) were successfully deposited by the colloidal method [1] on carbon materials (AC-activated carbon, CX-carbon xerogels and CNT-carbon nanotubes) as received/prepared and with different treatments, namely: oxidized with HNO_3 (-ox); and oxidized with HNO_3 and subsequently treated with NaOH (-ox-Na) [2].

The catalytic activity of the obtained materials was assessed for the single-pot hydrocarboxylation of cyclohexane to cyclohexane carboxylic acid, in H_2O/acetonitrile, under mild conditions (50 °C, 2 atm of CO). The best results were obtained with –ox-Na materials, followed by –ox and originals. Au/CNT-ox-Na exhibited the best performance, yielding cyclohexanecarboxylic acid up to ~90% yield, and excellent recyclability, maintaining 98.5% of the initial activity after 6 consecutive catalytic cycles.



Scheme 1. Hydrocarboxylation of cyclohexane catalyzed by Au NPs supported on carbon materials.

Green metric values of carbon efficiency also confirmed the improvement brought by this novel catalytic system to the hydrocarboxylation of cyclohexane. These results are relevant towards the sustainable production of carboxylic acids.

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INFLUENCE OF THE SURFACE CHEMISTRY OF THE SUPPORT ON THE CONVERSION OF CELLULOSE

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The production of fine chemicals and biofuels from lignocellulosic biomass is one of the most important topics in green and sustainable chemistry [1]. The one-pot hydrolytic hydrogenation of cellulose to sugar alcohols over heterogeneous catalysts is one of the most efficient pathways for a sustainable society dependent on cellulosic biomass. Sorbitol is one of the most important sugar alcohols, since it can be used as sweetener and in pharmaceuticals, cosmetics and textiles, and for the synthesis of many fine chemicals [2]. The aim of this work is the development of an efficient catalytic system for the direct conversion of cellulose to sorbitol by testing Ru catalysts supported on CNT with different surface chemistries.

Commercial carbon nanotubes (CNT_0) were oxidized with HNO_3 (CNT_1) in order to introduce oxygen-surface groups, and then thermally treated at different temperatures (400, 700 and 900 °C). Ru catalysts were prepared by the incipient wetness impregnation of the different supports. Supports, catalysts and cellulose were characterized by N_2 adsorption at -196 °C, TEM, TPR, TPD and XRD.

The catalysts were tested in the one-pot conversion of cellulose. The oxidative treatment of the supports enhanced the rate of hydrolysis of cellulose, but the selectivity to sorbitol achieved was lower (Figure 1). As conclusion, Ru/CNT_0 was the most efficient catalyst for the selective production of sorbitol from cellulose. Comparing the modified materials, the thermal treatment decreased the selectivity to sorbitol.

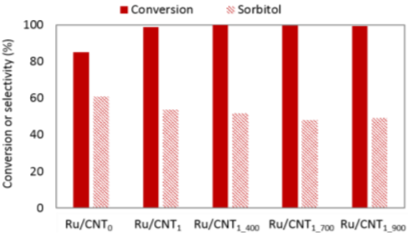

Figure 1. Conversion of cellulose and selectivity to sorbitol after 5 h of reaction.

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PREPARATION OF MULTIWALLED CARBON NANOTUBE HYBRID MATERIALS: CATALYTIC PERFORMANCE

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The application of CNTs as supports for immobilization of typical homogeneous catalysts started in the 90's and since then a huge increment on this field has been observed, mainly due to their thermal stability, tolerance against poisoning and ease of surface functionalization.[1,2] Chiral BINOL and phosphorous based molecules are among the most important ligands for preparation of transition metal complexes with application in homogeneous catalysis. Their immobilization onto solid supports, to allow the reutilization of catalysts, is still a great challenge. Herein, we present innovative methodologies to promote the immobilization of these ligands onto carbon nanotubes and their preliminary evaluation as catalysts for carbonylation (with rhodium) and for alkylation (with titanium) reactions.[3]

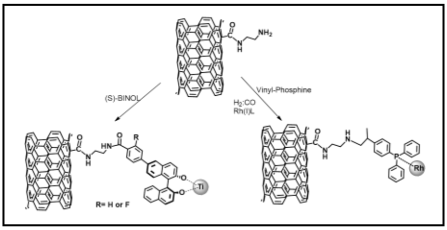

Figure 1. Structure of MWCNTs hybrid material.

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EXFOLIATED CARBON NITRIDE AS PHOTOCATALYST FOR THE SELECTIVE PRODUCTION OF ALDEHYDES

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Graphitic carbon nitride (g-C_3N_4) is a metal-free polymeric material, which has been attracted much attention for photocatalytic applications since it can be effectively activated by visible light. One of the major drawbacks of this material is its low surface area, derived from the strong stacking of C_3N_4 layers. Thermal exfoliation can be used as an efficient technique for producing g-C_3N_4 nanosheets, thus increasing the surface area of the resulting materials [1].

In the present work, thermally exfoliated g-C_3N_4 was used as catalyst for selective photocatalytic conversion of a set of aromatic alcohols into the respective aldehydes in aqueous medium, natural pH, ambient temperature and pressure, and using light emitting diodes (UV-LEDs) as highly-efficient and low cost radiation sources.

The results indicate that the photocatalytic activity is greatly influenced by the nature of the substituent in the *para*-position. The highest efficiency was obtained for the synthesis of 4-methoxy benzaldehyde, with a 76% yield and 78% selectivity at the end of 4 hours of irradiation (Fig. 1). The results will be discussed in light of the electron-donating and electron-withdrawing nature of the substituents in the starting molecule.

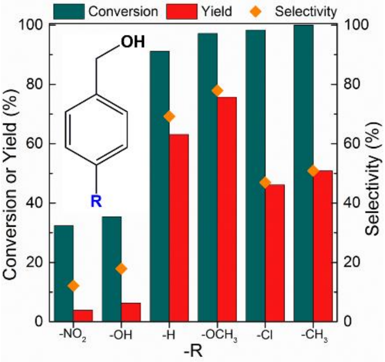

Figure 1. Effect of **-R**: conversion, yield and selectivity using exfoliated g- C_3N_4 after 4 h of irradiation.

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SELECTIVE SYNTHESIS OF AROMATIC ALDEHYDES USING CARBON NANOFIBER/ZnO PHOTOCATALYSTS

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Heterogeneous photocatalysis as been proving to be a promising alternative to traditional thermal catalytic synthesis processes [1]. Aromatic aldehydes are organic compounds widely used as flavouring and fragrance agents in food, pharmaceutical and cosmetic industries [2]. In the present work, composite materials based on zinc oxide (ZnO) and carbon nanofibers (CNF) were used for the photocatalytic synthesis of a series or aromatic aldehydes. The photocatalytic efficiency of composites with different CNF contents (from 5 to 20 *wt.*%) was assessed for the production of vanillin (V) through oxidation of vanillyl alcohol (VA) under UV-LED irradiation. The best performing material was that containing 10 *wt.*% of CNF, reaching 50% of VA conversion, and 20% yield and 40% selectivity towards V at the end of 8h of irradiation. Finally, ZnO and 10% CNF/ZnO were tested for the conversion of other aromatic alcohols namely anisyl alcohol and piperonyl alcohol into the respective aldehydes, anisaldehyde (A) and piperonal (P) (Fig. 1). The relative efficiency of ZnO and CNF/ZnO depended on the target reaction, being the synergetic effect promoted by the presence of the carbon phase more evident for the production of vanillin.

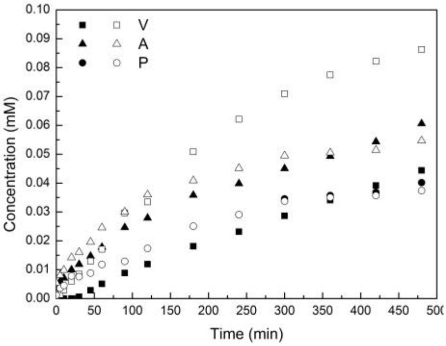

Figure 1. Photocatalytic production of aromatic aldehydes by ZnO (closed) and 10%CNF/ZnO (open).

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METALLIC CATALYSTS SUPPORTED ON MODIFIED CARBON NANOTUBES FOR BROMATE REDUCTION IN WATER

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Bromate has been found in water treatment plants at concentrations with a significant cancer risk for life-time exposures. Its principal source is the ozonation of bromide during water treatment [1]. Catalytic reduction of bromate into bromide using hydrogen over supported metal catalysts has been showing to be a promising technology for its removal from water [2,3].

In this work we aim to evaluate the influence of the textural and surface chemical properties of multi-walled carbon nanotubes (MWCNT) on the performance of Pd, Cu and Pd-Cu catalysts for the bromate removal. Thus, commercial MWCNTs were subjected to the following treatments: i) liquid-phase oxidation with nitric acid, followed by inert gas-phase thermal treatments in order to incorporate different types and amounts of oxygen-containing surface groups; ii) mechanical treatment by ball milling, and iii) doping with nitrogen. The catalytic bromate reduction in water (10 mg/L) was carried out in a semi-batch reactor under hydrogen at room temperature and atmospheric pressure.

The performance of the different supported metallic catalysts is highly influenced by the textural and surface chemical properties of the support. The N-doped carbon nanotubes are the best supports for this catalytic process, while the supports with high amounts of oxygen-containing surface groups decrease the catalytic performance of the metallic phases for bromate reduction.

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SYNERGETIC EFFECT BETEWEN N-DOPED CNT AND ZnO FOR THE PHOTOCATALYTIC SYNTHESIS OF VANILLIN

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The application of heterogeneous photocatalysis has been gaining increasing attention in the field of green organic synthesis[1]. Zinc oxide (ZnO) is a photocatalyst that can be considered a suitable candidate to substitute the benchmark titanium dioxide (TiO_2), due to the favourable electronic properties, greater morphological versatility and lower cost. On the other hand, carbon materials have shown beneficial effects on the photocatalytic activity of this type of semiconductors by inducing synergies, between the metal oxide and the carbon phase[2]. In the present work, ZnO prepared by a solid-state thermal process was combined with different contents of nitrogen doped carbon nanotubes (N-CNT). The efficiency of the materials was assessed in the photocatalytic oxidation of vanillyl alcohol into vanillin under room temperature, atmospheric pressure and using an energy efficient and low-cost light source (UV-LED). In general, the coupling of N-CNT with ZnO led to an increase in the yield of the photocatalytic production of vanillin (Fig. 1). Among the tested materials, the best performance towards vanillin production was obtained using 5%N-CNT/ZnO. A further increase in the N-CNT content led to a decrease in the efficiency of the process. The role of N-CNT in the efficiency of the composite materials will be discussed in light of the characterization results.

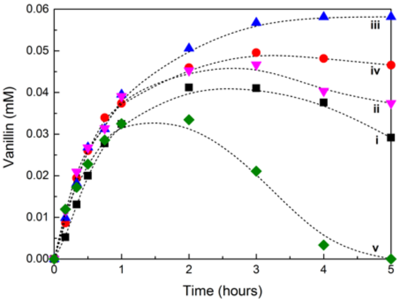

Figure 1. Vanillin production using neat ZnO (i), and 1%N-CNT/ZnO (ii), 5%N-CNT/ZnO (iii), 10%N-CNT/ZnO (iv) and 20%N-CNT/ZnO (v) composites.

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CARBON NANOTUBE-TiO_2 MATERIALS FOR THE PHOTOCATALYTIC SYNTHESIS OF CINNAMALDEHYDE

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Heterogeneous photocatalysis is considered a promising alternative route for the selective synthesis of fine chemicals [1]. Compared to conventional processes, it has the enormous advantage of operating under mild temperature, exempted of using hazardous reagents and with the prospect of using new low energy consumption irradiation sources. Selective conversion of alcohols into the corresponding aldehydes is one of the most important organic syntheses processes, Aldehydes are widely used in food, beverages, fragrances and as pharmaceutical precursors. In the present work TiO_2 (anatase, Sigma-Aldrich) was coupled with carbon nanotubes (CNT), seeking for enhanced catalytic activity resulting from synergic electronic effects between the metal oxide and the carbon phases [2]. The efficiency of the materials was assessed in the photocatalytic oxidation of cinnamyl alcohol (CA) into cinnamaldehyde (CAL) at room temperature, atmospheric pressure and using an energy efficient and low-cost light source (UV-LED). The coupling of CNT with TiO_2 led to an increase in the yield (*Y*) and selectivity (*S*) towards CAL production (Fig. 1). The introduction of Pt nanoparticles on both TiO_2 and CNT-TiO_2 materials further increased both *Y* and *S* (Fig. 1). The role of CNT and Pt nanoparticles in the efficiency of the photocatalysts will be discussed in light of the characterization results.

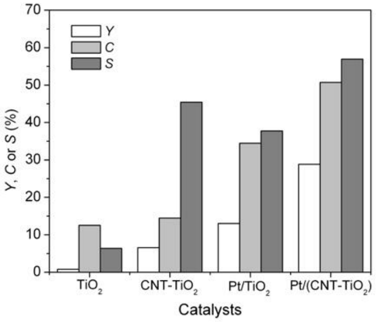

Figure 1. CA conversion (*C*) and CAL yield (*Y*) and selectivity (*S*) at 4 h irradiation using neat and Pt-loaded TiO_2 and CNT-TiO_2 photocatalysts.

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GREEN OXIDATION OF XYLENES USING C-SCORPIONATE VANADIUM HYBRID MATERIALS

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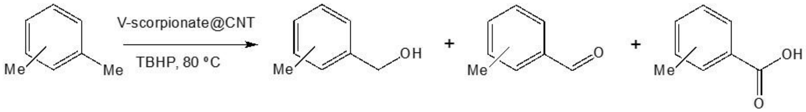
Currently, oxidation of *para*-xylene to produce terephthalic acid, a high value chemical mainly used in polyethylene terephthalate (PET) manufacturing[1,2], is conducted in a homogeneous cobalt:manganese catalytic system, in the presence of the highly corrosive bromide dissolved in aqueous acetic acid (Amoco process) [2]. Thus, halogen free catalytic systems are needed.

Herein, we report a new process for the selective oxidation of a methyl group of xylenes, catalyzed by C-scorpionate vanadium complexes supported at carbon nanotubes (CNT), to the corresponding alcohols, aldehydes and acids (no hydroxylation of the aromatic ring) under very mild conditions (Scheme 1) [3].



Scheme 1

Thus, our catalytic system is a significant finding towards the development of a greener process for *p*-xylene oxidation. The effects of reaction parameters, such as reaction time, temperature, type and amount of oxidant are reported and discussed.

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APPLICATION OF Au NPs/CARBON MATERIALS IN SOLVENT FREE 1-PHENYLETHANOL OXIDATION

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The Au(1%)/carbon materials[1] were used as catalysts for the oxidation of 1-phenyl ethanol to acetophenone (as a model reaction, see Fig. 1) with aqueous *tert*-butyl hydroperoxide (TBHP), under solvent free conditions and using a several reaction conditions.

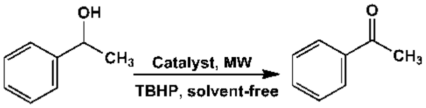

Figure 1 - Oxidation of 1-phenylethanol to acetophenone.

The differences in the catalytic activity of the hybrid materials are discussed (see Fig. 2) in ligth of the diferent supports.

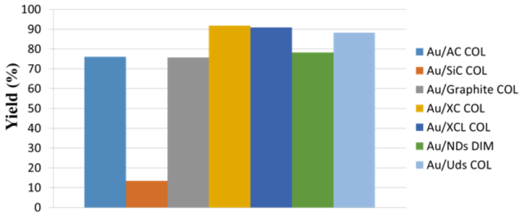

Figure 2. Yield of acetophenone. Reaction conditions : catalyst (5 µmol), 1-phenyl ethanol (2.5 mmol), TBHP (5mmol), 2 hours.

Acknowledgements. FCT for projects UID/QUI/00100/2013, PTDC/QEQ-ERQ/1648/2014 and PTDC/QEQ-QIN/3967/2014. QREN, ON2, FCT and FEDER for Project NORTE-07-0124-FEDER-000015. The LA LSRE-LCM acknowledges Project UID/EQU/50020/2013 co-financed by FCT and FEDER through Programme PT2020 and Programme COMPETE (FCOMP-01-0124-FEDER-123456). SACC acknowledges Investigador FCT program (IF/01381/2013/ CP1160/CT0007).

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$PMo_{11}V$@N-CNT AS ELECTROCHEMICAL NANOSENSOR FOR DETERMINATION OF ACETAMINOPHEN

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Since the discovery of carbon nanomaterials there has been much experimental and theoretical interest in investigating their physical and chemical properties[1-3]. Their unique structures and outstanding properties make them suitable and extremely attractive for a great number of applications such as electronics, energy and sensing[1-3]. Among these are the carbon nanotubes (CNT) which are highly used in the modification of electrodes especially due to their availability, cost-effectiveness and excellent physicochemical and electrochemical properties. CNT based sensors have the advantage of showing higher selectivity and sensitivity, lower detection limits and resistance to surface fouling and to passivation.

Their structure can be further improved by chemical doping with heteroatoms such as nitrogen (N-CNT) which can contribute to improve their intrinsic electrocatalytic activity, and when used as support, this type of doping can enhance the interaction between the CNT support and the catalyst, creating a new catalytic system with better performance. Several species have been used for the functionalization of CNT such as, polyoxometalates (POMs). Among their unique properties, the ability to reversibly accept and release a large number of electrons under marginal structural rearrangement producing the mixed-valence coloured species makes them suitable for several applications.

Herein we present a new nanocomposite ($PMo_{11}V$@CNT-N) as an electrochemical nanosensor for the determination of acetaminophen in the presence of tryptophan.

Acknowledgements. The Fundação para a Ciência e a Tecnologia (FCT), FEDER under Programme PT2020 (Project UID/QUI/50006/2013- POCI/01/0145/FEDER/007265) and Programme FCT–UT Austin, Emerging Technologies (Project UTAP-ICDT/CTM-NAN/0025/2014) is acknowledged for the financial funding. Thanks are also due to COST Action CM-1203 PoCheMoN.

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DIFFERENT APPROACHES FOR SURFACE FUNCTIONALIZATION OF S-DOPED HYDROCHARS

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Hydrochars are carbon materials that are prepared from renewable biomasses, e.g, glucose, maltose, sucrose or starch, that can present spherical morphology. These materials have been tested in different areas showing high electrical conductivity and excellent chemical stability. As-synthesised and further activated samples have also been used as adsorbents, catalysts or catalyst supports.[1]

The aim of this study was to evaluate the catalytic properties of sucrose, glucose and fructose derived hydrochars in esterification of butanol with acetic acid. Even though the materials present acidic surface properties, as demonstrated by the Boehm titration results, and pH_{pzc} values of ca. 2.0, the catalytic assays revealed that the nature of acid surface groups is a determinant factor for this type of reaction. In fact, according to the literature, to achieve high catalytic activities it is necessary to have a high number of sulfonic groups.[2] In this sense, S-doped hydrochars were synthetized by different ways: one-pot synthesis where the mixture of the sugars aqueous solution and different amounts of S-containing compound (*p*-toluenesulfonic acid, isethionic acid sodium salt, 4-sulfophtalic acid) were submitted to hydrothermal treatment; post-synthesis treatment of the sugar derived hydrochars (a) with concentrated H_2SO_4, and (b) by impregnation with S-containing compound followed by a second hydrothermal treatment.

The H_2SO_4 treated sucrose derived hydrochar allowed a quicker reaction (80% conversion after 2h), and to achieved almost total conversion after 6h of contact time.

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NANOPARTÍCULAS METÁLICAS MAGNÉTICAS REVESTIDAS COM CARBONO PARA A REMOÇÃO DE BROMATO EM ÁGUAS

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Ao longo dos últimos anos, tem havido um crescente interesse em estudar as nanopartículas superparamagnéticas. As nanopartículas metálicas magnéticas (MNP) podem ser revestidas com uma camada de materiais diferentes para melhorar a sua estabilidade e para introduzir novas propriedades de superfície [1]. O bromato na água tem sido associado a um risco significativo de cancro, tornando-se um dos poluentes frequentemente detetados na água potável e nas águas residuais, especialmente em processos que envolvam ozonização. A redução catalítica tem sido reconhecida como uma técnica de tratamento eficaz para remover iões através da sua redução sobre catalisadores metálicos (normalmente metais nobres) na presença de um agente redutor, normalmente hidrogénio [2]. Assim, este trabalho tem como objetivo sintetizar e caracterizar MNP e também MNP revestidas por carbono (C-MNP) para serem aplicadas como catalisador na remoção de bromato em água.

Para tal prepararam-se MNP, constituídas por metais não-nobres (Fe, Co ou Mn) baseadas em núcleos de FeO, que posteriormente foram revestidas com carbono por deposição química de fase vapor, utilizando etano ou mistura de etano com amónia como precursores a diferentes temperaturas. A redução catalítica de bromato em água (10 mg / L) foi realizada num reator semi-fechado na presença de hidrogénio à temperatura ambiente e pressão atmosférica. Os resultados obtidos revelam que estas MNP apresentam atividade catalítica para a redução de bromato em água, apesar de não terem metais nobres na sua constituição. As remoções de bromato mais elevadas foram observadas na presença de MNP revestidas com carbono.

Agradecimentos. Este trabalho foi desenvolvido no âmbito do projeto "AIProcMat@N2020 - Advanced Industrial Processes and Materials for a Sustainable Northern Region of Portugal 2020", com referência NORTE-01-0145-FEDER-000006, cofinanciado pelo Programa Operacional Regional do Norte (NORTE 2020), através do Portugal 2020 e do Fundo Europeu de Desenvolvimento Regional (FEDER) e do Projeto POCI-01-0145-FEDER-006984 - Laboratório Associado LSRE-LCM - financiado FEDER, através do COMPETE2020 – Programa Operacional Competitividade e Internacionalização (POCI) e por fundos nacionais através da Fundação para a Ciência e a Tecnologia I.P.

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Co-Mn LDH SUPPORTED IN OXYDIZED NANOTUBE COMPOSITES FOR OXYGEN EVOLUTION REACTION

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Oxygen Evolution Reaction (OER) is one of the reactions that occurs in the cathode of the Unitized Regenerative Fuel Cell (*i.e.*, a fuel cell combined with an electrolyser). It presents slow kinetics, leading to considerable electrochemical overpotential requirements. Traditionally, IrO_2 or RuO_2 and their alloys have been employed as electrocatalysts in OER due to their relatively low overpotential and high current density. However, Ir/Ru-based electrocatalysts suffer from low stability, high cost and scarcity. In order to bring this technology to a competitive commercial standing, it is necessary to develop electrocatalysts that counteract these disadvantages. Non-precious metal oxides supported on carbon materials have proven to be good options to replace current alternatives [1].

In the present work three types of electrocatalysts for OER were prepared. Layered Double Hydroxides (LDH), with a Co/Mn molar ratio of 4:1, were supported in carbon nanotubes oxidized with HNO_3 (CNT_HNO_3), in CNT_HNO_3 thermally treated in N_2 at 350 °C and in CNT_HNO_3 thermally treated in N_2 at 900 °C, using the incipient wetness impregnation method. The desired LDH structure was confirmed by X-Ray diffraction and thermogravimetric analyses. The textural parameters were determined from the N_2 adsorption isotherms. In order to obtain different metal oxide structures, the electrocalatalysts were once again submitted to a thermal treatment in a N_2-atmosphere at 350 °C. Only the composite with CNT_HNO_3 without thermal treatment kept the LDH structure.

Linear Sweep Voltammetry revealed that the lowest onset potential for OER was observed for the composite with CNT_HNO_3 treated at 350 °C in the electrocatalyst series without thermal treatment and in the electrocatalyst series with thermal treatment, which points out that only the removal of the carboxylic acids of the oxidized nanotubes is favourable for OER.

Acknowledgements. This work is a result of the projects “UniRCell”, with the reference POCI-01-0145-FEDER-016422 and of Project POCI-01-0145-FEDER-006984 – Associate Laboratory LSRE-LCM funded by ERDF through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) – and by national funds through FCT - Fundação para a Ciência e a Tecnologia.

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$MnFe_2O_4$@CNT-N AS A CARBON-BASED MATERIAL FOR THE CONSTRUCTION OF ELECTROCHEMICAL NANOSENSOR WITH APPLICATION IN PHARMACEUTICAL DETERMINATION

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Carbon nanotubes have been attracting increasing interest due to their structure, easy functionalization, high surface area and electrical properties, which make them attractive for application in the fabrication of electrochemical nanosensors.

For the first time, a glassy carbon electrode modified with N-doped carbon nanotubes functionalized with $MnFe_2O_4$ nanoparticles ($MnFe_2O_4$@CNT-N) has been prepared and applied for the electrochemical determination of caffeine (CF), acetaminophen (AC) and ascorbic acid (AA). The electrochemical behaviour of CF, AC and AA on the bare GCE, CNT-N/GCE and $MnFe_2O_4$@CNT-N/GCE were carefully investigated using cyclic voltammetry and square-wave voltammetry. Compared to bare GCE and CNT-N modified electrode, the $MnFe_2O_4$@CNT-N modified electrode can remarkably improve the electrocatalytic activity towards the oxidation of CF, AC and AA with an increase in the anodic peak currents of 52%, 50% and 55%, respectively. The sensitivity values at the $MnFe_2O_4$@CNT-N/GCE, for the individual determination of AC, AA and CF and in the biomolecules mixtures showed that the quantification of AA and CF show no interferences from the other biomolecules; however, AA and CF interfered in the determination of AC, with the latter biomolecule showing the strongest interference. Nevertheless, the obtained results showed that $MnFe_2O_4$@CNT-N composite material acted as an efficient electrochemical sensor towards the selected biomolecules highlighting the properties of carbon-based nanomaterials.

Acknowledgments. The Fundação para a Ciência e a Tecnologia (FCT), FEDER under Programme PT2020 (Project UID/QUI/50006/2013- POCI/01/0145/FEDER/007265) and Programme FCT–UT Austin, Emerging Technologies (Project UTAP-ICDT/CTM-NAN/0025/2014) is acknowledged for the financial funding.

FLAVOUR SYNTHESIS USING ACTIVATED CARBON AS SUSTAINABLE ACID CATALYST

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The objective of this work was to develop and study carbon based heterogeneous catalysts for catalytic reactions of interest, within the scope of green chemistry. Activated carbons prepared via sol gel synthesis and then physically activated with CO_2 (sample RFC2) as well as a commercial carbon (sample NCN) were studied in esterification reactions for the production of flavours. This material is an eco-friendly choice for catalyst, which combines excellent textural and chemical properties. Also, the preparation of activated carbon via sol gel method results in very tuneable material with highly pure composition which may be important for some applications. [1]

Table 1 presents the main characterization results. The sol gel derived carbons presented lower surface area. Both carbon presented low pHpzc values revealing a very acidic surface resulting from the post synthesis treatment with HNO_3. These carbons also presented significant mesoporosity.

Table 1: Samples Characterization

Samples	A_{BET} (m^2/g)	V_{micro} (cm^3/g)	V_{total}	pH_{pzc}
NCN	1030	0.30	0.56	3.8
RFC2	658	0.18	0.29	3.2

These characteristics allow them to be active in the esterification reaction with very high conversion after 24 h. The catalysts proved to be efficient in the esterification reaction of hexanol, isoamyl alcohol and octanol with acetic acid to produce pear, banana and orange flavours, respectively. The latter are approved compounds for food additives by the European Food Safety Authority.

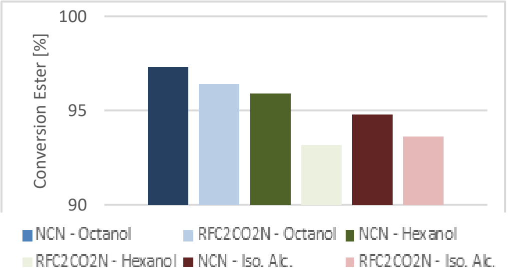

Figure 1. Conversion values to ester for each esterification reaction after 24 h reaction time

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NEW SULFONIC ACID FUNCTIONALIZED CARBON NANOTUBES: CATALYTIC APPLICATIONS

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The research strengthening on the development of sustainable processes to produce biochemical platform molecules and biofuels is mainly determined by the foreseen dependence decrease on the petroleum-based products. The use of renewable feedstocks (from renewable sources) and sustainable heterogeneous catalytic processes are important goals to achieve this challenge.[1]

The introduction of acid properties on materials in order to develop heterogeneous acid catalysts is one of the main challenges on catalysis due the wide range of industrial applications and their superior advantages when compared with the homogeneous acid catalysts, the traditional mineral acids. Over the past few decades, carbon nanomaterials have been extensively studied and have found numerous promising applications in science and technology. The thermal and mechanical properties of carbon nanotubes (CNTs) point them as good candidates for the preparation of heterogeneous acid catalysts by functionalities introduction to create acid active sites.[2] In the present work sulfonic acid functionalized multi-walled carbon nanotubes were prepared by covalent functionalization[3] and their performance as heterogeneous acid catalysts was evaluate in esterification reaction of free fatty acids (FFA) in the presence of alcohols and in the condensation reaction of furfural with 2-methylfuran. These catalytic processes are very useful for the preparation of bio-products and biofuels from waste oils and biomass.[4,5]

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NEW MONOLITH WITH ZEOLITE AND ACTIVATED CARBON FOR CO_2 CAPTURE

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Over the years, due to the industrialization, reduction of carbon dioxide emissions is an important challenge of industries. For that, diverse technologies can be studied, such as, adsorption processes. In adsorption processes, the development of new materials is an emerging challenge in order to increase the CO_2 adsorption capacity of material and the efficiency of the process of materials development. In this work, a new hybrid material composed by 13X zeolite and activated carbon as adsorptive raw materials was produced by extrusion. Textural characterization was carried out with N_2 adsorption isotherm at 77 K, CO_2 adsorption at 273 K, thermogravimetric analyses and mercury intrusion porosimetry. Pure gas adsorption equilibrium isotherms of carbon dioxide and nitrogen were measured with a gravimetric method using a Rubotherm® suspension balance at three temperatures, 303, 333 and 373 K. The experimental points were well described by Dual-Site Langmuir model. After that, binary breakthrough curves were performed at 298 K and 2.4 bar with different feed mixtures. These experimental results of adsorption equilibrium were validated by multicomponent extension of the Dual-Site Langmuir isotherm. A mathematical model was applied to predict the dynamic behaviour of the adsorption breakthrough curves.

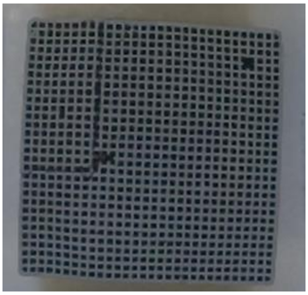

Figure 1. Composite monolith 50×50×50 mm

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CORN COB DERIVED-CARBONS AS ADSORBENTS FOR BIOGAS UPGRADING TO BIOMETHANE

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Corn production generates about 151 Mt of corn cob residues that are usually left in the crop field. However, the amount of cob waste produced often exceed the organic-C needed for soil conditioning. The conversion of this surplus into carbon adsorbents represents an added-value to these byproducts.

Biogas is a key bioenergy source that will contribute worldwide for low carbon bioeconomy. Apart from the digestate, the final product obtained in the anaerobic digestion of biomass is a gas with an interesting Low Heating Value mainly composed by 50-70% (v/v) CH_4 and 30-50% (v/v) CO_2 and trace amounts of H_2O, H_2S, CO, H_2 and NH_3. If biogas is suitably cleaned up to be upgraded to biomethane ($CH_4 > 97\%$ v/v), it will be similar to natural gas [1,2].

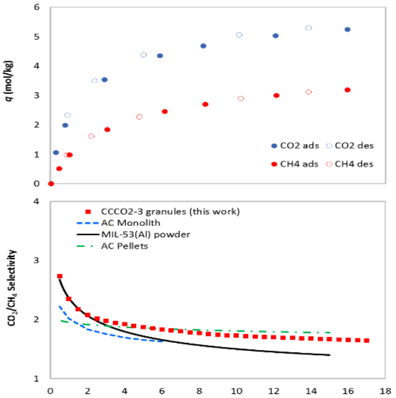

Figure 3. Top: CO_2 and CH_4 adsorption/desorption equilibria at 30ºC in CCCO2-3 sample. Bottom: Equilibrium selectivity as a function of pressure at 30°C for CO_2/CH_4. The results are compared with data of other ACs[1,2] and a metal-organic framework (MOF), MIL-53(Al) [3].

In this work, corn cob waste was submitted to physical activation with CO_2, at 800ºC, for different activation times (0.5, 1, 2 and 3 h). The best activated carbon (AC) was obtained with 2 h of activation time (CCCO2-3) and is being studied as adsorbent in an adsorption-based biogas refining process (Table 1). The CO_2 and CH_4 adsorption/desorption equilibria was measured using a standard volumetric/manometric unit. The adsorption capacities of these gases onto AC were investigated, as well as the CO_2/CH_4 equilibrium selectivity (Fig.1). CCCO2-3 showed a strong affinity towards CO_2 compared to CH_4, making it suitable for biogas upgrading.

Table 1. Textural properties of the CCCO2-3 carbon.

Activated Carbon	A_{BET} (m^2/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)
CCCO2-3	630	0.214	0.251

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CRITICAL FACTORS FOR AN EFFICIENT TWO-PHOTON EMISSION OF GRAPHENE QUANTUM DOTS

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Fluorescence imaging of biosystems is by far one of the most successful applications of nonlinear fluorophores. In this presentation, emphasis will be laid upon our recent study on the photophysics and nonlinear emission properties of nitrogen doped graphene quantum dots (N-GQD) as part of a new strategy to improve the nonlinear response of molecular materials. N-GQDs can be described as a 2-4 nm graphene core decorated with various oxygen and nitrogen containing functional groups on the surface (Fig. 1).[1] The fundamental question that we are striving to answer is what are the critical structural properties of the GQD for an efficient two-photon induced emission. The few existing reports where the TPA cross-section of GQD and carbon dots has been actually quantified seem to converge into a couple of critical factor for observation of an efficient nonlinear absorption, namely doping with nitrogen and crystallinity. Our conclusion, after production of GQD following many different reported procedures is that none of those factors seem to be sufficient to guarantee a high TPA cross-section of GQD.

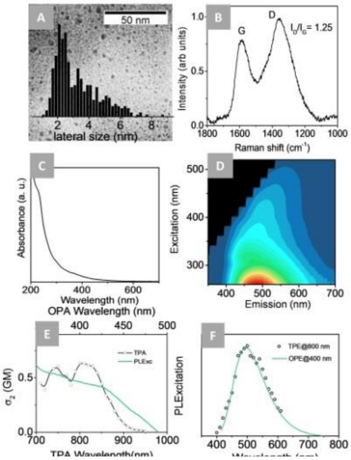

Figure 4. N-GQD with a lateral size distribution peaking at 2 nm (A), with D and G bands in the Raman spectrum indicative of structural order (B), unstructured UV-Vis absorption spectrum (C), excitation dependent emission (D), two-photon absorption and emission spectra overlapping with the linear excitation and emission spectra (E and F).

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TWO-PHOTON BRIGHTNESS IN HEPTAGON-CONTAINING NANOGRAPHENES

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Planar polycyclic aromatic hydrocarbons (PAHs), such as graphene quantum dots (GQDs), have been extensively investigated in recent years due to their exceptional optical properties that enabled applications in bioimaging, sensors, optoelectronic devices and nanomedicine. However, due to their uncontrolled synthetic procedures the final material is quite heterogeneous making it impossible to control its properties and engineering the material for specific applications. To overcome this limitation, we initiated the study of the photophysical properties of PAH mimicking the structure of GQD. The step-by-step synthetic procedure of these molecules is well controlled leading to a homogenous material [1]. For a set of distorted nanodisks containing non-hexagonal rings on the edge, the effect of the nature of the edge groups, the distortion from planarity and the conjugation length on the photophysical properties were studied, with emphasis on the two-photon absorption and emission. Figure 1 illustrates the typical spectroscopic properties of one of the studied molecules showing a moderate TPA cross section (~ 500 GM).

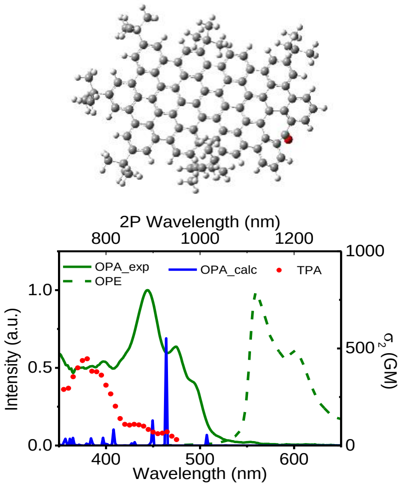

Figure 1. Experimental and calculated One-photon absorption (OPA), experimental Two-photon absorption (TPA) and One-photon emission (OPE) of the molecule represented above.

Acknowledments. The authors thank the group of A. G.Campaña for providing the compounds. The Fundação para a Ciência e a Tecnologia is acknowledge for financial support (IF/00759/2013, post-doc grant SFRH/BPD/75782/2011 and UID/NAN/50024/2013).

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GRAPHENE-BASED MAGNETIC NANOPARTICLES AS DUAL STIMULI-RESPONSIVE DRUG RELEASE

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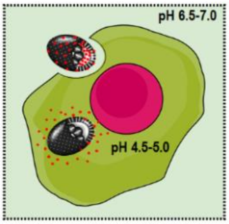

Figure 1. MDDS controlled release

Magnetic drug delivery systems (MDDS) have been attracting much attention due to the possibility to combine synergisticaly therapeutic applications, such as magnetic hyperthermia and drug delivery [1,2]. This thermo-chemotherapeutic approach improves the cellular uptake of drugs by cell membrane permeability, the inhibition of DNA-repair and the acceleration of the cytotoxic chemical reaction [3]. Commonly, these nanoparticles are designed with a superparamagnetic core coated with a metal or non-metal structure, such as gold, silica or polymers. However, this approach usually presents some drawbacks, such as low drug loading capacity, low saturation magnetization and/or lack of stimuli-responsive release. In this work, graphene-based magnetic nanoparticles were developed as super-drug nanocarriers, exhibiting extraordinary high loading contents of the anticancer drug Doxorubicin (91 %, ratio 1:1, w/w), high saturation magnetization (~70 emu/g), dual pH- and thermal-responsive controlled release and good biocompatibility even at high concentrations. These results shed light on the development of new hybrid nanomaterials with high potential to be applied in nanomedicine for cancer treatment, combining magnetic targeting, hyperthermia and controlled drug delivery.

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OPTIMIZATION OF CARBON-BASED MAGNETIC DRUG NANOCARRIERS SYNTHESIZED BY GREEN ROUTES

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Green routes, considering the use of plant extracts with high reducing power, have been investigated as alternative methods to obtain superparamagnetic cores for biomedical applications (1). Usually, these magnetic cores are further coated either with metal or non-metal materials. In particular, carbon-coated nanoparticles have several advantages in comparison to other coatings, since they usually offer higher chemical and thermal stability, larger surface area, biocompatibility and easier functionalization (2,3). In this work, different plant hydromethanolic extracts with high reducing power (i.e., *Tamus communis* L. shoots, *Crateagus monogyna* Jacq. flowers and *Rubus ulmifolius* Schott flowers) were investigated in the synthesis of magnetic cores for carbon-coated yolk-shell magnetic nanoparticles (CYSMNPs). Overall, the extract of *Rubus ulmifolius* has shown great ability to produce highly magnetic cores. To enhance the colloidal stability of the as-synthesized CYSMNPs, the nanocomposites were chemically functionalized with nitric acid at 60 ºC, during 3h. This chemical treatment allows the incorporation of carboxylic acid groups on the carbon-based shell, leading to a dramatic change on the sample pH_{PZC} values (from highly basic to highly acid, before and after the treatment, respectively). Moreover, the drug loading efficiency (DLE, %) and drug loading capacity (DLC, mg/mg) were investigated in different working solutions (e.g. PB pH 6.0, PBS pH 7.4, PB pH 8.0). The results show that the highest DLE (99,6%) and DLC (0,996 mg/mg), with a ratio 1:1 (w/w), occurred with the CYSMNPs functionalized after 3 hours in PB pH 8.0. This can be explained mainly due to the solution, whose pH is approximately the pKa of the drug (Doxorubicin, pKa 8.3), which allows greater electrostatic affinity between the drug (positively charged) and the CYSMNPs (negatively charged), consequently a higher drug loading. Therefore, this research demonstrates the outstanding ability to use the developed and optimized green CYSMNPs, as super-drug nanocarriers with great ability to load high content of the anticancer drug Doxorubicin.

Acknowledgements. Project POCI-01-0145-FEDER-006984 – Associate Laboratory LSRE-LCM funded by FEDER through COMPETE2020 - POCI – and by national funds through FCT - Fundação para a Ciência e a Tecnologia. R.O.R. acknowledges the Ph.D. scholarship SFRH/BD/97658/2013 granted by FCT.

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NON-ENZYMATIC GLUCOSE SENSING WITH FLUORESCENT CARBON DOTS

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Diabetes is a chronic disease manifested by improper blood glucose levels, and is a major health problem worldwide [1]. If left untreated, diabetes can lead to cardiovascular disease, neuropathy, blindness and ulceration, among other problems. Given this, the sensitive detection of improper glucose blood levels is essential for a proper treatment and for reducing the possibility for health problems.

Glucose sensing is generally achieved with sensors based on glucose oxidase enzyme [2]. However, the immobilization of the enzyme on the electrode is very challenging and high cost, and it is highly affected by temperature, pH and humidity. Thus, non-enzymatic sensors, with simpler and lower cost usage, should be developed.

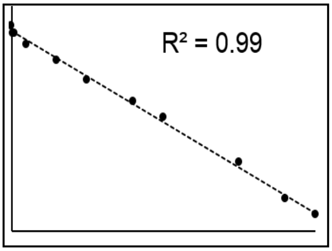

Figure 1. Fluorescence as a function of glucose.

Inspired by this goal, we have developed non-enzymatic glucose sensors based on fluorescent carbon dots. These are carbonaceous nanoparticles with attractive analytic properties, such as water solubility, high fluorescence quantum yield, biocompatibility and good photostability [3-5]. The carbon dots were obtained by microwave-assisted synthesis, which is a rapid, simple and low cost method for carbon dot synthesis [3-5]. The reactivity towards glucose was achieved with a strategy based on boronic acid-diol chemistry [6]. The developed carbon dots were then able to detect and quantify glucose in the biological concentration range of 0-100 m*M* (Figure 1).

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DEVELOPMENT OF RATIOMETRIC FLUORESCENT SENSORS BY CARBON DOT MIXING: APPLICATION IN GLUCOSE SENSING

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Carbon dots are fluorescent carbonaceous nanoparticles usually with dimensions less than 10 nm [1-4]. They possess very attractive analytic properties, such as water-solubility, high photostability, high fluorescence quantum yield, biocompatibility, low toxicity and are easy to functionalize [1-4]. These unique properties have led to promising applications in optical sensing of several analytes of interest, as biomolecules, metal ions and free radicals [1-4].

Such assays are based on changes of emission intensity of the sensor when in contact with the target analyte. However, fluorescence intensity can be affected by a variety of factors, which can lead to interferences in the measurements [1,4]. Thus, ratiometric fluorescent probes are more robust sensors, due to a reduced number of false-positives [1,4].

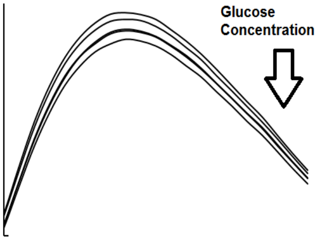

Figure 1. Responsive peak in the presence of glucose.

On an ongoing project, fluorescent ratiometric sensors (based on carbon dots) were developed and applied on the field of glucose sensing. This was achieved by mixing carbons responsive to glucose with unresponsive ones, with different emission peaks. This resulted on a dual emission (430 nm *vs* 550 nm), which intensity ratio allows for glucose quantification. With this work, we present a simple, rapid and low cost approach for the development of more robust ratiometric sensors.

Acknowledgments. This work was made in the framework of projects PTDC/QEQ-QAN/5955/2014 (funded by FCT/MEC and COMPETE-POFC), NORTE-01-00145-FEDER-000028 (funded by NORTE2020) and POCI-01-0145-FEDER-006980 (funded by COMPETE2020).

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CARBON MATERIALS FOR ENTEROSORPTION AND HEMOPERFUSION: THE DICLOFENAC CASE-STUDY

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Most of the registered intoxications is attributed to the excessive ingestion of pharmaceutical drugs, either voluntarily or accidentally, which constitutes a public health problem. The detoxification can be done either with a single dose of activated carbon as enterosorbent, or as a continuous process of extracorporeal hemoperfusion by using activated carbon cartridges in the case of high blood plasma concentrations [1].

Diclofenac (DCF) is an anti-inflammatory drug, with increasing consumption and high toxicity at low concentrations, constituting a high risk to acute intoxication.

The main aim of this work was to study the application of activated carbons from several sources and with different treatments, as decontamination agents of DCF present in the gastrointestinal tract and blood plasma in the case of acute intoxication/overdose. A medicinal carbon typically used on acute intoxications was used as reference material (Cref). *In vitro* studies were performed under simulated physiological conditions.

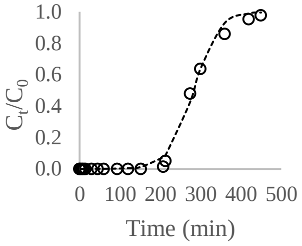

Figure 1. Breakthrough curve of CX8 carbon. Dashed line – Thomas model; dots – experimental data.

Table 1. Properties of the carbons.

	A_{BET} (m^2/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)	pH_{PZC}
Cref	1340	0.312	0.798	7.5
CX8	1194	0.364	0.640	9.4

From the 14 carbons studied, physically activated xerogel CX8 (CO_2, 800°C, 8 hours) presented the best performance, both in kinetics and in uptake capacity. The textural properties and the marked basic surface chemistry (Table 1) of this carbon played a major role in its best performance.

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VALORISATION OF TEAK SAWDUST BY THE PRODUCTION OF ACTIVATED CARBON

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The valorisation of wood wastes by the production of added value materials is one of the possible strategies to expand the income sources and increase the economic activity. This approach is very important in particular for the developing countries like East Timor.

There are a quite number of studies regarding the preparation of activated carbons (ACs) from a diversity of precursors [1, 2]. However, there is scarce information concerning the production of ACs using teak sawdust as precursor.

In this work, the wood wastes of Tectona grandis tree (from East Timor) were used as a precursor to the ACs production by chemical activation, with potassium hydroxide, at 973 K and by physical activation, with carbon dioxide at different temperatures.

The influence of carbonization temperature and activation time were studied, which have a significant effect on the activated carbons porous structure.

A set of experimental technics like nitrogen adsorption at 77 K, Fourier transform-infrared spectroscopy, elemental analysis and determination of the point of zero charge were used to characterise all ACs.

The good results obtained allow us to state that teak sawdust is an excellent precursor for ACs production.

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GRAPHENE OXIDE LAYER-BY-LAYER-FILMS DEPOSITION IN OPTICAL FIBRE DEVICES

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Optical fibre sensors based on tapered, microphere and knot resonator were fabricated by depositing contrast graphene oxide (GO) layers thought the layer-by-layer (LBL) technique [1]. The LBL films were prepared from aqueous solutions of poly(ethyleneimine) (PEI) (Mw) 750 000 g/mol) and GO 2 mg/mL, dispersion in H_2O, with concentrations of 10^{-3} M and 10^{-2} M, respectively. The chemicals were obtained from Aldrich and the corresponding molecular structures are depicted in Figure 1. The PEI cationic solution, GO anionic solution and ultra-pure water were placed in cups. The fibre sensors active areas were then alternately dipped following the order aforementioned. After this, the films were dried with soft nitrogen flow, and a bilayer film is accomplished. The above steps were repeated until 8 bilayer films were produced in fibre sensor active regions $(PEI/GO)_8$.

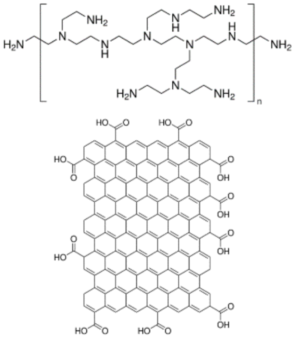

Figure 1. poly(ethyleneimine) (PEI) and below: graphene oxide (GO).

In the meeting, will be presented three configurations of graphene-based fiber sensors for liquid measurement. The microsphere presented a better solution when compared with the other structures due to its robustness and high sensitivity to the measured parameters, taking advantage of being an interferometric configuration.

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UNDERSTANDING RATE JUMPS IN CATALYTIC CARBON GASIFICATION BY OXYGEN

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Rate jumps are sometimes observed in catalytic carbon gasification by air or oxygen following a minor increase in temperature ($v.g.\ \Delta T = 5°\mathrm{C}$). Their occurrence has been reported (Table 1) but the phenomenon is not well understood. We show that the rate jump phenomenon can be explained by the "carbonworm" mechanism, due to a jump in the nano-particles temperature. The dominant effect of the size of the particles is consistent with the observation of Devi et al.: significant decrease of the jump observed in Cu, Ni and Ca systems due to size increasing by sintering – much lower dispersion [4]. The guess that the enormous increase in the mobility of the catalyst species near the Tammann temperature is the *cause* for the jump in char reactivity, should be reversed: the mobility is a *consequence* of the temperature jump.

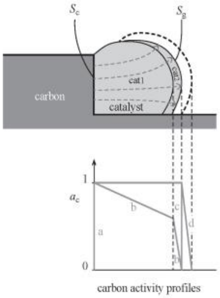

Fig. 1. C activity profiles.

Table 1. Examples of observed rate-jumps is carbon gasification by air/oxygen.

Carbon	Gas	Catalyst	Temp/ºC	Year
Coal char	Air	Cu	200-400	1987
Graphite	Air	Tl_2O_3	500	1987
Activated C	O_2	MoO_3	400-800	1990
CMC	Air	Cu	200-300	1990
CMC	Air	Ni	200-400	2001
Olive husk	O_2	(ashes)	>450	2007
CMC	Air	Ca, K	250-450	2010

The real cause is a local sintering-like surface effect promoting a good contact catalyst/coke. A good contact facilitates the supply of carbon atoms, diffusing fast to the other side where the surface reaction takes place. That exothermic surface reaction increases the temperature of the particles, further accelerating the rate, until the level of the mass transfer through the external film operates as a rate-limiting ceiling (check Figs. 1,2). Two different solid phases may operate under steady-state gasification at each side.

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REMOVAL OF DRUGS FROM WATER BY ADSORPTION ONTO PAPER PULP-BASED ACTIVATED CARBONS

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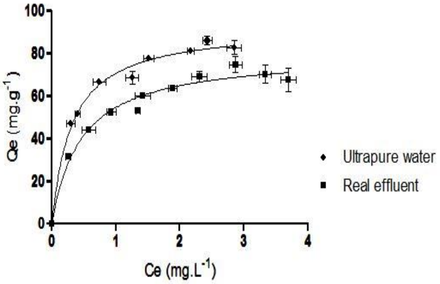

Figure 5. Langmuir isotherms for bleached pulp activated with H_3PO_4 in two different batch adsorption tests: ultrapure water and real effluent.

The occurrence of pharmaceuticals in aquatic environments is generalized, becoming a serious public health problem. A sustainable solution to address this issue and treat contaminated water is based on the adsorption of drugs onto activated carbons, produced from residual or cheap precursors, such as, raw and bleached pulp. In this work, paper pulps derived from the paper production process were activated with two chemical activation agents (K_2CO_3 and H_3PO_4) and then pyrolysed at 800ºC for 150 min and washed with HCl. The adsorption kinetic and capacity of the resulting carbons were determined by performing batch adsorption tests with 5 mg L^{-1} solution of carbamazepine (CBZ) in ultrapure water. As wastewater treatment plants (WWTP) are the main pathway of drugs into aquatic environments and even into the public water supply, batch adsorption tests were also performed using effluents, collected from an urban WWTP and enriched with CBZ. Batch tests showed a better performance for the carbon produced from bleached pulp and activated with H_3PO_4. As schematized in Figure 1, adsorption tests with ultrapure water reached slightly better adsorption capacity (about 90 mg of removal CBZ per gram of carbon), compared to the tests with real effluents that reached about 80 $mg.g^{-1}$. Also, using a low adsorbent dose (0.050 g L^{-1}), 80% of CBZ removal was reached in ultrapure water. For the same carbon and same adsorbent dose, but with real effluents, the removal of CBZ from solution decreased, however remaining considerably high (60%), which proves the good adsorptive capacity of these carbons even with real effluents, being an effective method to treat contaminated waters.

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GRANULAR ACTIVATED CARBON PRODUCED FROM PRIMARY PAPER MILL SLUDGE

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Primary paper mill sludge (PS), a residue produced in large amounts by paper industry, is mainly constituted by cellulose and has already shown potential to be used as raw material to the production of carbon adsorbents for the removal of pharmaceuticals from water [1]. The production of activated carbons (AC) from PS using potassium hydroxide as activating agent resulted in a powdered AC (PAC). However, for the application of the produced adsorbents in fixed-bed columns, a granular AC (GAC) is preferred. Hence, in this work, lignosulfonate was used as binder agent for PS aiming the subsequent production of a GAC by pyrolysis and chemical activation. The final produced GAC (PSA) was tested in a kinetic study (under batch mode) for the adsorption of carbamazepine (CBZ), an anti-epileptic pharmaceutical frequently found in water systems. For a comparison purpose, the same adsorption study was performed with a commercial GAC from NORIT (GACN). The results showed that PSA differs from GACN in the time needed to attain the equilibrium: 48h and 24h, respectively. However, the predicted CBZ adsorbed at the equilibrium is of 43.5 mg g^{-1} onto PSA and 52.8 mg g^{-1} onto GACN, for a concentration of 0.070 g L^{-1} of carbon, indicating a similar performance in terms of adsorptive capacity. Future work will focus on the fixed-bed utilization of PSA.

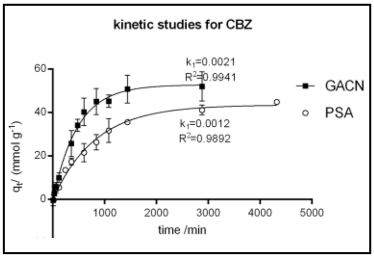

Figure 1. Kinetic study for the adsorption of CBZ onto PSA and commercial GAC (GACN).

Acknowledgments. This work was funded by FEDER through COMPETE 2020 and by national funds through FCT by the research project PTDC/AAG-TEC/1762/2014. V. Calisto also thanks FCT for her postdoctoral grant (SFRH/BPD/78645/2011). Authors thank FCT the financial support to CESAM (UID/AMB/50017/2013) and to FCT/MEC through national funds, the co-funding by FEDER (within the PT2020 Partnership Agreement and Compete 2020), and RAIZ - Instituto de Investigação da Floresta e do Papel, for kind collaboration.

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WASTE-BASED CARBONS: A COMPETITIVE OPTION FOR PHARMACEUTICALS ADSORPTION FROM WATER

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Pharmaceuticals' consumption has been increasing in the last few decades which can be associated to the improvement in health-care and science sectors investment and to the increase of life expectancy. Since conventional sewage treatment plants are usually inefficient in the removal of these compounds, the release into sewage water, through excretion by humans and animals, causes their ubiquity in treated wastewater and consequently in receiving waters. Therefore, removal of pharmaceuticals from water constitutes a great challenge for the scientific community. Adsorption onto activated carbon (AC) is considered an efficient and versatile treatment for that purpose. However, as a major drawback, ACs present poor economic feasibility, which has motivated the search for low-cost adsorbents. On the other hand, there is a need to implement sustainable waste management procedures and to exploit the potential economic value of wastes. Consequently, waste-based adsorbents have been an important focus of attention.

Using primary sludge from a paper industry as precursor material, AC was performed by chemical activation with KOH in a precursor:activating agent ratio of 1:1. Impregnated material was stirred during 1 h and left to dry at room temperature, which was followed by pyrolysis (800 °C; 150 min of residence time) in an inert atmosphere. Afterwards, AC was subjected to a washing step with HCl. BET surface area of the produced AC was measured (1627 m^2 g^{-1}), being much higher than those of the commercial ACs used for comparison (500-1000 m^2 g^{-1}). The produced carbon was used for the removal of three pharmaceuticals' therapeutic classes – the antiepileptic carbamazepine, the antibiotic sulfamethoxazole, and the anti-depressant paroxetine. Adsorption experiments were carried out under batch operation mode. Produced AC presented fast kinetics and very high maximum adsorption capacities for all the pharmaceuticals tested (around 200 mg g^{-1}). Adsorption experiments were also performed with commercial carbons for comparison. It was proven that the produced materials can compete with commercially available ACs in terms of adsorptive characteristics.

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CP55

NITROGEN DOPED CARBON NANOTUBES FOR THE CATALYTIC WET OXIDATION OF PHENOL

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In recent times, large amounts of wastewater contaminated with recalcitrant and bio-toxic organic pollutants have been produced. These organic compounds render infeasible the traditional treatment options [1]. New and more efficient technologies started to be developed in order to treat these effluents.

In this work, the oxidation of phenol by catalytic wet oxidation (CWO) over several types of carbon nanotubes (CNTs) was studied. Commercial CNTs and CNTs treated in a ball mill, with and without nitrogen precursor (to introduce nitrogen functionalities), were characterized and tested as catalysts. The experiments were performed in both batch and continuous mode, and the influence of several reaction parameters (reaction temperature, dissolved oxygen concentration and initial phenol concentration) was studied. Temperature was the most influential parameter, an optimal temperature of 160 ºC being determined.

The presence of N-functional groups in the CNTs improved their catalytic activity [2]. In batch mode, complete phenol degradation was achieved over the N-doped catalyst, while only 68% removal was observed for the undoped catalyst at the same reaction conditions (2 h of reaction at 160 ºC and 6 bar O_2). In continuous mode, an experiment with a higher initial phenol concentration (500 mg L^{-1}) was performed at 160 ºC and 12 bar O_2. Complete phenol removal was achieved for the first 7 h of reaction and 80% phenol removal was observed in the steady state, up to 80 h of reaction, over N-doped catalyst. Several regeneration attempts were investigated, for the N-doped catalyst, a significant regeneration being achieved by thermal treatment at 600 ºC under nitrogen atmosphere.

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CARBON NANOTUBES AS PICKERING INTERFACIAL CATALYSTS FOR THE CWPO OF OILY WASTEWATER

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Amphiphilic carbon nanotubes (ACNTs) were tested as Pickering emulsifiers and interfacial catalysts in the removal of pollutants from biphasic systems by using CWPO (catalytic wet peroxide oxidation). ACNTs were synthesized by catalytic CVD [1, 2] in a fluidized-bed reactor by feeding: 1) ethylene alone for 30 min (E30); 2) acetonitrile/N_2 for 20 min, followed by ethylene for 20 min (A20E20), or 3) 10 min (A20E10); 4) ethylene for 10 min, followed by acetonitrile/N_2 for 20 min (E10A20); or 5) acetonitrile/N_2 alone for 30 min (A30). ACNTs were first tested as catalysts for the degradation of 2-nitrophenol (2-NP), used as target lipophilic pollutant, in aqueous phase and under conditions similar to those previously reported [2]. The most active catalyst was the lipophilic ACNT E30 sample. Then, ACNTs were tested for 2-NP removal from the biphasic water-cyclohexane medium (used to simulate oily wastewater). Only the amphiphilic A20E20, A20E10 and E10A20 samples stabilized the emulsions and showed catalytic activity for 2-NP removal from biphasic media by using CWPO. This catalytic activity was attributed to the formation of Pickering emulsions, enabling the decomposition of H_2O_2 into hydroxyl radicals, at the hydrophilic section of the catalyst, and the adsorption and further reaction of 2-NP with hydroxyl radicals, at the lipophilic section. Under biphasic conditions, the lack of activity of the most lipophilic ACNT (E30) sample was explained by its distribution in the organic phase and a negligible H_2O_2 conversion. On the other hand, the highest conversion of H_2O_2 was achieved using the most hydrophilic ACNT (A30) sample, distributed in the aqueous phase, but without pollutant conversion.

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CORE-SHELL MAGNETIC CARBON NANOCOMPOSITES FOR CATALYTIC WET PEROXIDE OXIDATION

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The application of heterogeneous metal/magnetic phases in catalytic wet peroxide oxidation (CWPO), either directly as catalyst or included in distinct support/hybrid materials, has been receiving great attention from the scientific community. Under this context, our recent work has been mainly focused on the development and application of composite materials combining highly active and magnetically separable iron-based materials with the easily tuned properties of carbon-based materials [1]. As a result, the outstanding performance of a hybrid magnetic graphitic nanocomposite (MGNC) catalyst – composed by a magnetite (Fe_3O_4) core and a graphitic shell – was recently reported [2].

Seeking to improve catalytic performance, two additional magnetic materials were prepared and encapsulated within a graphitic shell. The resulting MGNC materials were applied as catalysts in the CWPO of 4-nitrophenol (4-NP) aqueous solutions with high load (5 g L^{-1}). The MGNC material with the highest catalytic activity and stability for CWPO was the subject of additional studies, including the assessment of the (i) adsorption influence on the removal of 4-NP by CWPO, (ii) mineralization achieved in terms of total organic carbon removals, (iii) chemical oxygen demand removals, (iv) efficiency of hydrogen peroxide consumption, (v) heterogeneous nature of the catalytic system, (vi) participation of hydroxyl radicals in the CWPO process and (vii) 4-NP oxidation mechanism. In addition, a lab-scale magnetic separation system was designed for in-situ catalyst recovery after the CWPO reaction stage.

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CARVÕES DERIVADOS DE ALGAS MARINHAS PARA CATALIZADORES NA CONVERSÃO DA BIOMASSA

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As algas marinhas apresentam-se como precursores promissores para a obtenção de materiais de carbono uma vez que são compostas, maioritariamente, por celulose, carbohidratos, lípidos e proteínas. Isto, em conjunto com a sua grande disponibilidade, faz com que sejam uma potencial fonte de carbono para a produção de materiais sustentáveis com alto teor de heteroátomos. Para além da química superficial, uma estrutura porosa adequada pode ser decisiva no rendimento prático dos materiais de carbono. Infelizmente, a complexa estrutura polimérica dos materiais derivados da biomassa dificulta a modificação das suas propriedades texturais. Neste trabalho, foram preparados materiais de carbono com uma mesoporosidade bem definida e com uma química superficial variada por meio de uma pirólise de algas marinhas. Apesar do seu alto teor de cinzas, os carvões apresentam uma mesoporosidade e também um conteúdo muito alto em diferentes heteroátomos. Por exemplo, uma amostra carbonizada a 800 °C apresenta 28,03 % (em massa) de oxigénio, 3.75 % de azoto e 2.01 % de enxofre. A presença de 0.4% de fósforo foi também verificada por XPS.

Estes materiais foram testados como catalisadores sólidos na reação de hidrólise da celobiose a glucose, que é o passo crítico e limitante dos processos de conversão da biomassa. Utilizando condições de pressão e temperatura moderadas, verificaram-se rendimentos de 50 % na obtenção da glucose em água. O rendimento foi considerado dependente do tipo e da quantidade de fósforo e oxigénio presente nas amostras.

Agradecimentos. Este trabalho foi desenvolvido no âmbito do projeto "AIProcMat@N2020 - Advanced Industrial Processes and Materials for a Sustainable Northern Region of Portugal 2020", com referência NORTE-01-0145-FEDER-000006, cofinanciado pelo Programa Operacional Regional do Norte (NORTE 2020), através do Portugal 2020 e do Fundo Europeu de Desenvolvimento Regional (FEDER) e do Projeto POCI-01-0145-FEDER-006984 - Laboratório Associado LSRE-LCM - financiado FEDER, através do COMPETE2020 – Programa Operacional Competitividade e Internacionalização (POCI) e por fundos nacionais através da Fundação para a Ciência e a Tecnologia I.P. K. Eblagon agradece à FCT pela bolsa de pós-doutoramento SFRH/BPD/110474/2015.

ADVANCED ELECTRICALLY CONDUCTIVE ADHESIVES FOR APPLICATION IN ELECTRONICS

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Electronic packaging, or assembly of packed electronic components on printed circuit boards (PCBs), present challenges that require innovative solder pastes and electrically conductive adhesives to face the increasing complexity of PCB assembly.

Current commercially available conductive adhesives are based on epoxy matrices with a high load of silver (~80 %), typically in the form of micro flakes. Several studies reported improvements obtained by the use of multidimensional materials, such as silver nanowires and micro flakes, or multiple scales as micro and nano-particles [1]. Carbon nanotubes have also been used as fillers for electrically conductive adhesives [2].

In this work epoxy resin composites were produced with different carbon fillers including, carbon nanotubes (single- and multi-wall, SWCNT and MWCNT), graphite nanoflakes (as-received and exfoliated), carbon nanofibers (CNF) and chopped carbon fibers (CF) to achieve thermal stability, low electrical resistance and vibration damping. Different concentrations of each carbon material, separately or combined, were explored. The concentration ranges tested were, 0.001-0.3 wt.% for SWNT, 0.001-3 wt.% for MWNT, 0.01-7 wt.%, for graphite nanoflakes, 0.3-13 wt.% for CNF and 1-35 wt.% for CF.

The ECAs were produced by manually pre-mixing the epoxy and carbon filler and then using a three roll mill to induce nanoparticle dispersion. The mixture was processed to obtain a good dispersion of the fillers and the epoxy was cured after mixing with the hardener by heating for 1 hour at 80 °C. The effect of the different fillers and concentrations on the electrical and rheological properties of the ECAs were evaluated.

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GRAPHENE OXIDE/TiO2 PHOTOCATALYSTS FOR HYDROGEN PRODUCTION FROM WATER

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The photocatalytic activity of TiO_2 is limited by the aggregation of nanoparticles and the fast recombination of electrons and holes. Graphene oxide, with high specific surface area and unique electronic properties, is considered a good candidate for enhancing TiO_2 activity [1]. Graphene oxide–TiO_2 composites were prepared from graphene oxide (GO) obtained by Hummers method and TiO_2 P25 from Evonik (P25). Different metals (M: Pd, Au, Ir, Pt, Ni, Ag) were used as co-catalysts. The photocatalytic tests were performed using aqueous solutions containing 10 *%vol.* methanol as hole scavenger. The production of H_2 from water was carried out under both UV and visible light irradiation and monitored by GC-TCD. The best performing materials were those loaded with Pt and Pd (Fig. 1). The highest activity was obtained for the Pt/GO-TiO_2 under UV irradiation, producing 2565 µmol of H_2 after two hours, contrasting with 1742 µmol obtained using Pd/GO-TiO_2. When irradiated using visible light, the Pd-loaded composite performed better that the Pt-loaded one. These results will be discussed in light of the characterization of the materials.

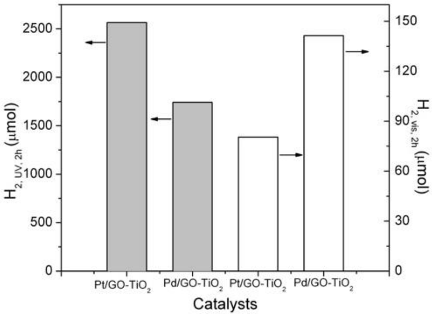

Figure 1. H_2 production using GO-TiO_2 loaded with Pt and Pd under UV and visible light irradiation.

Acknowledgements: This work was financially supported by Project POCI-01-0145-FEDER-006984 – Associate Laboratory LSRE-LCM funded by FEDER through COMPETE2020 – Programa Operacional Competitividade e Internacionalização (POCI) – and by national funds through FCT. CGS and LMPM acknowledge the FCT Investigator Programme (IF/00514/2014 and IF/01248/2014, respectively) with financing from the European Social Fund and the Human Potential Operational Programme. NN thanks Minister of Higher Education and Scientific Research TUNIS-GABES University for her scholarship.

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GRAPHITIC CARBON NITRIDE AS PHOTOCATALYST FOR PHENOL DEGRADATION USING VISIBLE LIGHT

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Heterogeneous photocatalysis is widely used in several environmental applications, including the degradation of organic pollutants in water and wastewater treatment. Graphitic-carbon nitride (g-C_3N_4) is a material that has recently attracted the interest of the scientific community, since it can be used as a semiconductor photocatalyst without the need to add metals or metal oxides. Of note is the variety of photocatalysts that have been produced from g-C_3N_4 with the specific purpose of being used with visible light [1].

In the present study, pristine g-C_3N_4 was prepared and a fraction of this sample was treated at 500 °C (g-C_3N_4-T). These materials were tested in the photocatalytic degradation of phenol in liquid phase and compared with the benchmark material for this treatment process (TiO_2-P25). From the 3 samples, the thermally treated material shows the highest photocatalytic activity (Fig. 1) when the same catalyst load (1 gL^{-1}) is used throughout.

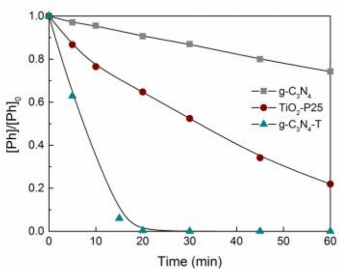

Figure 1. Concentration of phenol (normalized) for different photo-catalysts at identical loads.

Several operating conditions were tested and additional studies are underway to understand the mechanism of degradation under the reaction conditions.

Acknowledgments. This work was financially supported by: Project POCI-01-0145-FEDER-006984 – Associate Laboratory LSRE-LCM funded by FEDER through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) – and by national funds through FCT. M.J.L. acknowledges FCT for the research grant PD/BD/52623/2014, while A.M.T.S. and C.G.S. acknowledge the FCT Investigator Programme (IF/01501/2013 and IF/00514/2014, respectively) with financing from the European Social Fund and the Human Potential Operational Programme.

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PHOTOCATALYTIC OZONATION IN THE PRESENCE OF CARBON NANOTUBES AND TiO_2 COMPOSITES

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Photocatalytic ozonation (PCO) is an Advanced Oxidation Process carried out to eliminate pollutants from water and using a combination of radiation, ozone and a suitable catalyst. In this work, we study the effect of functionalization on the carbon nanotubes (MWCNT) used to prepare the composites with TiO_2. The assessment was made during organic compounds degradation by PCO. The results on oxamic acid (OMA) removal in the presence of the composites with the same composition prepared by sol-gel (SG) method [1] and synthetized in the ball milling (BM) [2], is shown in Figure 1. The preparation by SG technique led to slower OMA removal rate than that by MB. The order of catalytic activity can be attributed to the good contact between anatase TiO_2 particles and MWCNT promoted by the increase of TiO_2 diameter during MB preparation, as well as by the presence of rutile phase. The presence of Fe on MWCNT is useful, increasing the OMA degradation from 85% to 92% after 60 min of reaction. It is expected that the presence of Fe promotes the O_3 decomposition into $HO^\bullet$ radicals and enhances the surface reactions.

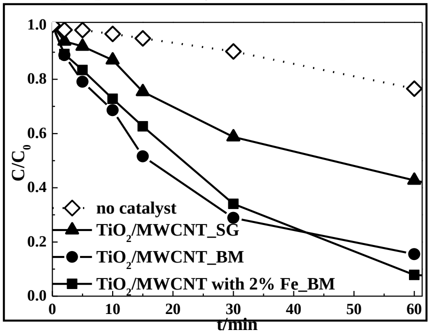

Figure 1. OMA removal by PCO in the presence of prepared composites.

Acknowledgments. This work is a result of project “AIProcMat@N2020 - Advanced Industrial Processes and Materials for a Sustainable Northern Region of Portugal 2020”, with the reference NORTE-01-0145-FEDER-000006, supported by Norte Portugal Regional Operational Programme (NORTE 2020), under the Portugal 2020 Partnership Agreement, through the European Regional Development Fund (ERDF) and of Project POCI-01-0145-FEDER-006984 – Associate Laboratory LSRE-LCM funded by ERDF through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) – and by national funds through FCT - Fundação para a Ciência e a Tecnologia. C. A. Orge acknowledges the FCT grant (BPD/90309/2012).

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MIXED OXIDES SUPPORTED ON CARBON NANOTUBES AS EFFICIENT CATALYSTS FOR HYDROGEN EVOLUTION REACTION

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Platinum free electrocatalysts for efficient hydrogen production is of great concern in the field of modern electrocatalysis and green chemistry. In the literature several materials can be found such as sulphides, carbonides, carbon based metal-free, oxides of transition metals etc [1-2]. However, till date no material fulfills the requirements to substitute platinum.

In this work we repport the electrochemical characterization of cryptomelane supported on commercial and functionalized carbon nanotubes in acid medium (0.5 M H_2SO_4) at room temperature by open circuit potential, cyclic voltammetry, linear sweep voltametry, electrochemical impedance spectroscopy (EIS) and square wave voltammetry (SQW). Its behaviour was compared with MoC, MoS_2 and cobalt-manganese layered double oxide (LDH) as well as platinum (20% in carbon black). We found that cryptomelane is a promissor substitute of platinum for the hydrogen evolution reaction (HER) with onset potentials differing only of few units of mV and with current exchange densities in the same order of magnitude. However, Tafel slopes, EIS and SWV point out to different mechanisms. We believe that the knowledge of the processes preciding HER might give an insight on how to fabricate efficient catalysts for hydrogen production.

Acknowledgments. This work is a result of the projects “UniRCell”, with the reference POCI-01-0145-FEDER-016422 and project “AIProcMat@N2020 - Advanced Industrial Processes and Materials for a Sustainable Northern Region of Portugal 2020”, with the reference NORTE-01-0145-FEDER-000006, supported by Norte Portugal Regional Operational Programme (NORTE 2020), under the Portugal 2020 Partnership Agreement, through the European Regional Development Fund (ERDF) and of Project POCI-01-0145-FEDER-006984 – Associate Laboratory LSRE-LCM funded by ERDF through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) – and by national funds through FCT - Fundação para a Ciência e a Tecnologia..

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SOLAR FUELS BY PHOTOCATALYTIC REDUCTION OF CO_2 OVER GRAPHENE-BASED COMPOSITES

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The combustion of coal, oil and natural gas supply close to 90% of our current energy needs, however the CO_2 emitted during the burning of fossil fuels is strongly implicated as the main drivers of climate change and acidified oceans. One option lies in using solar energy, which is an abundant, clean and sustainable resource, to photocatalytically convert CO_2 with water into a solar fuel. Graphene derivatives/metal oxide composites have been found to be efficient photocatalysts on account of the vital role of graphene as an electron acceptor/transporter, which reduces the recombination rate of photoexcited electron–hole pairs [1].

In the present work, CdS/reduced graphene oxide (rGO) composites were prepared with different graphene oxide (GO) loadings (3.0, 6.0 and 12.0 wt.%) and with *thermal treatment at 400 ºC* (N_2 atmosphere). The composites were applied in the photocatalytic reduction of CO_2 using different types of water (i.e. distilled water, brackish water and seawater) as reducing agent. The presence of rGO in the composites was found to enhance the CO_2 photoreduction in aqueous phase, with formation of both methanol and ethanol, among other sub-products (Fig. 1). The effect of type of water as well as copper metal as co-catalyst on the photocatalytic CO_2 reduction were also systematically investigated.

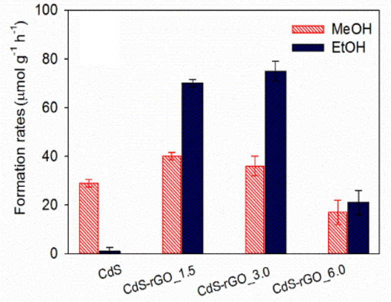

Figure 1. Methanol and ethanol formation rates using CdS and CdS-rGO composites using distilled water at 180 min.

Acknowledgements. This work was financially supported by Project POCI-01-0145-FEDER-006984 – Associate Laboratory LSRE-LCM funded by FEDER through COMPETE2020 – Programa Operacional Competitividade e Internacionalização (POCI) – and by national funds through FCT. LMPM and AMTS acknowledge the FCT Investigator Programme (IF/01248/2014 and IF/01501/2013, respectively) with financing from the European Social Fund and the Human Potential Operational Programme.

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TWO-COLUMN RELAY SMB PROCESS FOR GAS-PHASE SEPARATIONS USING ACTIVATED CARBON

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A new two-column, relay, simulated moving bed process (2-column R-SMB) for gas-phase separations has been designed using an activated carbon as adsorbent. R-SMB processes differ from classical SMB by avoiding the partial withdrawal of products, since the outlet streams are handled in a relay mode. The outlet streams are either fully collected as product/waste or completely recycled to another column. In this work, the relay concept is applied for the first time in 2-column SMB processes and gas-phase separations.

The process is designed and optimized through model-based computational simulation and the results obtained are validated experimentally. For the purpose, a new lab-scale unit was designed and assembled and the simplest case of a binary gas-phase separation of an isothermal trace system is studied. For the purpose, the separation of carbon dioxide/methane mixtures using activated carbon as adsorbent and nitrogen as carrier gas is evaluated as a proof-of-concept.

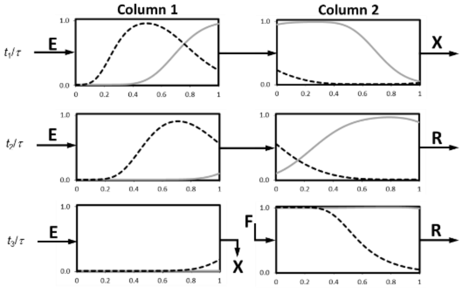

Figure 1. CSS gas-phase mole-fraction internal profiles at the end of each sub-step of a half-cycle of the 2-Column R-SMB (solid grey line: CH_4; dashed black line: CO_2).

The scheme designed allows obtaining 99% purity (eluent free basis) in both extract and raffinate products. Figure 1 presents the simulated internal profiles, at cyclic steady state (CSS) at the end of each sub-step of an optimized half-cycle. The process performance is compared with classical four-zone SMB and asynchronous port switching schemes, showing that at low-feed throughput the process performances are coincident.

Acknowledgements. Financial support from FCT/MCTES (Portugal) through projects EXCL/QEQ-PRS/0308/2012, PTDC/AAC-AMB/108849/2008, PTDC/CTM/104782/2008, grant SFRH/BPD/103533/2014 (Rui Ribeiro) and FCT Investigator contract IF/01016/2014 (Isabel Esteves) is gratefully acknowledged. This work was partially supported by LAQV which is financed by national funds from FCT/MCTES (UID/QUI/50006/2013) and co-financed by the ERDF under the PT2020 Partnership Agreement (POCI-01-0145-FEDER - 007265).

NEW TRENDS ON FLEXIBLE CARBON-BASED SUPERCAPACITORS: TOWARDS SMART TEXTILES AND MICRO-DEVICES FOR ENERGY STORAGE

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The fast growth of the market of wearable electronics boosted the need for smart and sustainable portable energy storage solutions. Supercapacitors emerged as a clean and safe energy storage technology due to their high power density, long cycle life, fast charging and stability. The integration of flexible supercapacitors in textiles has been a major quest for Protection, Sports, Medicine and Military applications in order to produce wearable energy storage devices to power sensors, flexible displays, among others [1].

Engineered nanomaterials opened new horizons in the clothing industry, for the design of high-performance textiles with new functionalities and improved comfort to the user. In particular, carbon-based nanomaterials and transition metal oxide nanoparticles are promising building blocks for the fabrication of smart energy storage textiles combining high-performance, lightness and flexibility [1,2].

In this work, we will provide an overview of our recent achievements in the design of smart textiles and micro-devices for energy storage based on supercapacitor technology. We will start by presenting the design of flexible electrodes through the coating of fabrics and flexible plastic substrates with functional carbon-based nanomaterials. Subsequently, the assembly of the electrodes and electrolyte into the final smart supercapacitors will be presented. Finally, the influence of the type/composition of the electrodes on the performance of the resulting flexible SCs will be discussed as well as their market potential.

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FLEXIBLE CARBON-BASED MICROSUPERCAPACITOR FABRICATED BY LITHOGRAPHY

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The Era of the Internet of Things and the rapid evolution of miniaturized electronic devices, such as wireless devices and sensors, have stimulated the development of micro/nano flexible and all-solid-state energy storage devices [1]. For that purpose, two main types of energy storage devices can be identified: microbatteries and microsupercapacitors (µ-SCs). µ-SCs have been pointed out as the most promising solution due to their long cycle life, high power density and fast charging [2,3]. These devices are normally produced by screen-printing and lithography. Carbon-based nanomaterials are promising electrode materials for µ-SCs due to their high specific surface area, good conductivity, mechanical stability and high operating temperature range [3].

In this work, we report on the fabrication of a flexible all-solid-state µ-SC based on nanostructured carbon electrodes coated on PET substrates. The µ-SC was produced by lithography, in a planar configuration, with the carbon-based electrodes separated by a solid-gel electrolyte (Figure 1). The topological and structural characterization was performed by SEM, EDS and XRD. The electrochemical performance was evaluated by cyclic voltammetry, galvanostatic charge/discharge and electrochemical impedance spectroscopy. The all-solid-state µ-SC showed an excellent performance, with a volumetric specific capacitance of 6.65 F cm^{-3} and an operation tension of ~2 V. This resulted in an energy density of 3.70 mWh cm^{-3} and a power density of 1.49 W cm^{-3}.

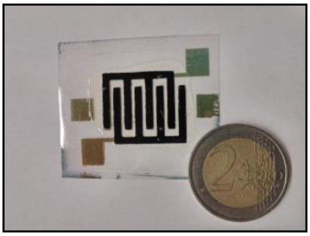

Figure 1. µ-SC based on carbon nanomaterials.

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SISAL-DERIVED HYDROCHARS AS PRECURSORS FOR PHARMACEUTICALS ADSORBENTS

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Hydrothermal carbonization (HTC) is the most suitable and up-scalable technology for biomass conversion into added-value end-products for a wide range of important applications [1,2]. In this study, biomass-derived activated carbons were obtained by a two-step activation procedure and the effect of an initial HTC in the properties of the carbons was evaluated. The materials were also tested regarding their adsorption capacities towards caffeine and paracetamol.

- The HTC treatment of sisal wastes (170−200 °C) allowed the synthesis of hydrochars, solids with numerous microspheres with diameters up to 5 µm, dispersed within the fibrous structure of the sisal precursor.
- Subsequent activation of the hydrochars with K_2CO_3 allowed a porosity development, and also the introduction of different surface functionalities on the final materials.
- The activated carbons obtained proved to have a superior performance as adsorbents for caffeine and paracetamol in liquid phase.

Although these materials require a **two-step synthesis procedure**, a higher adsorption capacity and/or affinity towards caffeine and paracetamol is obtained. Hydrothermal carbons can thus serve as suitable precursors to produce activated carbons with tuneable morphologies, porosities and functionalities.

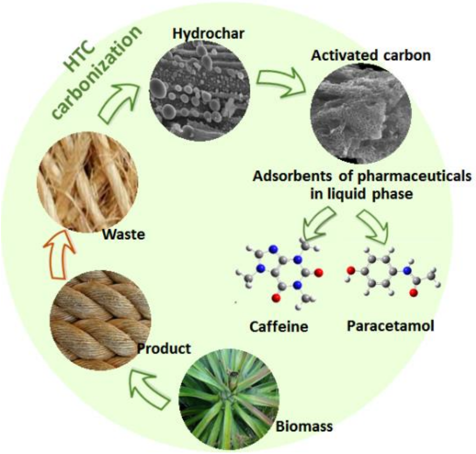

Figure 6- Schematic illustration of the synthesis procedure and target compounds.

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CHEMICAL COMPOSITION OF CHARCOAL PRODUCED AT DIFFERENT CARBONIZATION TEMPERATURES

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Charcoal is a C-rich material that can be obtained from the thermal decomposition of wood, in the absence or in the controlled presence of oxygen [1]. The final carbonization temperature directly affects the properties of charcoal, namely its elemental chemical composition. The increase of the carbonization temperature results in the decomposition of the wood chemical constituents, resulting in a loss of weight due to the volatilization of the organic matter and, consequently, concentrating the carbon in the resulting material [2].

In this study, the effect of the final carbonization temperature on the amounts of N, C, H, S and O contents of the charcoal obtained from wood of hybrids between *Corymbia citriodora* and *Corymbia torelliana*, carbonized at the temperatures of 350, 450 and 550 ºC, was studied. Table 1 presents the average values for the elementary chemical components of charcoal of the 3 evaluated thermal treatments. Table 1 shows that, for the H and O contents of the charcoal, reductions of 33 and 53% were respectively obtained, between the temperatures of 350 and 550 ºC. A different result was observed for the C content, as an increase in the final carbonization temperature lead to in an increase of its amount of about 20%. The contents of N and S remained practically the same with the increase of the final carbonization temperature.

Table 1. Nitrogen, carbon, hydrogen, sulfur and oxygen average contents in charcoal.

Temperature (ºC)	N (%)	C (%)	H (%)	S (%)	O (%)
350	1,13	71,06	4,32	0,01	23,46
450	1,12	80,79	3,69	0,01	14,45
550	1,12	84,97	2,92	0,01	10,98

Acknowledgements. TASV is grateful to EBWplus/Erasmus Mundus grant. SACC thanks Fundação para a Ciência e Tecnologia (FCT) for financial support (Investigador FCT program, IF/01381/2013/CP1160/CT0007), with financing from the European Social Fund and the Human Potential Operational Program. This work was supported by Project POCI-01-0145-FEDER-006984 – Associate Laboratory LSRE-LCM funded by FEDER through COMPETE2020 – POCI – and by national funds through FCT.

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CHEMICAL COMPOSITION OF *Corymbia citriodora* AND *Corymbia torelliana* HYBRIDS FOR ENERGETIC USE

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The evolution of the world energy consumption led mankind to seek more sustainable energy sources, intensifying the use of renewable energy sources, including forest biomass. Therefore, the use of wood as an energy source provides a favorable global carbon balance in relation to fossil fuels, due to the absorption of CO_2 through photosynthesis [1]. It is also known that the energetic value of wood is closely related to the elemental amounts of C, H and O, and the ratios between those chemical elements. Thus, the purpose of this work was to evaluate the bioenergetic potential of the hybrids of *C. citriodora* × *C. Torelliana* wood by elemental chemical analysis. Seven clones were used, with five trees per clone, with 3.75 years old, located in Itamarandiba, MG, Brazil. The quantification of C, H, N and S contents, based on the dry mass of wood, was determined by elemental analysis and the O content was determined by difference. The N/C, H/C and O/C atomic ratios were obtained considering the atomic mass of these atoms. The bioenergetic use of wood was satisfactory based on the inferences made from the elemental composition. In general, the different crossings had little influence on the C, H, O and S contents of the wood, and on the N/C, H/C and O/C ratios.

Table 1. C, H, N and O found in wood and N/C, H/C and O/C ratios. Cc × Ct = *C. citriodora* × *C. torelliana*; Ct × Cc = *C. torelliana* × *C. citriodora*.

Clone / Crossing	Elemental analysis (% in dry basis)				Atomic ratios		
	C (%)	H (%)	N (%)	O (%)	N/ C	H/C	O/C
1/ Cc × Ct	45,66 a	5,63 a	0,76 a	47,94 a	0,01 a	1,48 a	0,79 a
2/ Cc × Ct	43,59 a	5,48 a	0,81 a	50,12 a	0,02 a	1,51 a	0,86 a
3/ Cc × Ct	44,33 a	5,53 a	0,77 a	49,37 a	0,02 a	1,50 a	0,84 a
4/ Ct × Cc	45,11 a	5,57 a	0,81 a	48,51 a	0,02 a	1,48 a	0,81 a
5/ Ct × Cc	45,26 a	5,60 a	0,78 a	48,37 a	0,02 a	1,48 a	0,80 a
6/ Ct × Cc	45,44 a	5,61 a	0,75 a	48,20 a	0,01 a	1,48 a	0,80 a
7/ Ct × Cc	45,05 a	5,56 a	0,85 a	48,54 a	0,02 a	1,48 a	0,81 a

Acknowledgements. TASV is grateful to EBWplus/Erasmus Mundus grant. SACC thanks Fundação para a Ciência e Tecnologia (FCT) for financial support (Investigador FCT program, IF/01381/2013/CP1160/CT0007), with financing from the European Social Fund and the Human Potential Operational Program. This work was supported by Project POCI-01-0145-FEDER-006984 – Associate Laboratory LSRE-LCM funded by FEDER through COMPETE2020 – POCI – and by national funds through FCT.

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CHEMICAL CARACTERIZATION OF *Pinus sp.* WOOD

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The increasing demand of products and by-products of forestry industry, along with the global trend of conservation of natural ecosystems are challenges for forest science [1]. Wood components may vary in composition and quantity according to the species, from tree to tree, or even within the tree itself, along its structure [2]. Thus, the knowledge of the chemical properties of pine wood is indispensable in the search for better applications, since this species is very important in forest industry.

This work aimed to characterize the chemical properties of *Pinus sp.* wood. We used two 20 years old trees. Samples were randomly cut along the trees and reduced to sawdust for chemical analyses. Then, the 40/60 mesh sawdust was taken. The following chemical characterization were performed: moisture content, amount of extractives, soluble lignin, insoluble lignin, cellulose, hemicellulose and ash content. The characterization was performed in the Wood Science Laboratory at Federal University of Lavras, following the Brazilian standards. The total extractive content of the wood was 12.5% and ash content 1.72%. The lignin content of soluble and insoluble lignin was 2.36% and 22.7% respectively. The cellulose and hemicellulose contents were 50.62% and 12.36%, respectively. The wood showed high carbohydrate content and lower lignin content, being recommended for pulp production.

Table 1. Mean values of wood chemical components

Chemical component	Content (%)
Extractives	12,5
Soluble lignin	2,36
Insoluble lignin	22,7
cellulose	50,62
Hemicellulose	12,36
Ash	1,72

Acknowledgements. TASV is grateful to EBWplus/Erasmus Mundus grant. SACC thanks Fundação para a Ciência e Tecnologia (FCT) for financial support (Investigador FCT program, IF/01381/2013/CP1160/CT0007), with financing from the European Social Fund and the Human Potential Operational Program. This work was supported by Project POCI-01-0145-FEDER-006984 – Associate Laboratory LSRE-LCM funded by FEDER through COMPETE2020 – POCI – and by national funds through FCT.

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CARBON MATERIALS AS ADSORBENTS OF MULTI-RESISTANT BACTERIA

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At present one of the major environmental and public health problems is the existence of bacteria resistant to antibiotics mainly from hospital wastewater, one of the main sources of these bacteria. To remove these bacteria possible strategies are those involving activated carbon that due to their tunable properties can be a suitable adsorbent for different types of microorganism, for example Gram + or Gram – bacteria. In this context, the objective of this study was to verify the adhesion capacity of multi-resistant bacteria onto carbon materials.

Two carbon materials were tested: a commercial activated carbon (AC), assayed in two different granulometries, and a sawdust derived sample (SC) prepared by H_2SO_4 digestion followed by polycondensation of the saccharics units. The bacteria selected were multi-resistant strains of *Klebsiella pneumoniae*, *Escherichia coli*, *Pseudomonas aeruginosa*, *Staphylococcus aureus*. The adsorption test was performed according Naka et al. [1]. In any case in parallel with the adsorption assays, the growth of the bacteria was also assessed.

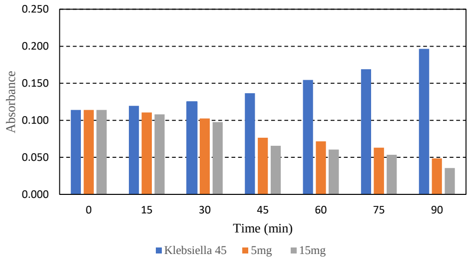

Figure 1. Number of bacteria (absorbance-600 nm) vs time for the bacteria growth and adsorption onto the mentioned amount (5 and 15mg) of carbon AC per 5mL of inoculated bacteria.

Figure 1 exemplifies the results obtained showing that carbon allows a continue decrease of bacteria amount in the liquid media despite the continuous increase of bacteria revealed by the blank experiment. As a final comment, it is possible to consider that carbon can be an efficient method for removal of multi-resistant bacteria present in hospital wastewater.

Acknowledgments. The financial support of FCT to CQB (PEst-OE/QUI/UI0612/2013) is acknowledged. A.S.M. thanks FCT for her postdoc (SFRH/BPD/86693/2012) fellowship.

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ATENOLOL ADSORPTION BY ACTIVATED CARBONS

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The presence of pharmaceutical compounds in the environment can have a tremendously harmful impact on public health. However, the high consumption of drugs and their inefficient removal by conventional wastewater treatment processes leads to their continuous release in the aquatic system. To overcome this problem, it is urgent to implement advanced technologies for water treatment, such as, adsorption onto activated carbons (ACs). To select a specific material it is essential to understand the factors ruling the adsorption mechanism of the targeted molecules [1-3].

In this work, we prepared ACs from a bio-waste (apple tree bark char), using KOH and K_2CO_3 as activating agents. The carbons obtained present high A_{BET} values, up to 2500 and 1965 $m^2\ g^{-1}$, when activated with KOH and K_2CO_3, respectively. The carbons' microporosity profile is also different: composed almost exclusively by wider micropores (KOH) or with significant volumes of narrow micropores (K_2CO_3). As a proof of concept, the adsorption of atenolol was assessed. Equilibrium isotherms (**Figure 1**) show a very steep initial rise revealing a high affinity of the molecule towards the surface but no saturation plateau is clearly observed. All the lab-made samples presented higher adsorption capacity and faster adsorption kinetics than the commercial carbons assayed as benchmark.

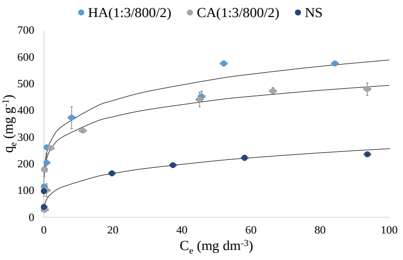

Figure 1. Atenolol adsorption isotherms.

Acknowledgements. The authors thank FCT, Portugal, for financial support to CQB center (Project UID/MULTI/00612/2013) and fellowships: SM(SFRH/BD/91767/2012), ASM(SFRH/BPD/86693/2012). Salmon&Cia (Norit) and Quimitejo are also thanked for supplying the commercial ACs.

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DEVELOPMENT OF CARBON/MnO_2 COATED ON NANOFIBER TEXTILE ELECTRODES FOR HYBRID SOLID-STATE SUPERCAPACITORS

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This work is focused on the design and development of hybrid solid-state energy storage devices with high capacitive performance. In particular, the work includes, the preparation of carbon composite electrodes based on a carbon nanofibers (CNF) supported on a cotton fabric. The coating of CNF to the cotton cloth is obtained by the dip and dry method. On these so-obtained composite substrates, further layers of activated carbon (Norit A Supra Eur) and manganese oxide (MnO_2) material have been subsequenlty deposited to enhance the electrochemical performances of negative and positive electrodes, respectively. The preparation of carbon-based active layers comprises the spreading on the negative CNF-substrate of a slurry containing the activated carbon (AC) material, graphite fibres and polyvinylidene difluoride (PVDF) in N,N dimethylacetamide (DMA). Whereas the positive electrode is prepared by spreading a slurry of MnO_2, carbon black, graphite fibers, PVDF in DMA. A 1M Na_2SO_4 solution impregnated in the porous paper separator (Nippon Kodoshi Corportion, Japan) and a polymer electrolyte membrane (Nafion 115) have been employed as electrolytes. The different supercapacitors were electrochemically characterized by cyclic voltammetry (CV), galvanostatic charge/discharge (G–CD), electrochemical impedance spectroscopy (EIS) and long-term cycling stability tests.

The hybrid carbon-based textile supercapacitors exhibited capacitance performance of 137 and 120 F/g with the porous separator and Nafion 115 membrane, respectively. Specially, the solid-state (Nafion membrane) hybrid device demonstrated very long stability in cycling (10000 cycles) and holding voltage condition at 1.6 V (more than 200 h). Besides, these textile-based capacitors also showed really slow self-discharge.

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INTERACTION DYNAMICS OF CARBON NANOTUBES WITH DISORDERED AND GLOBULAR PROTEINS

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The rich pool of protein structures combined with the nanoscale dimensions and properties of carbon nanotubes (CNTs), generates new horizons for emerging applications in the area of functional and smart materials and nanomedice.[1] Protein α-synuclein (14 kDa) is an intrinsically disordered protein composed by hydrophilic and hydrophobic blocks. This aggregation-prone protein is typically associated with neurodegenerative diseases. The lack of 3D structure and the hydrophobic-hydrophilic regions make this protein a good candidate to disperse carbon nanotubes in water/physiological conditions. Additionally, due to the α-synuclein role in neurodegenerative diseases, new applications in nanomedicine may emerge. Herein, we use UV/Vis spectroscopy, AFM and NMR diffusometry to characterize the SWNT aqueous dispersion and the α-synuclein binding dynamics to SWNT.[2] For the sake of comparison we dispersed SWNTs with a globular protein β-lactoglobulin (18.4 kDa). We observed higher dispersibility of SWNTs with α-synuclein in comparison to β-lactoglobulin protein.

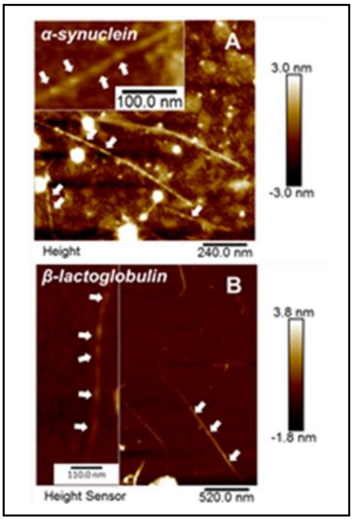

Figure 1. The white arrows in AFM images show adsorbed proteins on SWNTs (A) SWNTs dispersed with α-synuclein. The inset shows clear bead like structure on SWNTs (B) SWNTs dispersed with β-lactoglobulin.

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OPTIMIZING SURFACTANT-ASSISTED DISPERSIONS OF CARBON NANOTUBES: METRICS AND TRENDS

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The high aspect ratio and strong van der Waals cohesive forces (~40 $kT \cdot \text{nm}^{-1}$) of carbon nanotubes (CNTs) results in tightly agglomerated, bundled powders. Surfactants have been used as non-covalent exfoliants and dispersants of pristine CNTs in water, but a fundamental understanding of the dispersing mechanism is still lacking [1]. Well-controlled, systematic dispersing methods and reliable comparative metrics are warranted. This could greatly influence optimization of dispersions and future applications. Herein, we have investigated the ability of several ionic surfactants to exfoliate and disperse single and multiwalled CNTs, resorting to a stringently controlled sonication-centrifugation method. In order to quantify CNT concentration, combined TGA and UV−vis spectroscopy were used. Different single-tailed and double-tailed gemini surfactants, covering a wide range of molecular properties, were studied [2-4]. The dispersibility curves obtained permitted the definition and comparison of several metrics. In turn, this allowed us to assess and rationalize the effect of different molecular properties (aromatic rings, chain length, headgroup charge, *cmc*, covalent spacer length) on the dispersing performance (*viz.* effectiveness and efficiency) of the surfactant.

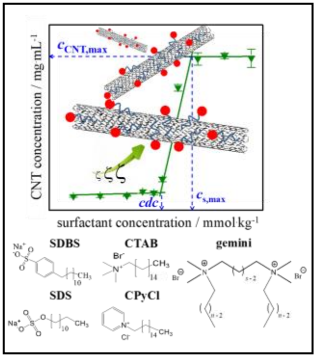

Figure 1. Performance metrics obtained from the dispersion curves for the different surfactants.

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A NOVEL MICRO-MESO STRUCTURED MIXER APPLIED FOR CO_2 HYDRATES PRODUCTION

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It is worldwide accepted that climate changes are occurring, being associated to the human use of fossil fuels. CO_2 emissions are a serious problem in electricity, oil and steel industries. Hydrate-based CO_2 capture (HBCC) is a process approach that involves the precipitation of CO_2 hydrates, concentrating large amounts of gas in solid crystals. Hydrates consist on a lattice of water that traps CO_2, being stable at low temperatures (< 10 ºC) and moderate pressures (30 bar). The most widely described problem of hydrates precipitation is the large amounts of energy that is released, inhibiting further precipitation. The use of stirred tanks or tubular reactors has shown to be insufficient, resulting in high reaction times and low productivities. Also, it has been shown that once the heat transfer limitations are overcome, precipitation can be fast as long intense mixing is achieved.

NETmix is a static mixer that consists of a network of mixing chambers interconnected by channels, and has the potential to be used in the production of hydrates, since it has the capacity to control the mixing quality and intensity, and has demonstrated to be an efficient heat exchanger for highly exo/endothermic processes. These capabilities arise from the fact that under proper hydrodynamic conditions, the flow inside the chambers evolves from a segregated and parallel flow to a chaotic oscillatory flow that induces strong local laminar mixing.

The objective of this work is to apply the NETmix technology in a continuous process, reducing mass and heat transfer limitations, thus enhancing the process kinetics and productivity. A lab-scale continuous HBCC process based on NETmix was designed for the treatment of 1 kg/h of CO_2, in a 20% wt. slurry. The slurry is obtained using a unit with residence time of 1 s, with no flow assurance problems. No gas is detected in a visualizing window, meaning that complete conversion from supersaturated CO_2 to hydrates is achieved. Energy balance to the NETmix unit agrees with the observation of fully converted CO_2 to hydrates.

NETmix has proven to be capable to produce CO_2 hydrates, which can be transported in pipelines. The reduction of the mass/heat transfer limitations, together with high mixing quality, allows the enhancement of the process kinetics. The cost of a HBCC process based on NETmix and further pipeline transportation is competitive to pipeline transportation of supercritical CO_2, the state-of-the-art transportation method.

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