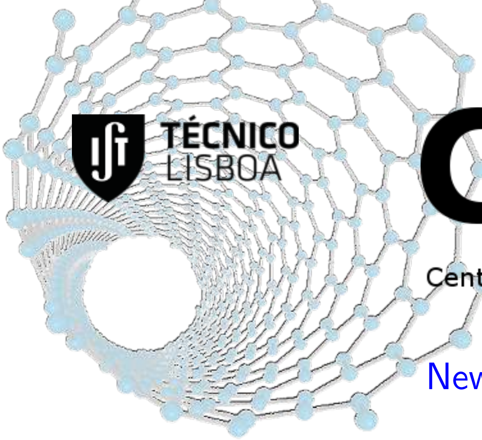

TÉCNICO LISBOA

CeFEMA

Center of Physics and Engineering of Advanced Materials

Newsletter September 2017

Editorial

Luís Amaral
João Figueirinhas

The CeFEMA newsletter intents to disseminate the research activities in materials science and condensed matter physics developed in the Center to a wide scientific and non-scientific community. In this third number, some of the most recent achievements or ongoing projects are highlighted. Nanocomposite and nanostructured membranes for applications from water treatment to medical devices and artificial organs are focused in two contributions. Functional mono- and few-atomic layer materials for nanoelectronics are also featured. Finally, another contribution reports on a work on NMR of liquid crystal dendrimers, which was reviewed in a recently published book by the authors. The featured works are good examples of the excellence and impact of the science developed in CeFEMA.

Tailoring structures and permeation properties of asymmetric nanocomposite cellulose acetate/silver membranes with bactericide activity

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In the 60s the synthesis by Loeb and Sourirajan [1] of integrally skinned cellulose acetate (CA) membranes for reverse osmosis (RO) led to the development at large scale not only of RO but also of the other pressure-driven membrane processes, nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF). Moreover the versatility on these membranes synthesis, by the wet phase inversion method, namely the formulation of the casting solution composition of different polymers and solvents and the setup of different casting conditions is a strong asset on the tailoring of a multiplicity of asymmetric structures with the creation of intrinsically different surfaces or different active layers [2-4]. Nanotechnology is currently used to enhance the performance of ceramic and polymeric conventional membranes and several concepts have been proposed, such as zeolitic and catalytic nanoparticle coated ceramic membranes, hybrid inorganic-organic nanocomposite membranes and aligned nanotube membranes. In a very thorough review Pendergast and Hoek [5] proposed a semi-quantitative ranking based not only on the performance enhancement but also on the commercial readiness, namely prediction and knowledge of costs, use of technology at large scale and existence of manufacturing infrastructures. Pressure-driven membrane processes are often associated to biofouling. By complying with the requisite of large scale manufacturing, our CA membranes prepared by the phase inversion technique offer multiple possibilities of developing novel materials as membrane/Ag nanoparticles composites [6] with bactericide activity and biofouling control. In CeFEMA/MemChem group nanocomposite membranes, CA/Ag nanoparticles, CA/silica, CA/fluorite, are investigated for application ranging from water treatments to medical devices.

[1] S. Loeb, S. Sourirajan, Adv. Chem. Ser. 38 (1963) 117. [2] T. Matsuura and S. Sourirajan, Fundamentals of Reverse Osmosis, National Research Council Canada, Ottawa, (1985), Chap. 3, p.165. [3] D. Murphy and M. N. de Pinho, J. Membrane Sci., 106 (1995) 245-257. [4] D. F. Stamatialis, C. R. Dias, M. N. de Pinho, Biomacromolecules, 1 (2000) 564-570. [5] M. T. M. Pendergast, E. M. V. Hoek, Energy Environ. Sci., 4 (2011) 1946-1971. [6] A. S. Figueiredo, M. G. Sanchez-Loredo, A. Mauricio, M. F. C. Pereira, M. Minhalma, M. N. de Pinho, J. Appl. Polym. Sci., 132 (2015), 41796.

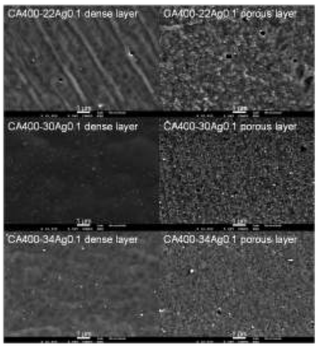

Figure:Dense and porous layers of the UF CA400-22Ag0.1, CA400-30Ag0.1, CA400-34Ag0.1 membranes with Ag nanoparticles (0.1 wt%) with hydraulic permeabilities of 13.6; 52.5 and 58.2 $kgm^{-2}h^{-1}bar^{-1}$

Development of mono- to few-layer TMDs for nanoelectronics

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Transition metal dichalcogenides (TMD) are a class of layered materials with chemical formula MX_2, where M is a transition metal and X a chalcogen. Just like graphite, they can be exfoliated down to a monolayer (2D), exhibiting new properties that are absent in bulk crystals. Some of the TMDs are semiconductors (e.g. M=Mo, X=S,Se) and this is one of the most exciting properties of these 2D materials in contrast to the zero bandgap of graphene. Furthermore, their band structure changes with the number of layers in a way that the indirect band gap in bulk and few-layer TMD crystals transforms into a direct band gap in the monolayer. Actually, semiconductor 2D TMDs have open the door for new studies in fundamental science and applications in nano-scale electronics and optoelectronics. Although exfoliation methods enable the production of nanolayers with a high degree of crystallinity, ideal for the characterization in the laboratory, they present limitations on the control of the number of layers and lateral sizes, not suited for technological applications. Currently, Chemical Vapor Deposition (CVD) is the most promising fabrication technique for achieving a reliable and scalable approach to the production of large-scale 2D materials. It was almost three decades ago when researchers from the LASYP Group started a lab at the FCUL focused on the growth and characterization of functional thin films (nitrides, carbides, complex oxides) by using CVD-based methods. With the launch of CeFEMA in 2015 and its structuring project GOLDmater, taking profit of the know-how on growth techniques and on 2D materials properties of several of its members, $MoSe_2$ was added aiming at exploring new physical properties with interest for devices technology.

Why $MoSe_2$? The CVD synthesis of large-scale monolayer $MoSe_2$ is more challenging than that of MoS_2 due to the lower chemical reactivity of Se as compared to sulphur; however, $MoSe_2$ shows a stronger light absorption in the solar spectrum range and the band gap of 1.5 eV for monolayer $MoSe_2$ is close to the optimal value required for solar spectrum related applications, e.g. single-junction solar cells and photoelectrochemical cells. Also, few-layer $MoSe_2$ has nearly degenerate indirect and direct band gaps, and an increase in temperature can effectively drive the system towards the 2D limit. Currently, we are optimizing the optical and electrical properties of CVD-grown mono- to few-layer $MoSe_2$ [1]. In parallel, we have been studying $MoSe_2$/ferroelectric hybrid structures where a switchable diode effect was found suggesting that these structures are promising candidates for non-volatile ferroelectric resistive memories [2]. This work is carried out in collaboration with researchers from Minho University.

[1] C. Almeida Marques, MSc in Physics, Ciências, ULisboa, November 2016 [2] J.P.B. Silva, C. Almeida Marques, J. Agostinho Moreira, O. Conde, arXiv:1705.04475

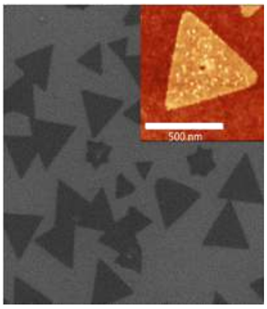

Figure:FE-SEM micrograph of $MoSe_2$ triangle flakes grown by CVD onto oxidized Si. Inset: AFM image.

Nanostructured membranes for artificial organs

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Artificial organs are associated to membrane based treatments clinically well established. They assure in extracorporeal circulation the metabolic functions of a failing organ like the hemodialyzer (HD) in the case of the kidney and the membrane blood oxygenator (MBO) in the case of the lung. In order to have technical and medical progress of HDs and MBOs two major factors need to be considered: 1) blood compatibility of the membrane/blood interfaces and 2) enhancement of the flow management/mass transfer associated to the metabolic functions of the artificial kidney and lung. The first factor is achieved through the tailoring of novel polymer membranes with specific chemical composition, morphology and topography for enhanced hemocompatibility [14]. In the case of the artificial lung this can be achieved through the synthesis of integrally skinned polyurethane urea (PUU) membranes with tailored surface topographies. The figure shows a direct correlation between the submicron roughness of the blood contacting surface and the degree of platelet adhesion for the PUU membranes where the smoothest membranes exhibited very low platelet adhesion and inhibition of extreme states of platelet activation [5]. In the case of the artificial kidney, blood compatibility can be achieved by the development of asymmetric cellulose acetate-silica (CA-Si) membranes by a modified version of the phase inversion method coupled to the sol-gel technique. The introduction of silica into the polymer matrix of cellulose acetate membranes provides functionalization anchor points for molecules known for their enhanced hemocompatibility properties, such as heparin, polyethylene glycol, etc.

The second factor is achieved through the synthesis of PUU and CA-Si membrane-fiber composites to assure flow conditions that minimize the boundary layer mass transfer resistance. In contrast with the state of the art, where boundary layers disruption is achieved by introduction of spacers over the flat sheet membranes, in our research group, the creation of secondary flows promoting mixing is achieved through the deposition of PUU and CA-Si microfibers at the blood contacting surface of the PUU and CA-Si membranes, respectively. In the case of the artificial lung, the efficiency of the PUU membrane-fiber composites is evaluated by oxygen and carbon dioxide permeation studies in a custom-built benchmark device under various flow and pressure conditions. With regard to the mass transfer studies associated to the metabolic functions of the kidney, also conducted in custom-built benckmark devices, particular emphasis is given to model solutions of molecules that are very difficult to remove by standard hemodialysis, namely the middle-sized molecules and the protein binding molecules such as $\beta 2$ macroglobulin and p-cresyl sulfate, respectively.

[1] Besteiro, M. C. et al. J. Biomed. Mater. Res. A 93, 954-964 (2010). [2] Faria, M., Geraldes, V. and de Pinho, M. N. International Journal of Biomaterials (2012). [3] Faria, M. and Pinho, M. N. D. Extracorporeal Blood Oxygenation Devices, Membranes for. in Encyclopedia of Membranes (eds. Drioli, E. and Giorno, L.) 737-755 (Springer Berlin Heidelberg, 2016). [4] Faria, M. and de Pinho, M. N. Eur. Polym. J. 82, 260-276 (2016). [5] Faria, M., Brogueira, P. and de Pinho, M. N. Colloids Surf. B Biointerfaces 86, 21-27 (2011).

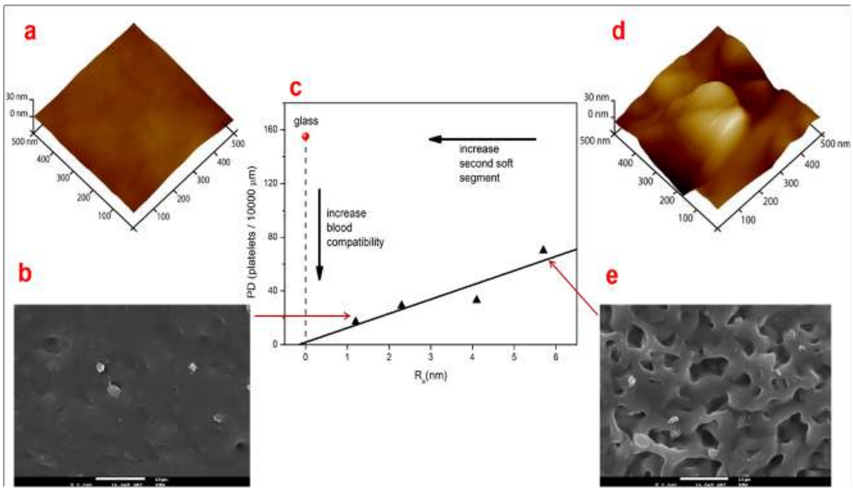

Figure (a, d) 3D AFM topography and (b, e) SEM images of the dense layer of the PUU 85 (a, b) and PUU 100 (d, e) membranes. (c) Platelet deposition (PD) vs. mean roughness (R_a) of the dense layer of PEUU membranes [5].

NMR of liquid crystal dendrimers

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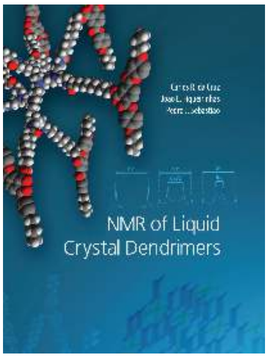
The study of new materials with potential and actual technological impact is one of the central purposes of CeFEMA. Dendrimers are among the most interesting materials with applications both in material science and biomedicine. Recently, as a result of more than one decade of investigations, three members of the Complex Fluids NMR and Surfaces (CFNMRS) group of the Centre published a book on Nuclear Magnetic Resonance of Liquid Crystal Dendrimers [1]. Dendrimers are hyperbranched molecules resulting from sequential iterative synthetic procedures. Unlike usual polymers, which molecules are composed by similar segments, linearly connected forming very long chains of repetitive chemical units, in the dendritic molecules each segment branches up into a certain number of similar units, forming a complex structure similar to a tree crown. The properties of a dendrimer are defined by the chemical nature of its segments, the multiplicity of the core (number of branches in the central unit),the degree of branching (number of branches starting at the end of each branch), and the generation (number of levels of branching, corresponding to the number of inner branching layers of the dendrimer). Contrary to conventional polymers, the dendrimer molecules are typically monodispersed, which means that, in a dendrimer sample, practically all the molecules have the same size, defined by the dendrimer generation. This way, the dimensions of a dendrimer (typically of the order of the nanometers) may be tuned by controlling the generation through the synthetic procedure. The outer shell of a dendrimer molecule corresponds to the peripheral branches associated to the external layer. In most applications, the outward branches of the dendrimer may be appropriately functionalized, using chemical units suitable for the desired purpose. Most of the interesting practical uses of dendrimers are based on this approach. If the dendrimers are functionalized with terminal units bearing liquid crystalline properties, peculiar materials known as liquid crystal dendrimers, can be obtained. Liquid crystal dendrimers combine the interesting properties of dendrimers with those of liquid crystals (anisotropic molecular organization, fluidity, anisotropic response to electric and magnetic fields, and anisotropic physical properties in general). The CFNMRS group of CeFEMA has a very long experience on the study of liquid crystals by means of NMR spectroscopy and relaxometry, characterizing both the molecular order and dynamics of those materials. In more recent years this expertise has been applied to study of other systems including liquid crystal dendrimers. The book recently published includes a general introduction to dendrimers, liquid crystal dendrimers and NMR, both in theoretical and experimental aspects applied to liquid crystalline materials, and an comprehensive review on the research work of the authors on this subject and a comparative study where the physical properties of many different liquid crystal dendrimers accessible thorough NMR are compared and analyzed.

[1] NMR of Liquid Crystal Dendrimers, Carlos R. Cruz, João L. Figueirinhas, Pedro J. Sebastião, Pan Stanford Publishing, 2016, ISBN 978-981-4745-72-7 (Hardcover), 978-981-4745-73-4 (eBook)



NMR of Liquid Crystal Dendrimers

News and Events

2016

News

CeFEMA at Industrial Technologies 2016 Creating a Smart Europe, Amsterdam, The Netherlands, June, 22, 2016

CeFEMA at infoday: Nanotechnologies, Advanced Materials and Advanced Mnufactoring and Processing, Biotechnology, Lisbon, July 7, 2016

Workshops

Workshop on graphene and other 2D materials
IST, December 5, 2016
CeFEMA Workshop
IST, December 12, 2016

Seminars

Cicle of CeFEMA Seminars, 7 held
CeFEMA Theory Group Seminars, 4 held
Other CeFEMA Seminars, 3 held

2017

Special Events

Emílio Ribeiro Conference on Quantum Chromodynamics and other matters
September 6, 2017

News

CeFEMA at EuroNanoForum 2017, Mediterranean Conference Centre, Valletta, Malta, June 21-23, 2017

Workshops

Mini-Workshop on Theoretical Condensed Matter Physics
February 21, 2017

Seminars

Cicle of CeFEMA Seminars, 4 held
CeFEMA Theory Group Seminars, 6 held

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