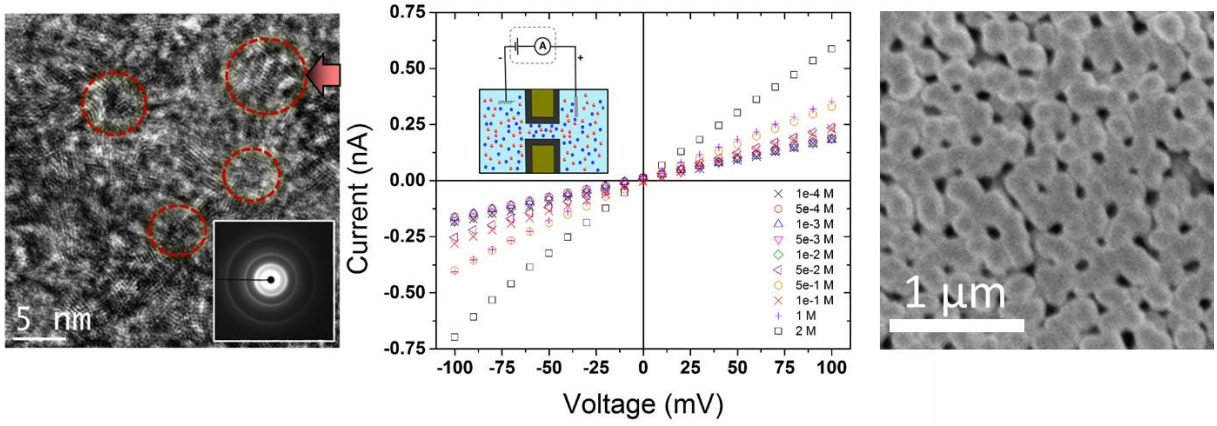
3D (nano)structured materials

Boron Nitride Nanoporous Membranes with High Surface Charge by Atomic Layer Deposition

ACS Applied Materials & Interfaces 9 (2017) 16669–16678

Involved PNM researchers: Philippe Miele, Mikhael Bechelany

In this work, we report the design and the fine-tuning of boron nitride single nanopore and nanoporous membranes by atomic layer deposition (ALD). First, we developed an ALD process based on the use of BBr_3 and NH_3 as precursors in order to synthesize BN thin films. The deposited films were characterized in terms of thickness, composition and microstructure. Next, we used the newly developed process to grow BN films on anodic aluminium oxide (AAO) nanoporous templates, demonstrating the conformality benefit of BN prepared by ALD, and its scalability for the manufacturing of membranes. For the first time, the ALD process was then used to tune the diameter of fabricated single transmembrane nanopores by adjusting the BN thickness and to enable studies of the fundamental aspects of ionic transport on a single nanopore. At pH=7, we estimated a surface charge density of 0.16 $C.m^{-2}$ without slip and 0.07 $C.m^{-2}$ considering a reasonable slip length of 3 nm. Molecular dynamic simulations performed with experimental conditions confirmed the conductivities and the sign of surface charges measured. The high ion transport results obtained and the ability to fine-tune nanoporous membranes by such a scalable method paves the way towards applications such as ionic separation, energy harvesting and ultrafiltration devices.



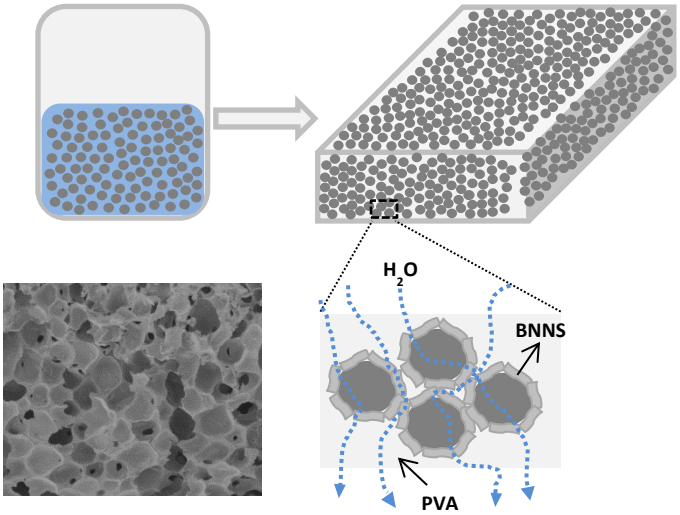
3D (nano)structured materials

Development of novel h-BNNS/PVA porous membranes via Pickering emulsion templating

Green Chemistry 20 (2018) 4319-4329

Involved PNM researchers: Julien Cambedouzou, Mikhael Bechelany, Philippe Miele

Polymer-based membranes play an important role in water filtration, in particular in the removal of particles, microorganisms and organic pollutants. Developing a reliable fabrication method for membranes presenting both high flux and good selectivity remains challenging. Polyvinyl alcohol (PVA) is a well-known polymer with promising perspectives due to its specific properties such as nontoxicity, biocompatibility and biodegradability susceptible to be of great interest within the context of developing green technologies. Herein, a new strategy to produce porous membranes based on PVA has been developed using emulsion templating involving hexagonal boron nitride nanosheets (h-BNNS) as stabilizer. The membranes displaying a pore size around 1 µm show a water performance over 2000 L m^{-2} h^{-1} bar^{-1} and a rejection efficiency of ~100 %. Moreover, the membranes did not significaly reduce their perfomance after particles filtration. The results indicated that the h-BNNS/PVA porous membranes fabricated via Pickering emulsion templating are good candidates to be used as microfiltration membranes



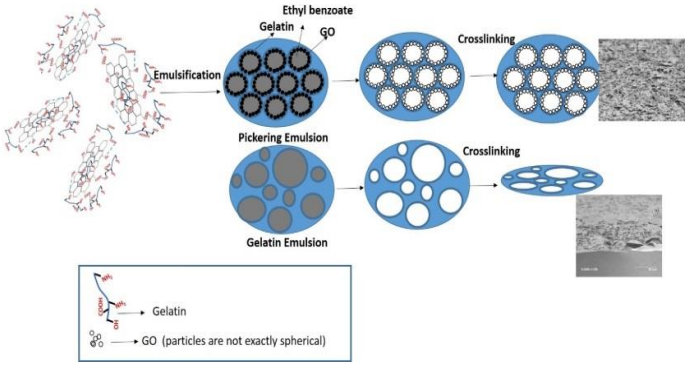
3D (nano)structured materials

Porous Gelatin Membrane Obtained from Pickering Emulsions Stabilized by Graphene Oxide

Langmuir 34 (2018) 1542-1549

Involved PNM researchers: Philippe Miele, Mikhael Bechelany

This paper presents a novel procedure to prepare porous membranes from water-soluble polymers involving the formation of Pickering emulsion. Gelatin is a biodegradable biopolymer obtained by the partial hydrolysis of collagen. Biopolymer such as gelatin is capable to adsorb at oil/water interface and results to decrease interfacial energy. Hence, gelatin is widely employed as an alternate for synthetic surfactants to stabilize emulsions in food industry. However, high molecular weight gelatin leads to large emulsion droplets and poor emulsion stability. The amphoteric nature of graphene oxide (GO) nanosheets was helpful to stabilize the oil/water interface and allows preparing stable gelatin/GO emulsion. Membranes fabricated using gelatin/GO display uniformly distributed porous structure. However, prepared membranes are highly hydrosoluble; hence the membranes were crosslinked without affecting their morphology. XRD results evidenced that gelatin effectively exfoliated the graphite oxide which is essential to stabilize the emulsion. Fabricated gelatin/GO membranes possess uniformly distributed pores and are highly stable in aqueous solution. Pure water filtration tests were conducted on the membranes. The permeability results proved that the membranes fabricated by Pickering emulsion are promising materials for filtration.



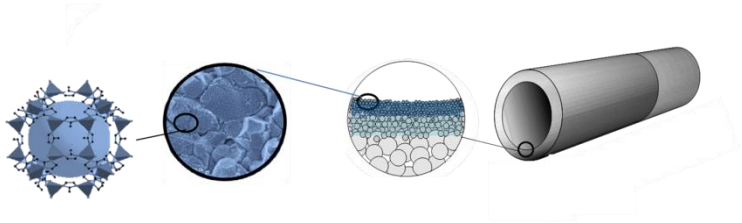
3D (nano)structured materials

An innovative Approach for the Preparation of Confined ZIF-8 Membranes by Conversion of ZnO ALD Layers

Journal of Membrane Science 475 (2015) 39-46

Involved MCP researchers: Mikhael Bechelany

An innovative eco-friendly approach has been developed for the synthesis of ZIF-8-based nanocomposite membranes. The method involves the Atomic Layer Deposition (ALD) of ZnO thin films on the grains of a macroporous ceramic support and their subsequent conversion to ZIF-8 using a 2-methylimidazole/methanol solution and solvothermal conditions. Despite of applying extremely low quantity of chemicals, reproducible and good quality ZIF-8-based membranes have been obtained, in which the ZIF-8 material was fully confined within the ceramic support macropores, thus leading to enhanced thermo-mechanical strength. A judicious choice of both the deposition conditions of ZnO layers and the solvothermal treatment parameters for their subsequent conversion to ZIF-8 were the key points for validation of this original protocol and evaluation of its potential for up-scaling on tubular industrial supports. The physico-chemical characterization of the ZIF-8/ZnO/α-Al2O3 nanocomposite membranes was completed by a study of their gas transport properties. Reproducible ZIF-8/ZnO/α-Al2O3 nanocomposite membranes were produced and tested in the separation of binary gas mixtures: membranes were found to extract H_2 from H_2/CO_2 and H_2/CH_4 equimolar gas mixtures with selectivities of about 7.8 and 12.5 respectively, measured at 100°C.



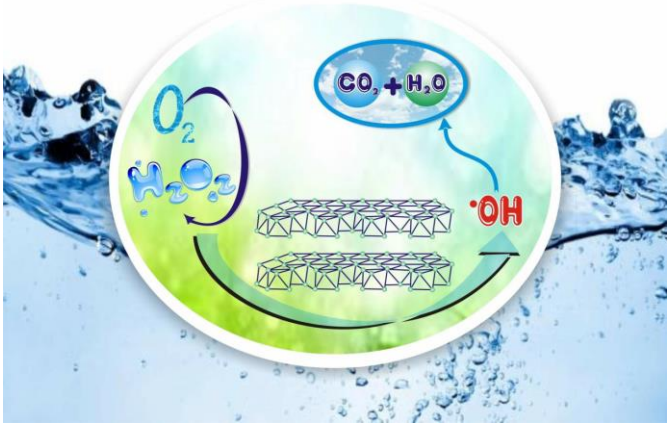
3D (nano)structured materials

Electrochemical mineralization of sulfamethoxazole over wide pH range using $Fe^{II}Fe^{III}$ LDH modified carbon felt cathode: Degradation pathway, toxicity and reusability of the modified cathode

Chemical Engineering Journal 350(2018) 844-855

Involved PNM researchers: Mikhael Bechelany

Hierarchical three-dimensional (3D) porous architecture $Fe^{II}Fe^{III}$ layered double hydroxide (LDH) multiwall was grown on carbon-felt (CF) substrate via solvothermal process. The as-deposited $Fe^{II}Fe^{III}$ LDH/CF cathode was composed of highly oriented and well crystallized interconnected nanowalls with high electrical conductivity and excellent catalytic activity over a wide pH range (pH 3 – 9) for heterogeneous electro-Fenton (HEF) degradation of antibiotic sulfamethoxazole (SMT) in aqueous medium. Mineralization efficiencies (in terms of TOC removal) of ~97%, 93% and 90% was achieved at pH 3, 6 and 9 respectively for $Fe^{II}Fe^{III}$ cathode during HEF treatment of 0.2 mM SMT solution at applied current density of 7.5 mA cm^{-2} using Ti_4O_7 anode. Comparative electro-Fenton (EF-Fe^{2+}) with 0.2 mM Fe^{2+} or electrooxidation with H_2O_2 production (EO-H_2O_2)studies using raw CF cathode at similar experimental conditions showed relatively lower mineralization with highest TOC removal efficiency of 77% and 64% obtained at pH 3 for EF-Fe^{2+} and EO-H_2O_2 respectively. Oxidative degradation of SMT in HEF system was by (i) Ti_4O_7($^{\bullet}OH$) generated at anode surface at all pH studied, (ii) surface catalyzed process and (iii) contribution from homogeneous catalyzed process at pH 3 due to leached iron ions. The prepared $Fe^{II}Fe^{III}$ LDH/CF exhibited excellent catalytic stability with good reusability up to 10 cycles of 4 h treatment at pH 6. Initial SMT solution showed relatively high toxicity but total detoxification of the solution was attained after 8 h of treatment by HEF with $Fe^{II}Fe^{III}$LDH/CF cathode. HEF with $Fe^{II}Fe^{III}$ LDH/CF cathode is an exciting technique for remediation of organic contaminated wastewater.



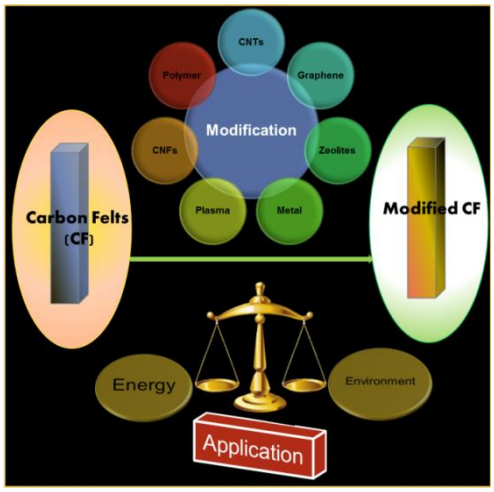
3D (nano)structured materials

Carbon felts based-electrodes for energy and environmental applications: a review

Carbon 122 (2017) 564-591

Involved PNM researchers: Mikhael Bechelany

Carbonaceous materials are abundantly used for electrochemical applications and especially for energy and environmental purposes. In this review, the carbon felt (CF) based-electrodes are discussed in a holistic manner. First of all, the study centers on the issues relevant to pristine CF materials such as manufacturing method and specific properties. The various methods and equations used to identify physical values of CF material are supplied. As main part of the review, the different modification methods for CF electrodes are described. The novel properties of fabricated materials are characterized by physical as well as electrochemical techniques. The strengths of each method are presented in the comparison with raw CF electrodes. The energy applications of CF based-electrodes are figured out in various fields such as vanadium redox flow batteries (VRFB), microbial fuel cells (MFCs), biofuel cells (BFCs), capacitors, solar cells and lithium ion batteries. For environmental applications, we focus our study on the wastewater treatment containing biorefractory pollutants by electro-Fenton (EF) process. The degradation result by EF technology using CF materials is impressive when most of toxic contaminants are mineralized to non-toxic compounds at the end of the electrolysis. To decrease the cost treatment and upgrade the treatment efficiency, the EF system has been improved by using modified electrodes or new catalyst sources. The CF materials are also investigated to apply in bio-fuel cell-Fenton in which electrons were produced from fuel cell (FC) towards zero-energy depollution. Finally, the sketches about EF pilot open new gates for application of CF materials in industrial areas.



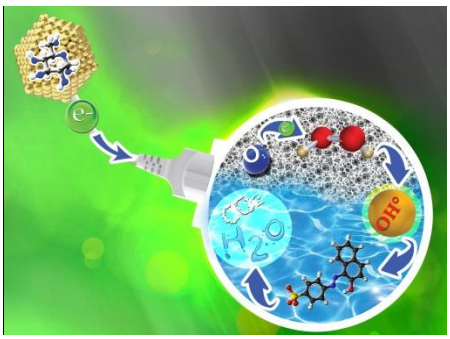
3D (nano)structured materials

Design of novel Fuel Cell-Fenton system: a smart approach to zero enegy depollution

Journal of Materials Chemistry A 4 (2016) 17686-17693

Involved PNM researchers: Mikhael Bechelany

A model azo dye pollutant, Acid Orange 7 (AO7), was removed efficiently from aqueous medium by a smart eco-friendly Fuel Cell - Fenton (FC-Fenton) system without any external power supply. In this approach, AO7 was degraded by electro-Fenton process at a designed cathode (Carbon Felt (CF)/porous Carbon (pC)) supplied by direct clean electrical energy from abiotic glucose oxidation at a CF/gold anode (CF@Au). The highly active cathode was fabricated by an attractive route combining Atomic Layer Deposition (ALD) of ZnO on commercial carbon felts (CFs) followed by subsequent solvothermal conversion of the metal oxide to a Metal Organic Framework (here ZIF-8). The as-prepared composite material was further calcined at high temperature under controlled atmosphere. A porous carbon-based (pC) support with high specific surface area and containing nitrogen as a dopant was thus obtained, enhancing both conductivity and electrocatalytic properties toward H_2O_2 production from oxygen reduction. Degradation kinetics of AO7 (0.1 mM initial concentration) at the CF@pC cathode was monitored by UV-vis spectrophotometry and High-Performance Liquid Chromatography (HPLC) to prove the efficiency of the composite material for the degradation of such a bio-refractory model molecule. Benefited from the H_2O_2 production rate (9.2 mg/L/h) by the carbon porous layer, AO7 (35.0 mg/L) was degraded by electro-Fenton process in acidic medium (pH=3) with removal efficiency reaching 90 % in 10 h. The durability of the system was extended for more than 2 months with an average power output of 170 mW m^{-2}, confirming this abiotic FC-Fenton system as a green promising future technology for both environmental and energy-related areas, including membrane-coupled reactor systems.



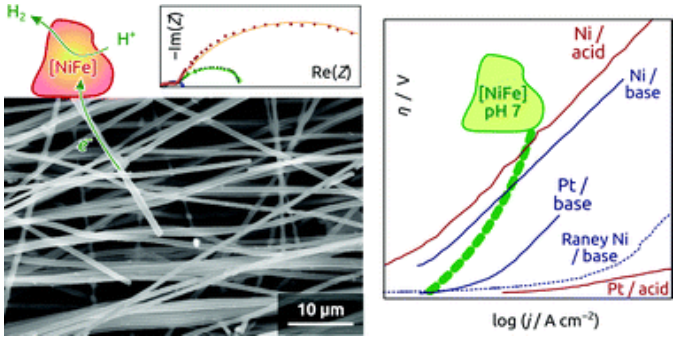
3D (nano)structured materials

An electrochemically functional layer of hydrogenase extract on an electrode of large and tunable specific surface area

Journal of Materials Chemistry A 4 (2016) 6487-6494

Collaboration: Friedrich-Alexander University Erlangen-Nürnberg (Germany)
Involved PNM researchers: Mikhael Bechelany

Electrode supports are generated by electrospinning of polyacrylonitrile fibers and subsequent coating of a thin electrically conductive TiO_2 layer by atomic layer deposition. The supports are then functionalized with a [NiFe]-hydrogenasecontaining membrane fraction from Escherichia coli and are characterized structurally and electrochemically. The hydrogenase suspension generates a micron-thick organic film around the fiber mat, which exhibits electrocatalytic activity for hydrogen evolution. Furthermore, the electrode geometric surface area is varied systematically via the electrospinning procedure, which reduces the charge transfer resistance and increases the hydrogen evolution current density to >500 µA cm^{-2} at 0.3 V overpotential.



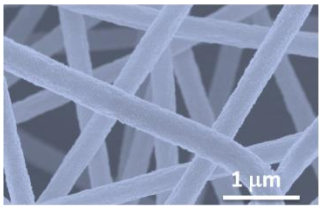
3D (nano)structured materials

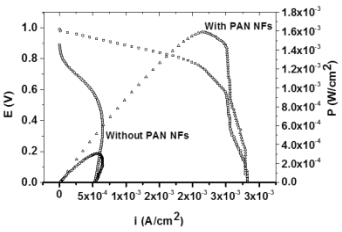
A highly efficient gold/electrospun PAN fibers material for improved laccase biocathodes for biofuel cell applications

Journal of Materials Chemistry A 2 (2014) 2794 – 2800

Involved PNM researchers: Mikhael Bechelany

We explored for the first time the ability of three-dimensional polyacrylonitrile/Gold material prepared by a low-cost and scalable synthesis method, based on the combination of electrospinning and sputtering, as new material with large surface area to provide high loadings of enzymes to enhance the electrochemical performances of enzymatic electrodes in biofuel cells (BFCs). An ethanol/O_2 BFC has been developed based on enzymatic reactions performed at both the cathode and anode with immobilization of the respective enzymes and mediators on the three-dimensional nanostructured electrodes. The power density delivered is 1.6 mW cm^{-2} at 0.75 V, which is five times the power density delivered by the BFC build on flat bioelectrodes. The greatly improved performance of these synthesized nanostructured electrodes makes them exciting materials for their implantation in biofuel cell applications.





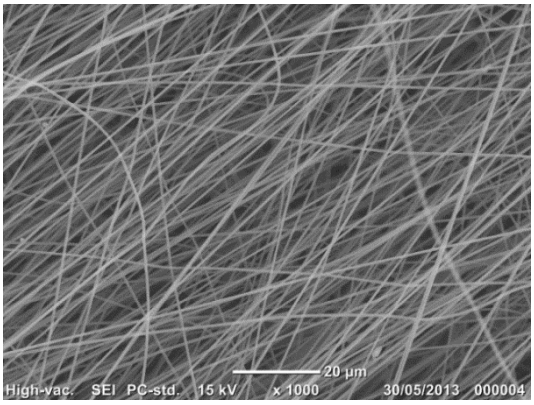
3D design of (nano) materials

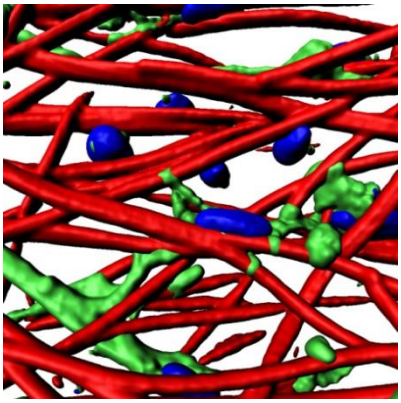
3D CELL CULTURE TECHNOLOGY: advanced enabling 3D scaffold to better mimic the tissue microenvironment for improved cell assays

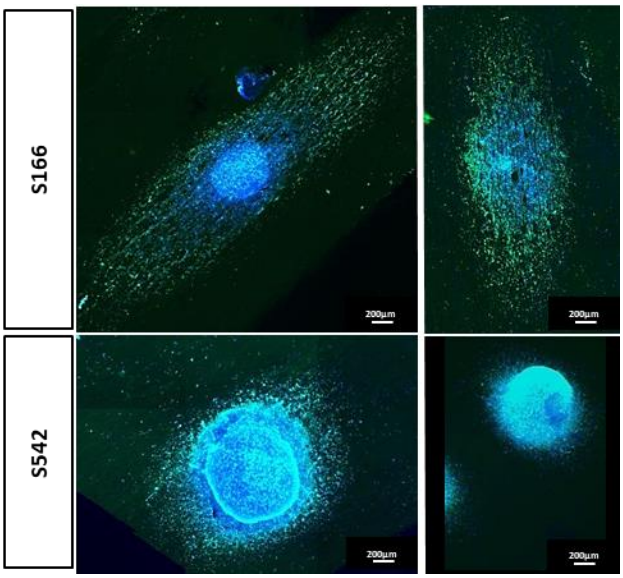
Brevet:
French Patent FR18 51324 (16/02/2018)

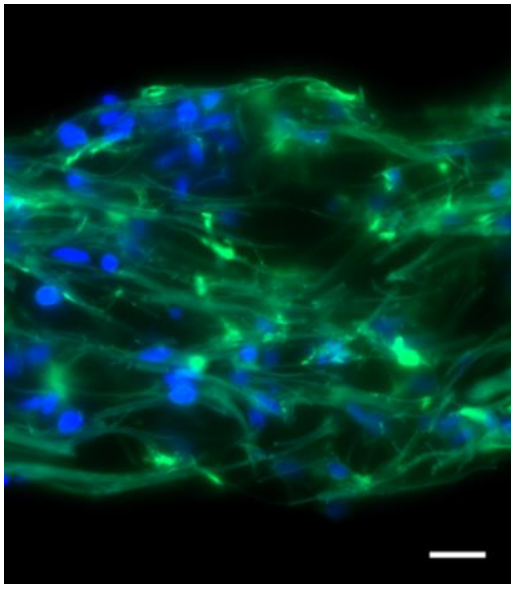
Collaboration: N. Bakalara, J. Vignon, C. Fabre, L. Bauchet, H. Duffau (INM, CHU St Eloi, Montpellier)
Involved PNM researchers: David Cornu and Julien Cambedouzou

We have developed a new porous membrane (3D Scaffold) made from electrospun fibers that mimics the chemical and mechanical environment of cells and thus offers biologists a new tool for in vitro expertiments enabling improved cell assays. Our 3D technology is inert and biocompatible. Cells live, migrate, proliferate and differentiate. Our technology opens up opportunities for biologists to carry out more relevant in vitro assays offering the possibility to reduce the use of animal experimentation. We have demonstrated the potentialities of our technology by studying the migration plasticity of Glioma Stem Cells.









3D design of (nano) materials

Soft templated mesoporous SiC from polycarbosilane grafted onto triblock copolymers

Materials Letters 185, 424-427, 2016 DOI: 10.1016/j.matlet.2016.09.041

Collaboration: ICSM Marcoule
Involved PNM researcher: Julien Cambedouzou

Mesoporous silicon carbide (SiC) presenting very large specific surface area was elaborated following an original soft-templating approach based on polymeric precursors. The polystyrene units of a poly(styrene-block-butadiene-block-styrene) triblock copolymer are used as a templating agent, while a polycarbosilane preceramic polymer is employed as SiC precursor. Thanks to the self-organization of polycarbosilane around PS blocks in liquid medium, and to the subsequent elimination of the copolymer during the polycarbosilane conversion into SiC, a mesoporous SiC can be formed. High specific surface areas of more than 400 $m^2 g^{-1}$ are measured on the final SiC, opening the doors to the viable production of SiC of controlled porosity.