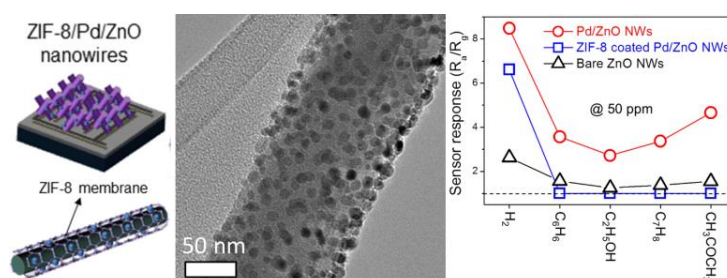


High-Performance Nanowire Hydrogen Sensors by Exploiting the Synergistic Effect of Pd Nanoparticles and Metal–Organic Framework Membranes

ACS applied materials & interfaces 10 (2018) 34765-34773

Collaboration: Inha University (Republic of Korea) and Adam Mickiewicz University in Poznan (Poland)
Involved PNM researchers: Mikhael Bechelany

Herein, we report the fabrication of hydrogen gas sensors with enhanced sensitivity and excellent selectivity. The sensor device is based on the strategic combination of ZnO nanowires (NWs) decorated with palladium nanoparticles (Pd NPs) and a molecular sieve metal organic framework (MOF) nanomembrane (ZIF-8). The Pd NPs permit the sensors to reach maximal signal responses, whereas the ZIF-8 overcoat enables for an excellent selectivity. Three steps were employed for the fabrication: i) coating of a miniaturized sensor with vapor grown ZnO NWs, ii) decoration of these NWs with Pd NPs by atomic layer deposition (ALD), and iii) partial solvothermal conversion of the tuned NWs surface to ZIF-8 nanomembrane. The microstructure and composition investigations of the ZIF-8/Pd/ZnO nanostructured materials confirmed the presence of both metallic Pd NPs and uniform ZIF-8 thin membrane layer. The integration of these nanomaterials within a miniaturized sensor device enabled the assessment of their performance for H₂ detection at concentrations as low as 10 ppm in the presence of various gases such as C₆H₆, C₇H₈, C₂H₅OH and CH₃COCH₃. Remarkably high response signals of 3.2, 4.7 and 6.7 (R_a/R₀) have been measured for H₂ detection at only 10, 30 and 50 ppm, whereas no noticeable response towards other tested gases was detected, thus confirming the excellent H₂ selectivity obtained with such sensor design. The results obtained showed that the performance of gas sensors towards H₂ gas can be greatly increased by both the addition of Pd NPs and the use of ZIF-8 coating acting as a molecular sieve membrane. Furthermore, the presented strategy could be extended towards the sensing of other species by a judicious choice of both the metallic NPs and MOFs materials with tuned properties for specific molecules detection, thus opening a new avenue for the preparation of highly selective sensing devices.



MOF-based membrane encapsulated ZnO nanowires for enhanced gas sensor selectivity

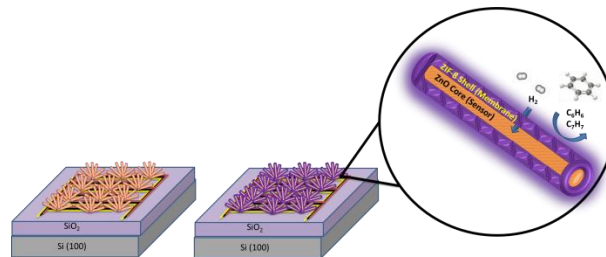
ACS Appl. Mater. Interfaces 8 (2016) 8323–8328.

Collaborations: Inha University (South Korea)

Involved MCP researchers: Mikhael Bechelany

Gas sensors are of a great interest for applications including toxic or explosive gases detection in both in-house and industrial environment, air quality monitoring, medical diagnostics or control of food/cosmetic properties. In the area of semiconductor metal oxides (SMOs)-based sensor, a lot of effort has been devoted to improve the sensing characteristics. In this work, we report on a general methodology for improving the selectivity of SMO_x sensors based on the coverage of ZnO nanowires with a thin ZIF-8 selective membrane barrier exhibiting molecular sieving properties. The as-prepared ZnO/MOF-based nanocomposite sensor shows improved sensitivity ratios of (S_{H_2})/($S_{C_7H_8}$) and (S_{H_2})/($S_{C_6H_6}$)

concentration up to enhancement, comparison to the sensor. This original way for different where gas or ionic such as sensing, photo(catalysis)



reaching for 10 ppm 3.5 and 2.8 times higher respectively in pristine ZnO nanowires strategy can pave the types of applications, selectivity is required biosensing, and electrodes.

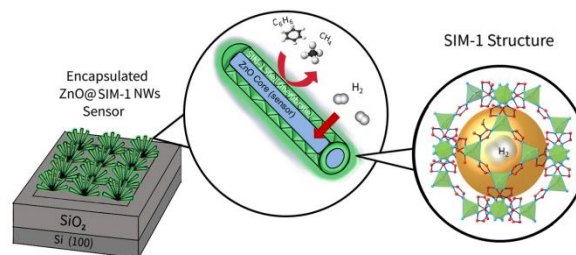
Design and fabrication of highly selective H_2 sensors based on SIM-1 nanomembrane-coated ZnO nanowires

Sensors & Actuators B: Chemical, Sensors and Actuators B 264 (2018) 410–418

Collaborations: Inha University (South Korea)

Involved MCP researchers: Mikhael Bechelany

High quality hydrogen sensors are of an utmost importance in many industrial applications to efficiently address the safety issues concerning the production, delivering, storage and use of H_2 gas. Recently a special effort has been devoted to modification of semiconductor metal oxides in order to improve their gas sensing characteristics. In this context here we report on the preparation of a novel ZnO-based semiconductor sensor modified by a thin SIM-1 hydrogen selective membrane serving as an efficient molecular sieving layer. Compared to pristine ZnO sensors, the optimized SIM-1 coated ZnO nanowires showed remarkable selectivity towards H_2 at high temperatures (300 °C) in the presence of numerous interfering gases (CH_3COCH_3 , CH_4 , C_7H_8 , C_2H_5OH and C_6H_6) thus confirming the efficiency of such sensor material for hydrogen detection.

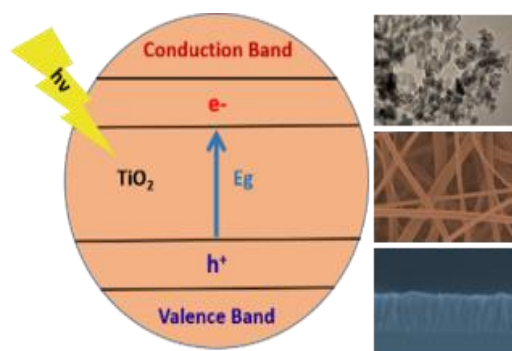


Recent Progress on TiO₂ Nanomaterials For Photocatalytic Applications

ChemSusChem 11 (2018) 3023-3047

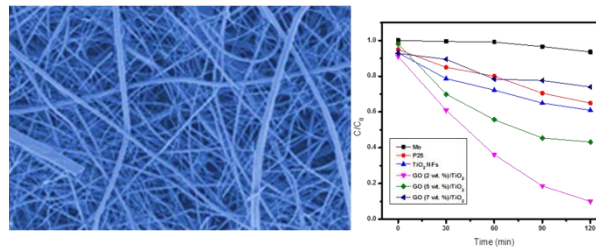
Involved PNM researchers: Mikhael Bechelany

Environmental and energy problems have drawn much attention due to the rapid population growth and the accelerated economic development. For instance, photocatalysis, “a green technology”, plays an important role in solar energy conversion owing to its potential to solve energy and environmental problems. Recently, many efforts have been devoted to improve the visible-light photocatalytic activity using titanium dioxide as photocatalyst due to its wide range of applications in energy and environment fields. However, the fast charge recombination and the absorption edge in the UV range limits the photocatalytic efficiency of TiO₂ under visible-light irradiation. Many investigations have been carried out in order to overcome the limitations of TiO₂ and therefore enhance its photocatalytic activity under visible light. The present literature review focuses on different strategies used to promote the separation efficiency of the electron-hole pairs and to shift the absorption edge of TiO₂ to the visible region. Current synthesis techniques used to elaborate several nanostructures of TiO₂ based material, recent progress in enhancing visible photocatalytic activity and the different photocatalysis applications will be discussed. Based on the studies reported in the literature, we believe that this review will help in the development of new strategies to further improve the visible light photocatalytic performance of TiO₂ based materials.



Enhanced visible-light photocatalytic performance of electrospun rGO/TiO₂ composite nanofibers*Journal of Physical Chemistry C* 121 (2017) 261–269Involved PNM researchers: Mikhael Bechelany

Reduced graphene oxide (rGO) / Titanium dioxide (TiO₂) composite nanofibers as photocatalytic materials were successfully elaborated by using electrospinning. The as-spun nanofibers with controlled ratio of rGO were annealed at 500°C under Nitrogen in a tubular furnace. Structural, morphological and optical characterizations demonstrate the success of rGO incorporation in the TiO₂ nanofibers. The performances of these nanocomposites for photocatalytic application have been evaluated. The presence of rGO sheets decreases the band gap energy of TiO₂ NFs from 3.2 eV to 2.9 eV. Hence, in the photodegradation of methyl orange (MO), a significant enhancement in the reaction rate was observed with rGO/TiO₂ (2wt. %) composite NFs compared to commercial TiO₂-P25. In addition, the kinetic of MO degradation by rGO/TiO₂ (2wt. %) composite NFs is 6 times higher than that by commercial TiO₂. Thus, the photocatalytic activity of the composites rGO/TiO₂ significantly increases the visible light photo-response and improves the separation of photo-induced electron-hole pairs of TiO₂.



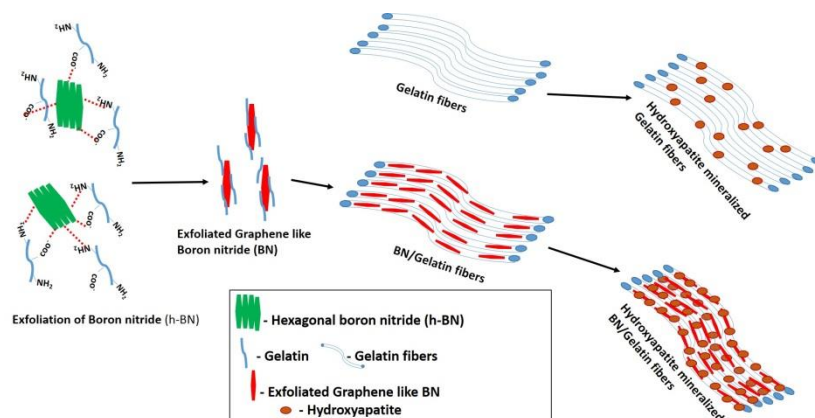
Design of Boron Nitride/Gelatin Electrospun Nanofibers for Bone Tissue Engineering

ACS Applied Materials & Interfaces 9 (2017) 33695-33706

Collaboration: IRCM (France)

Involved PNM researchers: Philippe Miele, Mikhael Bechelany

Gelatin is a biodegradable biopolymer obtained by collagen denaturation, which shows poor mechanical properties. Hence, improving its mechanical properties is very essential towards the fabrication of efficient nontoxic material for biomedical applications. For this aim, various methods are employed using external fillers such as ceramics or bioglass. In this report, we introduce boron nitride (BN) reinforced gelatin as a new class of two dimensional biocompatible nanomaterials. The effect of the nanofiller on the mechanical behavior is analyzed. BN is efficiently exfoliated using the biopolymer gelatin as shown through Fourier transform infrared (FTIR) spectroscopy and X-ray diffraction (XRD). The exfoliated BN reinforces gelatin electrospun fibers, which results in an increase in the Young's modulus. The ESM are stable after the glutaraldehyde cross-linking and the fibrous morphology is preserved. The cross-linked gelatin/BN ESM is highly bioactive in forming bone like hydroxyapatite as shown by scanning electron microscopy. Due to their enhanced mineralization ability, the cross-linked ESM have been tested on human bone cells (HOS osteosarcoma cell line). The cell attachment, proliferation and biocompatibility results show that the ESM are nontoxic and biodegradable. The analysis of osteoblast gene expression and the measurement of alkaline phosphatase activity confirm that these materials are suitable for bone tissue engineering.



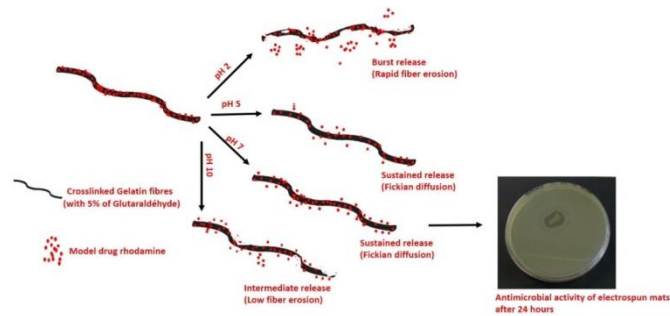
Novel biocompatible electrospun gelatin fibers mat with antibiotic drug delivery properties

Journal of Materials Chemistry B 4 (2016) 1134-1141

Collaboration: IRCM (France)

Involved PNM researchers: Mikhael Bechelany

The aim of this study was to synthesize stable gelatin electrospun mats (ESM) (cross-linked by Glutaraldehyde (GTA) vapors) with tunable drug release properties using pH as a stimuli. Gelatin ESM loaded with rhodamine as a model drug was first synthesized. The *in vitro* release of rhodamine was characterized to understand the mechanisms of drug release and the effects of both cross-linker concentration and pH on the drug release. An optimal cross-linker concentration of 5 % was evidenced to provide ESM allowing both sustainable release of drugs at pH 7 and burst release at pH 2. The release profiles were then fitted with a power law model to describe the release kinetic. Chlorhexidine antibiotic drug was finally loaded into the optimal electrospun mat and its bactericidal activity was demonstrated against Gram-negative (*E. coli*) and Gram-positive (*S. epidermidis*) bacteria by agar diffusion tests. This material was shown to efficiently destroy bacterial biofilms and prevent bacterial growth within a short time (3 h), while maintaining its antibacterial activity up to at least 72 h. This study provides a promising material, which could treat infected sites and prevent infections, with tunable drug releasing property using pH as a stimulus.



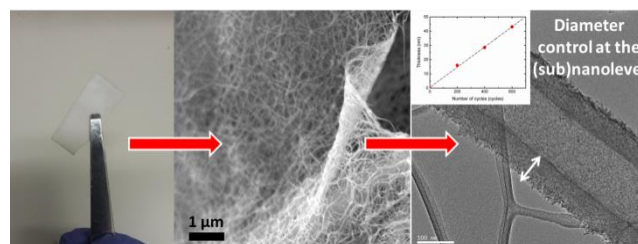
Novel and facile route for the synthesis of tunable Boron Nitride Nanotubes combining Atomic Layer Deposition and annealing processes

Advanced Materials Interfaces 5 (2018) 1800056

Collaboration: Adam Mickiewicz University in Poznan (Poland)

Involved PNM researchers: David Cornu, Philippe Miele, Mikhael Bechelany

The synthesis of tunable boron nitride nanotubes is the subject of intense research because of their potential applications in various fields, from smart textile materials to emerging environmental technologies. However, the preparation of these nanomaterials remains extremely challenging. Herein, we report proof-of-concept results on the scalable synthesis of boron nitride nanotubes with tunable dimensions. Combining atomic layer deposition (ALD) of boron nitride on carbon nanofibers template supports and successive annealing steps at high temperature, BN nanotubes with controllable properties have been prepared. The successive annealing steps enable the crystallization of BN and the combustion of the initial carbon supports. The self-limiting nature of the ALD process allows for the scalable coating of large scale carbon fibers matrix. High-resolution TEM measurements demonstrated the exquisite dimensions control at the nanoscale and the presence of crystalline BN. The proof-of-concept results presented allow for independent control of the inner and external diameter dimensions, opening up unique possibilities for the precise engineering of BN nanotubes properties. The nanotubes present good mechanical properties, are easy to handle, and the assessment of their sorption properties showed that they absorb up to 110 times their own weight in oils while repelling water, which opens prospects for water purification.



Electrospun fibers as electrode building blocks for electrocatalysis applicationsArticles:

Chemphyschem, 2018, DOI: 10.1002/cphc.201700447

Catalysts, 2017, DOI: 10.3390/catal7010031

J. Electrochem. Soc., 2017, Doi: 10.1149/2.0571702jes

ChemElectroChem, 2016, DOI: 10.1002/celec.201500537

Chempluschem, 2015, DOI: 10.1002/cplu.201402324

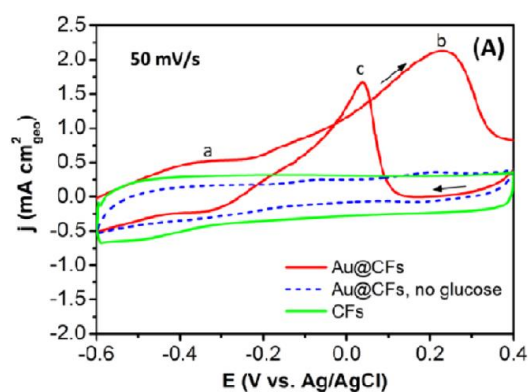
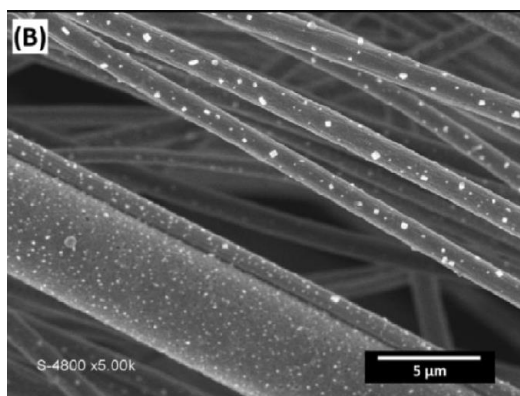
J. Phys. Chem. C, 2015, DOI: 10.1021/acs.jpcc.5b04352

Chemelectrochem, 2014, DOI: 10.1002/celec.201402142

Collaboration: Y. Holade, S. Tingry (IP2), Ch. Laurent, C. Estournes (CIRIMAT, Univ Paul Sabatier, Toulouse), E. Katz (Clarkson University, US), K. Servat, TW. Napporn, KB. Kokoh (IC2MP, Univ Poitiers)

Involved PNM researcher: David Cornu

The design and manufacture of efficient and selective electrodes is a crucial scientific challenge to support the development of sustainable energy, regardless of the fuel it uses: as simple as hydrogen or more complex as biomass wastes and electrochemical "cogeneration" processes that simultaneously produce electricity, heat and fuels. These interdisciplinary researches require synergistic efforts in electrochemistry and materials science. To this end, we are exploring the exceptional capabilities of electrodes developed from electrospun fibers for electrocatalysis.



Copper hexacyanoferrate functionalized single-walled carbon nanotubes for selective cesium extraction

New Journal of Chemistry 41(15) 41, 7705-7713, 2017 DOI: 10.1039/c7nj00879a

Collaboration: ICSM Marcoule; L2C Montpellier; ENSI Tunis

Involved PNM researcher: Julien Cambedouzou

Single-walled carbon nanotubes (SWCNTs) are functionalized with copper hexacyanoferrate (CuHCF) nanoparticles to prepare solid substrates for sorption of cesium ions (Cs^+) from liquid outflows. The high mechanical resistance and large electrical conductivity of SWCNTs are associated with the ability of CuHCF nanoparticles to selectively complex Cs^+ ions in order to achieve membrane-like buckypapers presenting high loading capacity of cesium. The materials are thoroughly characterized using electron microscopy, Raman scattering, X-ray photoelectron spectroscopy and thermogravimetric analyses. Cs sorption isotherms are plotted after having measured the Cs^+ concentration by liquid phase ionic chromatography in the solution before and after exposure to the materials. It is found that the total sorption capacity of the material reaches 230 mg g^{-1} , and that about one third of the sorbed Cs (80 mg g^{-1}) is selectively complexed in the CuHCF nanoparticles grafted on SWCNTs. The quantification of Cs^+ ions on different sorption sites is made for the first time, and the high sorption rates open interesting outlooks in the integration of such materials in devices for the controlled sorption and desorption of these ions.

