

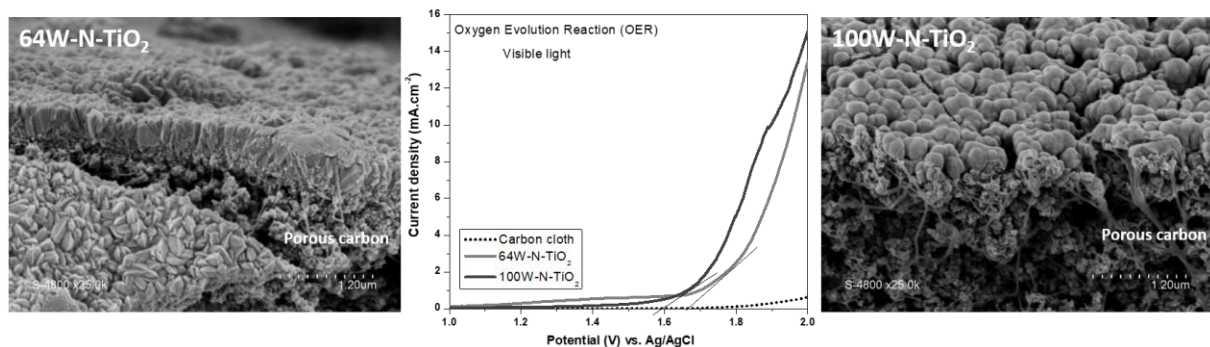
Optimization of N-doped TiO₂ Multifunctional Thin Layers by Low Frequency PECVD Process

Journal of the European Ceramic Society, 37(16) (2017) 5289-5303.

Collaboration: LCPM (Université Libanaise)

Involved PNM researchers: Stéphanie Roualdès, Vincent Rouessac

Direct coupling of separation and photocatalytic degradation using titania-based membranes is an attractive approach intensively investigated in air or water treatment devices. Such approach involving multifunctional titania layers can also be envisaged for other applications and in particular for H₂ production from solar light by water splitting, which is precisely the ultimate application aimed in this study. A one-step low-frequency Plasma Enhanced Chemical Vapor Deposition (PECVD) process, operating at temperature as low as 350°C, has been implemented to prepare single-oriented pure and N-doped anatase films. The layers have been synthesized using titanium isopropoxide as a precursor, and NH₃ as a doping agent. Optimized PECVD conditions have enabled to obtain homogeneous micro-columnar porous thin films with thicknesses close to 500 nm. Depth profiling XPS analyses have proved the nitrogen incorporation into TiO₂ lattice after ammonia introduction in the deposition chamber. As another proof of N-doping, Raman and XRD peaks shifting have been observed. Such thin films have been demonstrated as efficient photocatalytic materials which activity region can be tailored from UV to visible region by adjusting the proportion of doping agent in the plasma phase. Due to their microstructural and photocatalytic properties, the prepared thin layers should have an interest as anode materials in solar water splitting cells.

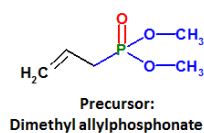


Phosphonic acid-based membranes as proton conductors prepared by a pulsed plasma enhanced chemical vapor deposition technique

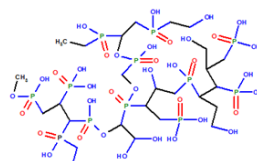
Thin Solid Films, 660 (2018) 506-515.

Involved PNM researchers: Stéphanie Roualdès, Vincent Rouessac

Among the electrolyte membranes for proton conduction in hydrogen production systems and fuel cells, phosphonic acid-based membranes are promising because of their advantage as good proton conductors in anhydrous medium which allows their use in systems operating at high temperature (80-150 °C) which is not the case of sulfonic acid-based ones such as the well-known Nafion[®] commercial membrane. In this study, a plasma polymerization process using a continuous or pulsed glow discharge has been implemented to prepare original Plasma Enhanced Chemical Vapor Deposition (PECVD also called plasma polymerization) phosphonic acid-based membranes using dimethyl allylphosphonate as a single precursor. The structural and proton transport properties of such membranes have been correlated with the plasma parameters in the deposition of films. The membranes prepared by pulsed plasma deposition method exhibit better proton conductivity than that of membranes prepared by continuous plasma deposition method, in direct relation with their specific structural properties. The optimal plasma membrane, obtained in a pulsed 100 W plasma discharge, has shown specific resistance to proton conduction twice less than Nafion[®] 212 one which is great for the final applications of such membrane.

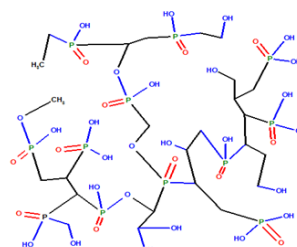


Plasma polymerization with
continuous plasma discharge



Highly cross-linked phosphonic acid-based polymer

Plasma polymerization using a
pulsed plasma discharge



Low cross-linked phosphonic acid-based polymer

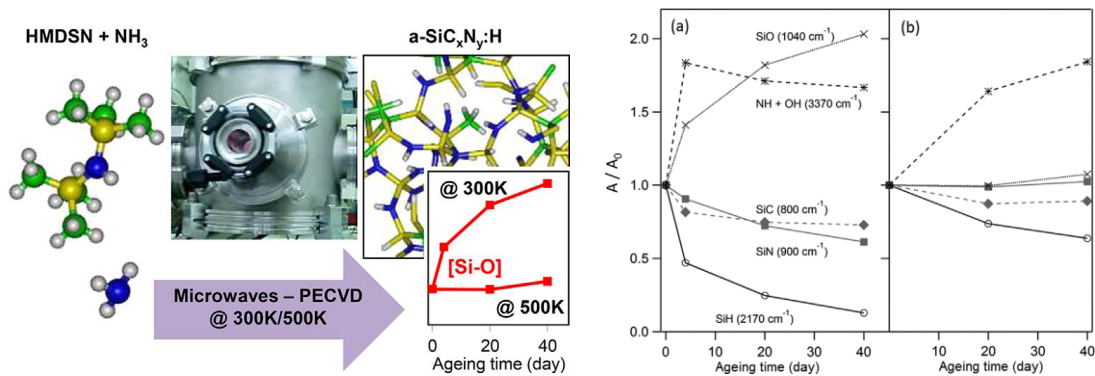
Microwave PECVD silicon carbonitride thin films: A FTIR and ellipsoporosimetry study

Plasma Processes and Polymers, 13 (2016) 258-265.

Collaboration: MCP cluster in DM3

Involved PNM researchers: Stéphanie Roualdès, Vincent Rouessac

Amorphous non-oxide $a\text{-SiC}_x\text{N}_y\text{:H}$ thin films have been synthesized at 300 or 500K from an Ar/HMDSN/ NH_3 gas mixture in a lab-scale microwaves PECVD reactor. These thin films have been characterized by FTIR spectroscopy and spectroscopic ellipsometry coupled with gas adsorption, in order to evidence the influence of PECVD synthesis conditions on the materials composition and microstructure. Deposition at high temperature (500 K) was found to yield more inorganic and more compact films in comparison with those obtained at room temperature. In addition, when considering long term aging at room temperature for more than 1 month, the films synthesized at high temperature were found to be more stable toward oxidation in (humid) air.

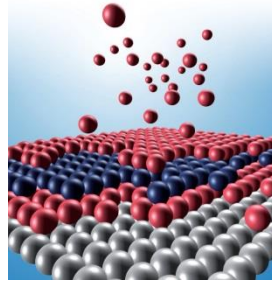


Atomic Layer Deposition of Nanostructured Materials for Energy and Environmental Applications: review

Advanced Materials 24 (2012) 1017-1032

Involved PNM researchers: Mikhael Bechelany

Atomic Layer Deposition (ALD) is a thin film technology that in the past two decades rapidly developed from a niche technology to an established method. It proved to be a key technology for the surface modification and the fabrication of complex nanostructured materials. In this progress report, after a short introduction to ALD and its chemistry, the versatility of the technique for the fabrication of novel functional materials will be discussed. Selected examples, focused on their use for the engineering of nanostructures targeting applications in energy conversion and storage, and on environmental issues, will be discussed. Finally, the challenges that ALD is now facing in terms of materials fabrication and processing will be also tackled.



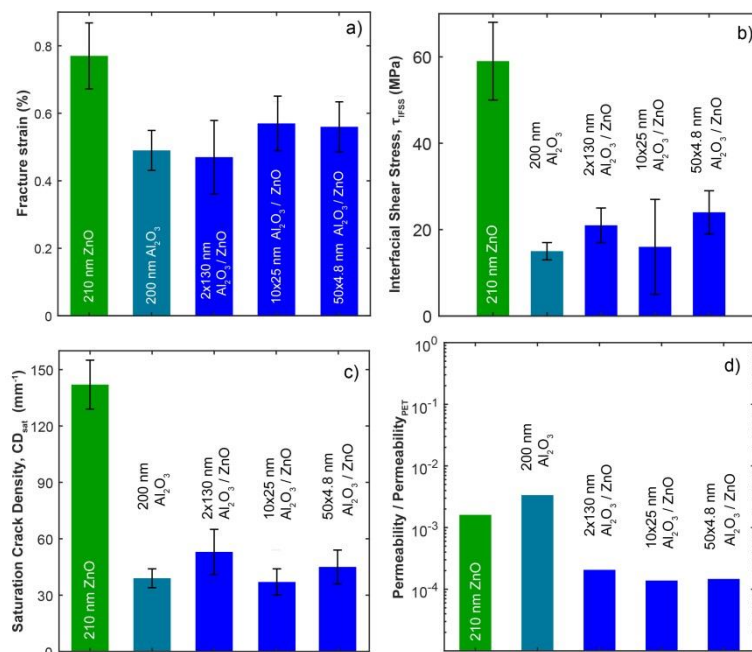
Fracture mechanics and oxygen gas barrier properties of $\text{Al}_2\text{O}_3/\text{ZnO}$ nanolaminates deposited by atomic layer deposition

Nanomaterials, 9 (2019) 88

Collaboration: EMPA (Switzerland)

Involved PNM researchers: Philippe Miele, Mikhael Bechelany

Rapid progress in the performance of organic devices has increased the demand for advances in the technology of thin-film permeation barriers and understanding the failure mechanisms of these material systems. Herein, we report the extensive study of mechanical and gas barrier properties of $\text{Al}_2\text{O}_3/\text{ZnO}$ nanolaminates films prepared on organic substrates by atomic layer deposition (ALD). Nanolaminates of $\text{Al}_2\text{O}_3/\text{ZnO}$ and single compound films of around 250 nm thickness were deposited on polyethylene terephthalate (PET) foils by ALD at 90 °C using trimethylaluminium (TMA) and diethylzinc (DEZ) as precursors and H_2O as the co-reactant.. STEM analysis of the nanolaminate structure revealed that steady-state film growth on PET is achieved after about 60 ALD cycles. Uniaxial tensile strain experiments revealed superior fracture and adhesive properties of compact ZnO films versus the compact Al_2O_3 film as well as versus their nanolaminates. The superior mechanical performance of ZnO was linked to the absence of a roughly 500 to 900 nm thick sub-surface growth observed for single Al_2O_3 films as well as for the Al_2O_3 initial layer the nanolaminates. In contrast, the gas permeability of the nanolaminate coatings was measured to be an order of magnitude less than their constituting compact oxides, which opens prospects for their applications as gas barrier layers for organic electronics, food and drug packaging industries. Direct interdependency between the gas barrier and the mechanical properties was not established enabling independent tailoring of these properties for mechanically rigid and impermeable thin film coatings.

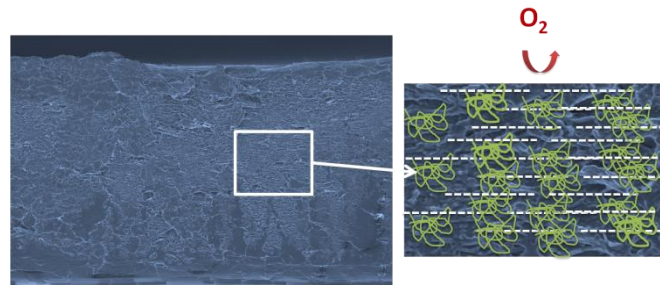


Graphene-like BN/Gelatin nanobiocomposites for gas barrier applications

Nanoscale 7 (2015) 613-618

Involvement PNM researchers: Philippe Miele, Mikhael Bechelany

We report a simple, effective and green way for the fabrication of gelatin–graphene-like BN nanocomposites for gas barrier applications. The reinforcement effect of graphene-like BN on the gelatin properties is discussed. The obtained graphene-like BN nanocomposites show good dispersion in the gelatin matrix and remarkable capability to improve the crystallinity and the barrier properties of gelatin. The barrier properties of gelatin/BN nanocomposites have been enhanced by a factor of 500 at 2 bar comparing to a gelatin film without graphene-like BN. The greatly improved performance and the high stability of these nanocomposites induce exciting materials for their implantation in gas barrier applications.

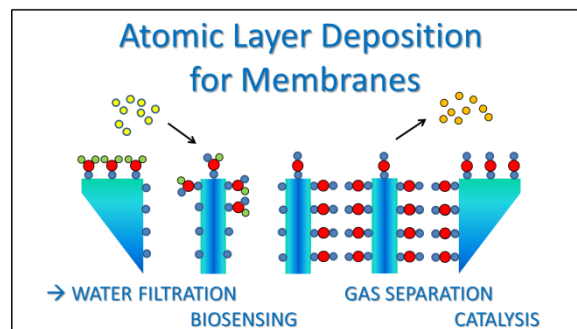


Atomic Layer Deposition for Membranes: Basics, Challenges and Opportunities

Chemistry of Materials 30 (2018) 7368-7390

Involved PNM researchers: Mikhael Bechelany

Atomic layer deposition (ALD) is a technology offering the possibility to prepare thin films of high quality materials on high aspect ratio substrates with precise thickness control, high uniformity and excellent conformality, a unique capability. Therefore, this route is particularly suited for the structural modification and pore tailoring of synthetic membranes. ALD coatings have been prepared on a wide variety of membrane substrates, from inorganic templated supports to porous polymers. This minireview aims to provide an extensive summary of the advances of ALD applied to membranes. A selected list of studies will be used to illustrate how the ALD route can be implemented to improve the operational performance of different inorganic, organic, hybrid or composite membranes. Furthermore, the challenges and opportunities of the route for this specific membrane application are also discussed. This work comprehensively shows the benefits of ALD and its application in various facets of membranes and membrane associated engineering processes, and will help exploiting the numerous prospects of this emerging and growing field.

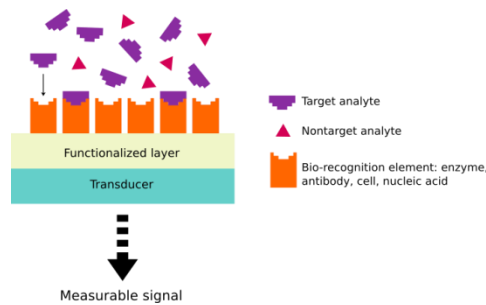


Atomic Layer Deposition for Biosensing Applications

Biosensors and Bioelectronics 122 (2018) 147-159

Involved PNM researchers: Mikhael Bechelany

Atomic layer deposition (ALD) is a thin film deposition technique currently used in various nanofabrication processes for microelectronic applications. The ability to coat high aspect ratio structures with a wide range of materials, the excellent conformality, and the exquisite thickness control have made ALD an essential tool for the fabrication of many devices, including biosensors. This mini-review aims to provide a summary of the different ways ALD has been used to prepare biosensor devices. The materials that have been deposited by ALD, the use of the ALD layers prepared and the different types of biosensors fabricated are presented. A selected list of studies will be used to illustrate how the ALD route can be implemented to improve the operational performance of biosensors. This work comprehensively shows the benefits of ALD and its application in various facets of biosensing and will help in exploiting the numerous prospects of this emerging and growing field.



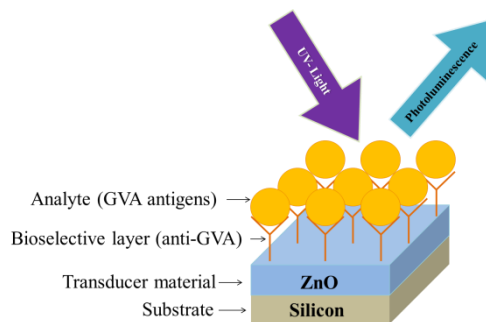
ZnO Films Formed by Atomic Layer Deposition as an Optical Biosensor Platform for the Detection of Grapevine Virus A-type Proteins

Biosensors and Bioelectronics 92 (2017) 763–769

Collaboration: Odessa National I. I. Mechnikov University (Ukraine)

Involved PNM researchers: Mikhael Bechelany

Novel sensitive optical biosensor for the determination of Grapevine virus A-type (GVA) proteins (GVA-antigens) has been designed. This biosensor was based on thin films of Zinc oxide (ZnO) deposited by atomic layer deposition (ALD). The ZnO-based films have demonstrated favorable surface-structural properties for the direct immobilization of antibodies against GVA-antigens in order to form a biosensitive layer sensitive to GVA-antigens. The immobilization was confirmed by intensity changes in the main near band emission (NBE) peak of ZnO and by the formation of intense photoluminescence band, discovered in the visible range around 425 nm, caused by the immobilized proteins. The GVA-antigen detection was performed by the evaluation of changes and behavior of corresponding luminescence band. The sensitivity of as-formed label-free biosensor towards the GVA-antigens was determined in the range from 1 pg/ml to 10 ng/ml, in addition, the selectivity of biosensor was evaluated.



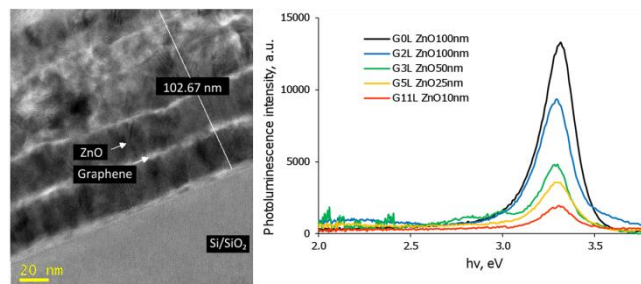
Tuning of Structural and Optical Properties of Graphene/ZnO Nanolaminates

Journal of Physical Chemistry C 120 (2016) 23716–23725

Collaboration: University of Latvia (Latvia) and Adam Mickiewicz University (Poland)

Involved PNM researchers: Mikhael Bechelany

Zinc Oxide (ZnO) and graphene (G) have been extensively studied because of their unique physical properties. Here, Graphene-Zinc Oxide (G/ZnO) nanolaminates were fabricated, respectively, by chemical vapor deposition and low temperature atomic layer deposition technique. The number of obtained G/ZnO layers was tuned from 1 to 11 with a total thickness of 100 nm for all prepared nanolaminates. The structure, optical properties and interaction between G and ZnO were studied by X-ray methods, TEM, AFM, Raman and optical spectroscopy. The obtained results were interpreted and analysed taking into account strain and charge effects of graphene in G/ZnO nanostructures. We demonstrate that the bottom graphene used as a substrate stimulated the formation of ZnO crystalline structure. *n*-doping of graphene caused by charge transfer from ZnO to graphene has been detected by blue-shift of G-band of Raman spectra of the nanolaminates. ZnO photoluminescence intensity was found to be dependent on the number of graphene layers in G/ZnO nanolaminate. *n*-doping of graphene could be tailored by controlling the construction of the G/ZnO nanolaminates for variety of applications such as, for example, selective adsorption of the target molecules on graphene surface. Thus, G/ZnO nanolaminates may find applications in optical, bio- and chemical sensors.



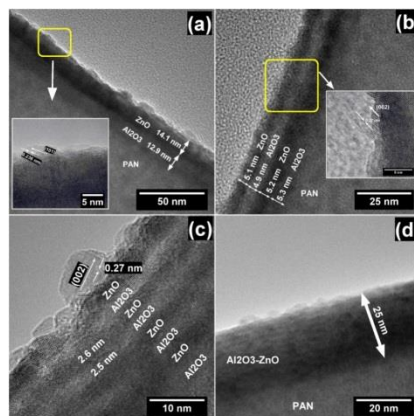
Enhancement of electronic and optical properties of ZnO/Al₂O₃ nanolaminate coated electrospun nanofibers

Journal of Physical Chemistry C 120 (2016) 5124–5132

Collaboration: University of Latvia (Latvia) and Adam Mickiewicz University (Poland)

Involved PNM researchers: Mikhael Bechelany

Nanolaminates are new class of promising nanomaterials with outstanding properties. Here we explored on the tuning of structural properties and the enhancement of electronic and optical properties of 1D PAN ZnO/Al₂O₃ nanolaminates designed by Atomic Layer Deposition (ALD) and electrospinning. The influence of ZnO/Al₂O₃ bilayer thicknesses on the fundamental properties of 1D PAN ZnO/Al₂O₃ nanolaminates has been investigated. Due to the quantum confinement effect, the shift of XPS peaks to higher energies has been observed. Work function of Al₂O₃ was mostly independent of the bilayers number whereas the ZnO work function decreased with an increase of the bilayer number. Photoluminescence of the 1D PAN ZnO/Al₂O₃ nanolaminates corresponded to emission bands in ZnO nanolayers. Due to quantum confinement and surface band bending, no excitonic peaks were observed. The defect emission band was affected by the band bending and defect concentration. The enhanced photoluminescence of the 1D PAN ZnO/Al₂O₃ nanolaminates allows applications in optical (bio)sensing field.

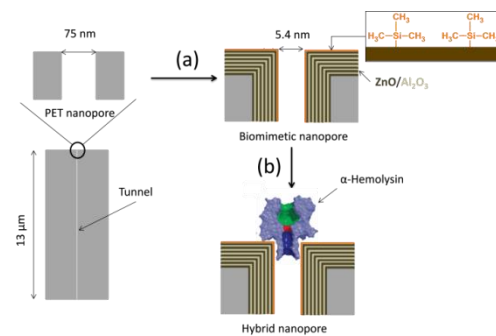


Polynucleotides slow translocation and discrimination through α -hemolysin inside a single track-etched nanopore designed by atomic layer deposition

Nanoscale 5 (2013) 9582 - 9586

Involved PNM researchers: Mikhael Bechelany

We report a hybrid biological/artificial nanopore by the direct insertion of non-modified α -hemolysin at the entrance of a high ratio (length/diameter) biomimetic nanopore. In this robust hybrid system, the protein exhibits the same polynucleotide discrimination properties than in biological membrane and the polynucleotide dwell time is strongly increased. This nanopore is very promising for DNA sequencing applications where the high DNA translocation velocity and the fragility of the support are the main bottlenecks.

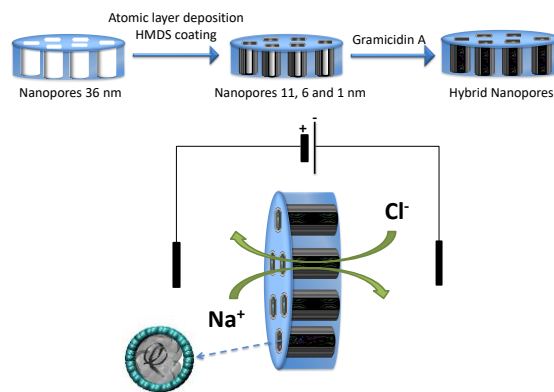


Enhanced Ionic Transport Mechanism by Gramicidin A Confined Inside Nanopores Tuned by Atomic Layer Deposition

Journal of Physical Chemistry C 117 (2013) 15306-15315

Involved PNM researchers: Mikhael Bechelany

The confinement and the understanding of ion transport through ionic channels when they are confined inside solid-state nanopores smaller than 10 nm remains a challenge. Here we report on the fabrication of biomimetic nanopores with high length (5 μm)/ diameter (smaller than 10 nm) ratio obtained using both track etched technique and atomic layer deposition on flexible membranes. These membranes present uniform hydrophobic nanopores with a low roughness inside the pores. Gramicidin A is then confined inside nanopores (diameter 10.6, 5.7 and ~ 2 nm) leading to NaCl ionic transport mechanism through a hybrid nanopore similar to the biological ones especially for small diameter (5.7 and ~ 2 nm).



Novel membranes made of exfoliated 2D nanosheets

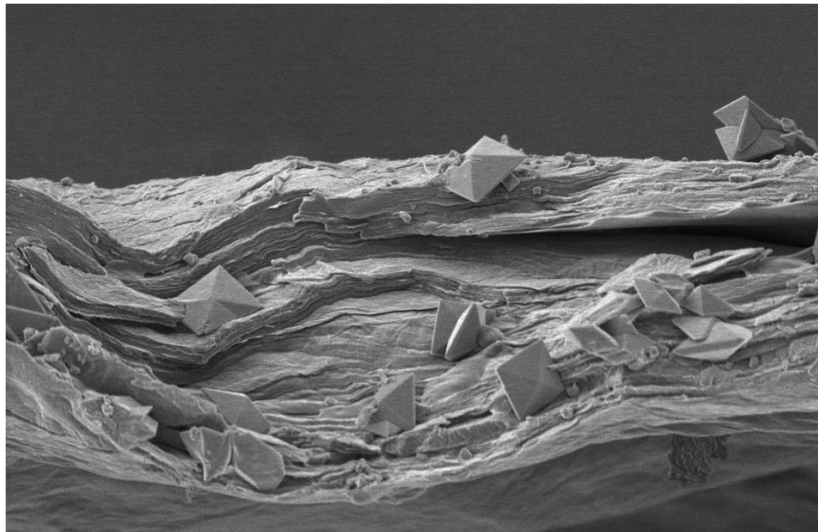
Articles:

Advanced Energy Materials, 4, 2014

Collaboration: Nicolao Onofrio (PolyU Hong Kong)

Involved PNM researchers: Damien Voiry, Mikhael Bechelany, Chrystelle Salameh, Philippe Miele

2D materials thanks to their high surface area have natural advantages as atomically thin membranes. They have recently been explored as barrier or membranes for both energy harvesting and for sieving molecules. The atomic thickness of 2D materials enables high flux while the presence of nanopores within the structures or between the flakes can theoretically lead to highly selective sieving. Our group aim to investigate the performance of 2D membranes made of exfoliated layered materials.



Microwaved reduced graphene oxide

Articles:

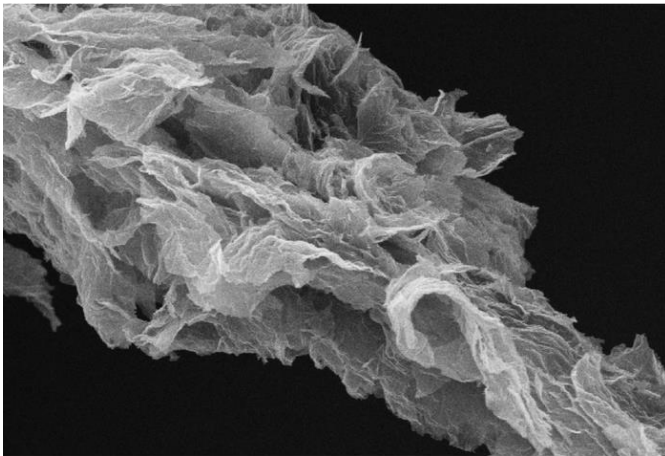
Science, 2016, 353, 1413-1416

Collaboration: Manish Chhowalla, University of Cambridge (UK)

Involved PNM researchers: Damien Voiry

Graphene oxide (GO) is the oxidized form of graphene. GO is interesting because it can be prepared large scale from graphite and it is water-soluble that makes it easy to process. Unfortunately graphene oxide contains high density of oxygen functional groups that completely suppress the properties of graphene and therefore GO is insulating. GO can be converted to reduced graphene oxide (rGO) by annealing or chemical reactions but it remains largely defected and poorly crystalline. As a consequence the exceptional properties of graphene cannot be recovered. Our approach is based on the use of microwave to carry out the reduction of the GO nanosheets.

Microwaves were previously examined to reduce GO but, to our knowledge, the effect of arcing had not been explored. This method, published in *Science* in Sept. 2016, is unique as its can reduce graphene oxide and convert GO to a material that closely resembles to pristine defect-free graphene. Microwaved reduced graphene oxide (MWrGO) exhibits high crystallinity and remarkable electronic properties. Such high reduction of GO is typically achieved via heating at 2000-3000°C, which is considerably limiting. Using our method, this can be down in a microwave oven within few seconds and minimal input power.



Synthesis of exfoliated materials 2D materials via CVD and chemical exfoliation

Articles:

Nano Letter, 2011, 11, 5111

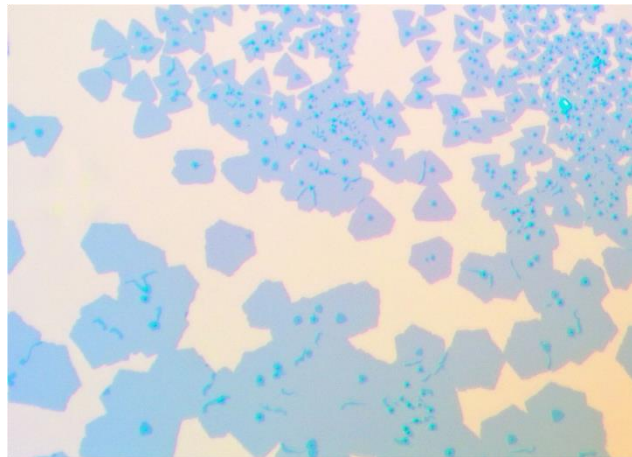
Nature Materials, 2016, 15, 1003–1009

ACS Nano, 2016, 10, 9899–9908

Collaboration: Daniel Kaplan, Picatinny Arsenal, NJ, USA

Involved PNM researchers: Damien Voiry

CVD growth and chemical exfoliation is a promising route to prepare large quantity of exfoliated 2D nanosheets. Yet it typically leads to materials with high density of defects and poor electronic and optical properties compared to CVD-grown and mechanically exfoliated samples. Chemical exfoliation routes include dispersion in organic solvents, surfactant-assisted dispersion in water or intercalation followed by exfoliation. The objective of our research is to develop methods in order to prepare chemically exfoliated 2D nanosheets and heterostructures with low concentration of defects, high crystallinity, uniform thickness and large dimension that can be used for energy conversion and opto-electronics.



Electrocatalysis from 2D materials and heterostructures

Articles:

Nature Materials, 2016, 15, 1003–1009

Nano Letters, 2013, 13, 6222

Nature Materials, 2013, 12, 850

Reviews:

Advanced Materials, 2016

Nature Reviews Chemistry, 2018, 2, 0105

Editorial:

ACS Nano, 2018, 12, 9635–9638

Collaboration: Nicoloas Onofrio (PolyU Hong Kong)

Involved PNM researchers: Damien Voiry

Exfoliated materials are highly regarded as potential candidates for the development of novel catalytic and electrocatalytic materials. 2D materials are typically used as active materials (doped graphene, transition metal dichalcogenides) or as support (graphene and reduced graphene oxide). Two-dimensional systems are fundamentally intriguing as their activity is largely influenced by the structure of the nanosheets, doping, alloying and strain. Our research aims to tackle the fundamental challenges for 1) understanding the origin of the electrocatalytic activity of 2D materials and 2) developing novel exfoliated materials and heterostructures with superior activity and made of earth-abundant elements.

