

# **Ion track polymer membrane, a versatile tool for research and applications**

**Marie-Claude DUBOIS-CLOCHARD**

Laboratoire des Solides Irradiés  
CEA2/CNRS/Ecole Polytechnique

FRANCE



# The site: the « Ecole Polytechnique » Engineer School

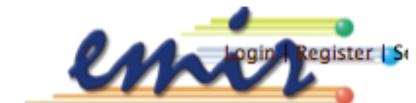
Plateau de Saclay (5km from CEA-Saclay site)



Laboratoire des solides Irradiés



EB facility  
2,5MeV



Grand Accélérateur National d'Ions Lourds



Mixt laboratory : CEA - Ecole Polytechnique – CNRS, UMR 7642

Management: Kees Van Der Beek

90 staff members – 6 teams among them XPnano : 8 permanent researchers

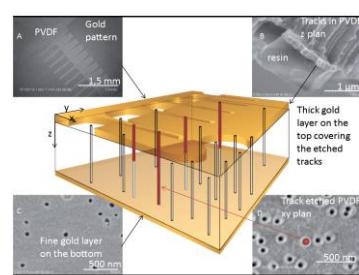


# Research Fields

## Energy



## Nanoelectronic

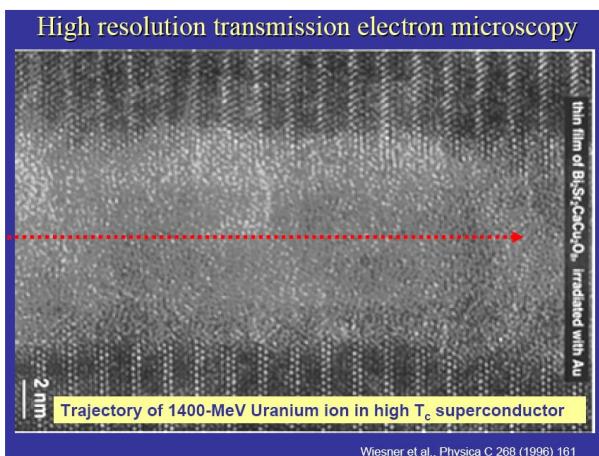
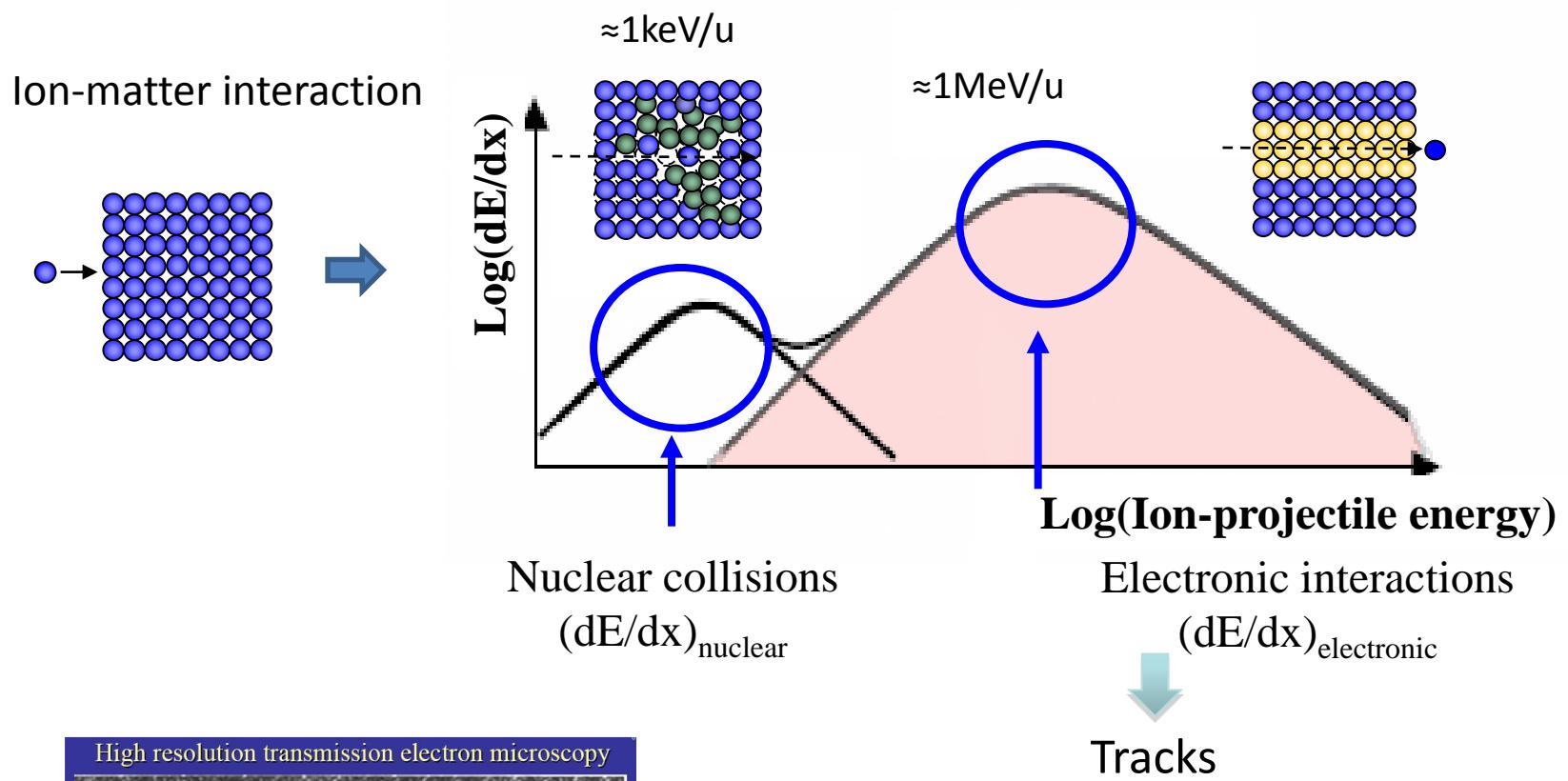


## Environment/Health



# Tracks formation

# Ion-matter interaction : Energy loss

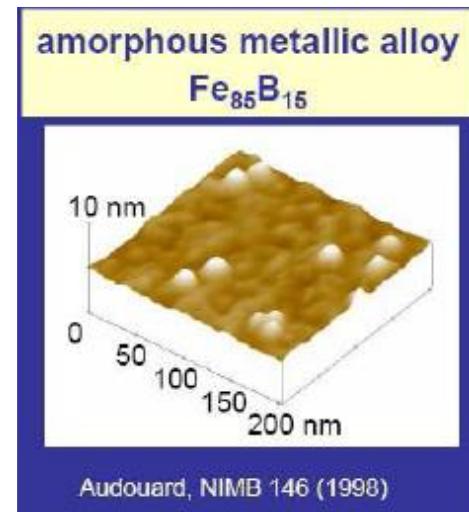
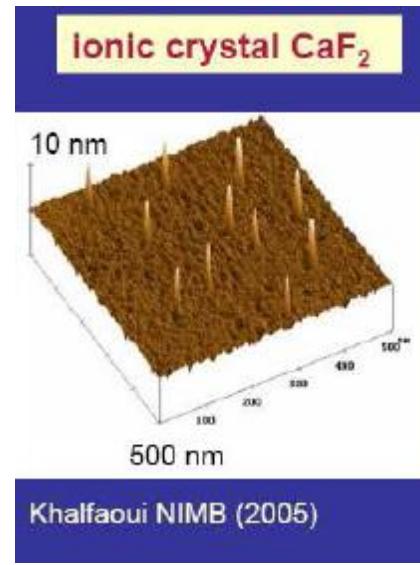
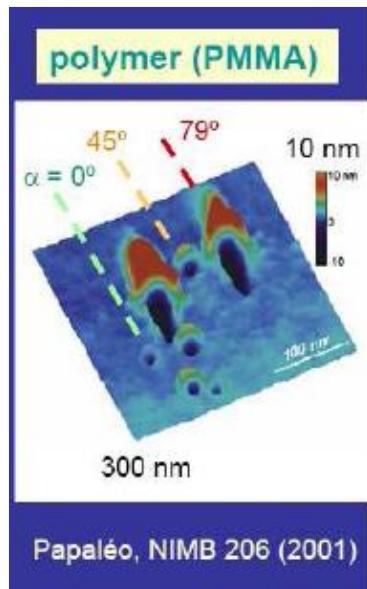


Deposited Energy per charged particle and per length unit

$$\left( \frac{dE}{dx} \right) \propto \frac{\text{keV}}{\text{nm}}$$

$$(dE/dx)_{\text{Total}} = (dE/dx)_{\text{nuclear}} + (dE/dx)_{\text{electronic}}$$

# Tracks at the surface of some solids



High sensitivity

Weak sensitivity

dE/dx  
threshold

## Insulators



Polymers



Oxydes



Spinsels

~1 keV/uma

## Semi-conductors



Amorphous Si



GeS, InP, Si<sub>1-x</sub>Ge<sub>x</sub>



Si, Ge

~20 keV/uma

## Metals



Amorphous alloys



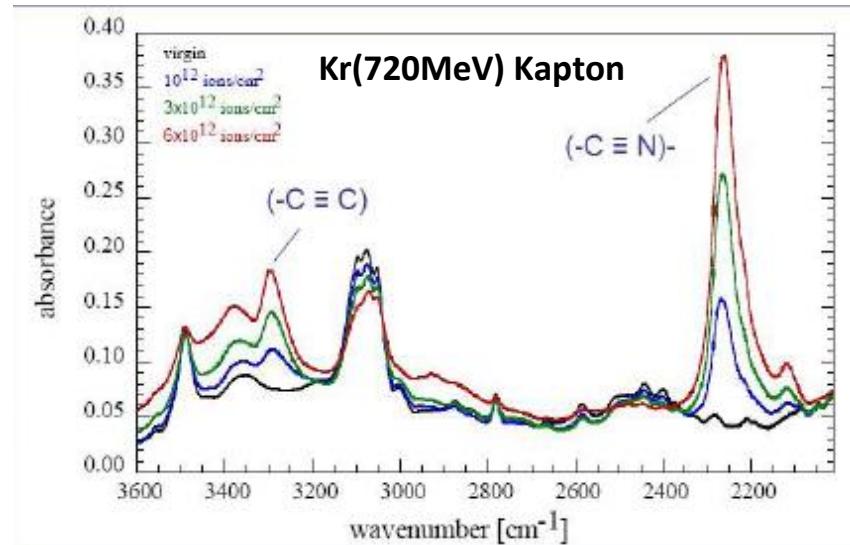
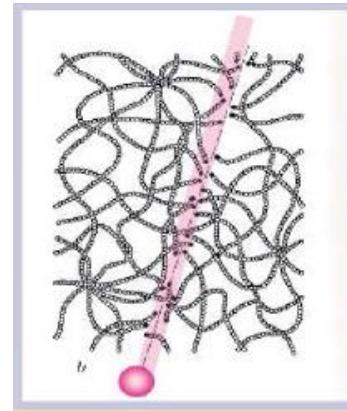
Fe, Bi, Ti, Co, Zr



Au, Cu, Ag ...

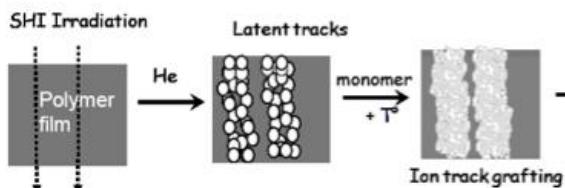
# Defaults in a latent track in a polymer film

- Chain scission
- Amorphization
- Gaz formation ( $\text{CO}_n$ ,  $\text{C}_n\text{H}_m$ , ...)
- Radical formation
- Cross-linking
- Multiple bonds (ex.  $\text{C}=\text{C}$ ,  $\text{C}\equiv\text{C}$ )

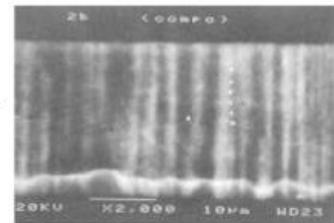


Steckenreiter et al, J. Polym. Sci. A37 (1999) 4318

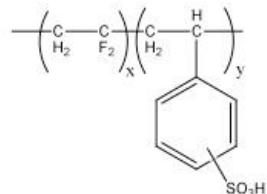
# Radiografted ion-track membranes for fuel cell: creation of proton conductive channels



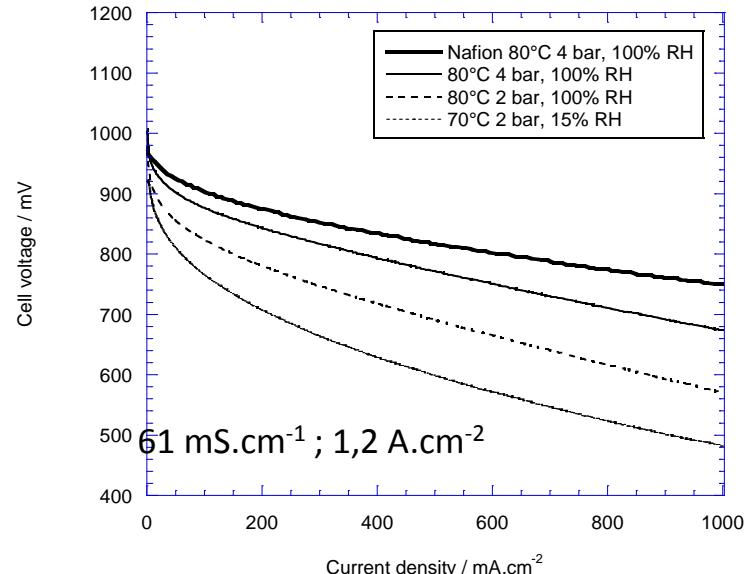
PVDF-g-PSSA  
10<sup>10</sup>ions/cm<sup>2</sup>Y=140wt%



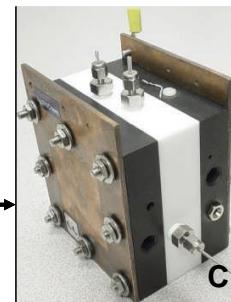
PVDF-g-PSA dopé au Césium  
5.10<sup>7</sup>ions/cm<sup>2</sup>Y=1.7wt%



Substitution électrophile



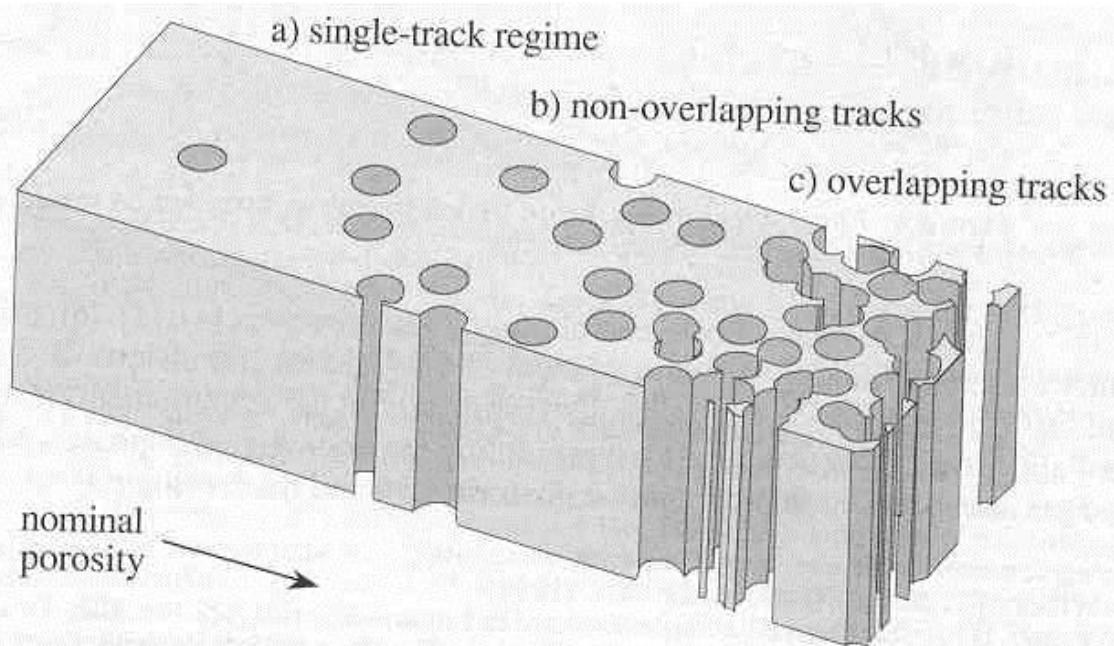
Identical efficiency as Nafion®



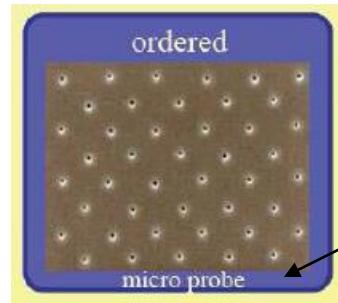
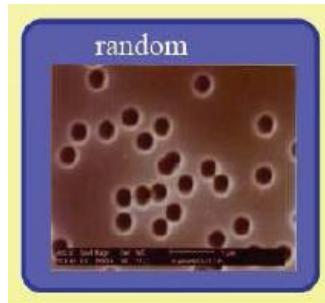
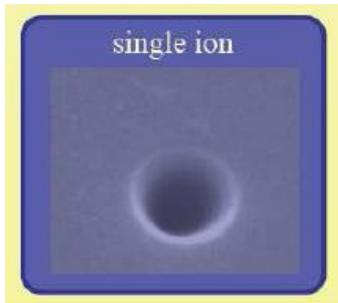
(A) PEMFC for automotive (ex: GENEPAC PSA-CEA), (B) Stack and (C) single cell.

Track revealing : track-etching

## 1srt application: membranes for filtration



Ions species: C... Xe... U Fluence:  $1\ldots 10^{13}$ ions/cm<sup>2</sup>

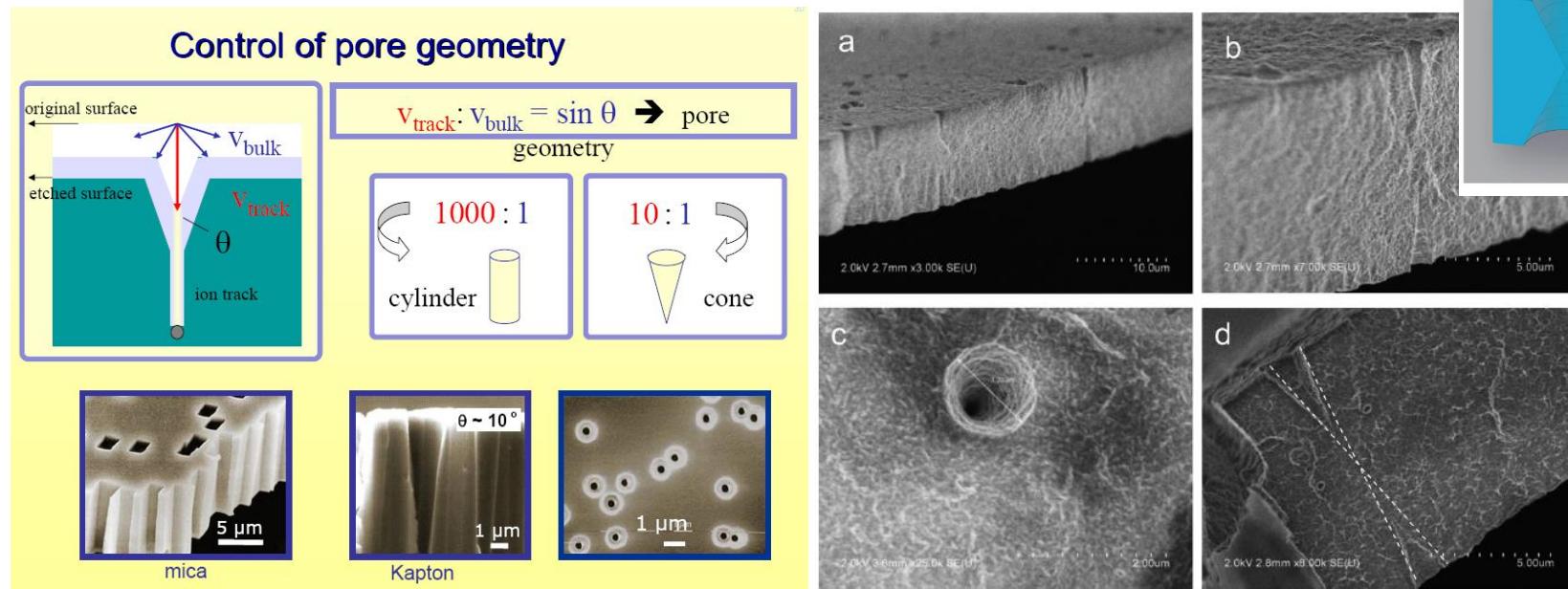


Commercial products (Nuclepore, Poretics)  
Millipore®, Whatman®...



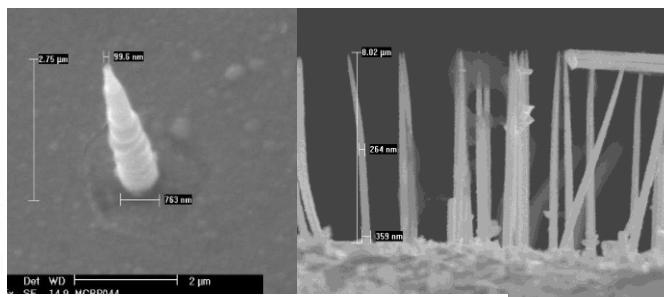
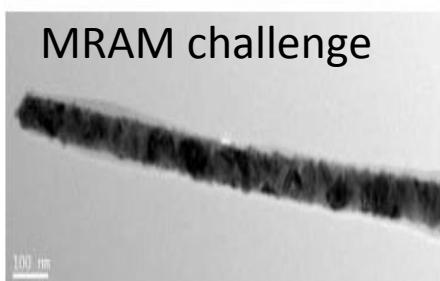
Developed at  
GSI - FAIR  
(Germany)

# Track etching

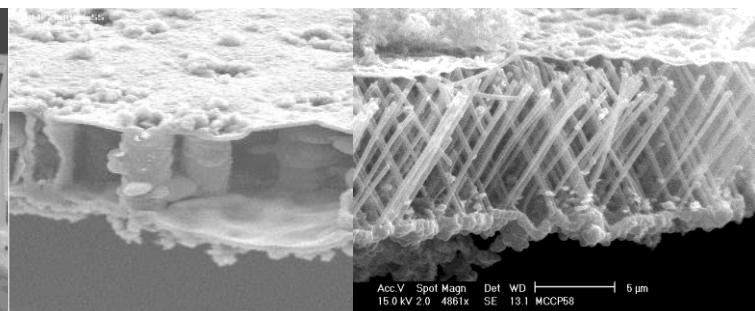


## Template synthesis

Cylindrical and conical metallic nanowires



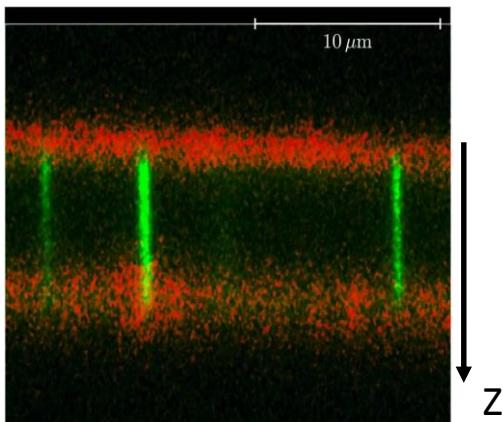
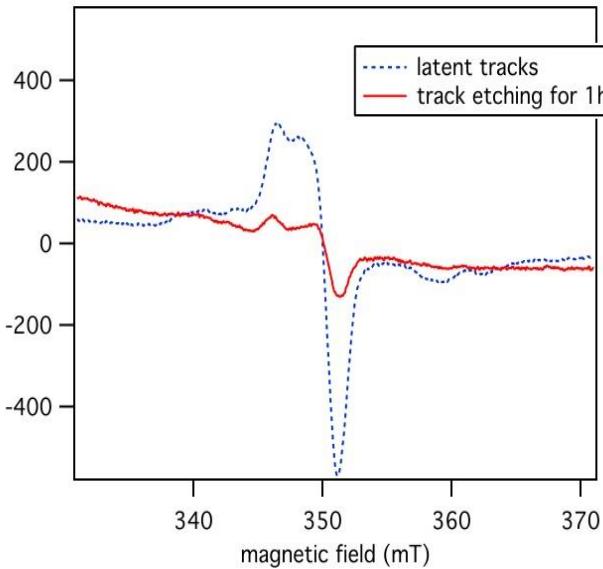
PPy nanotubes



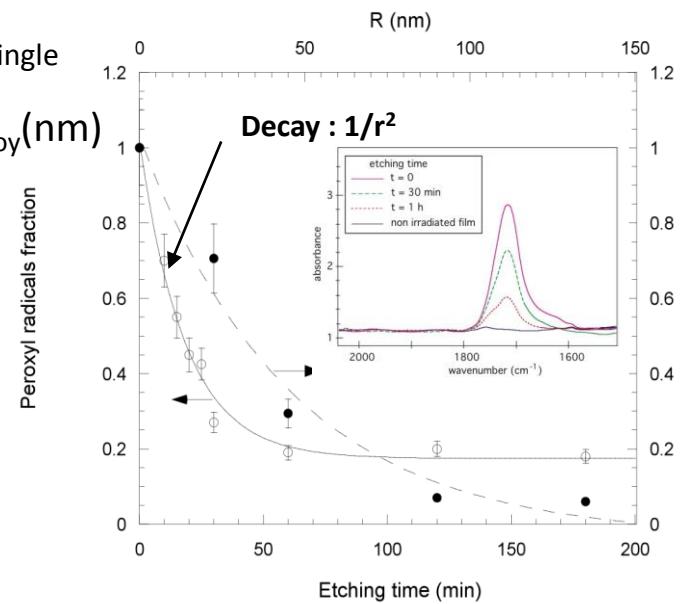
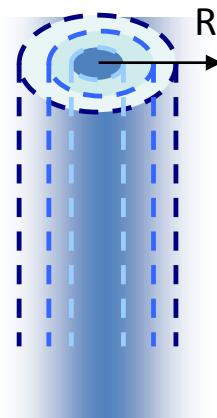
# Radiografted track-etched polymer membranes

# Radiation-induced grafting to chemically modify track-etched pore interior

Remanence of radicals after etching in PVDF



$f$  averaged and normalized to a single track



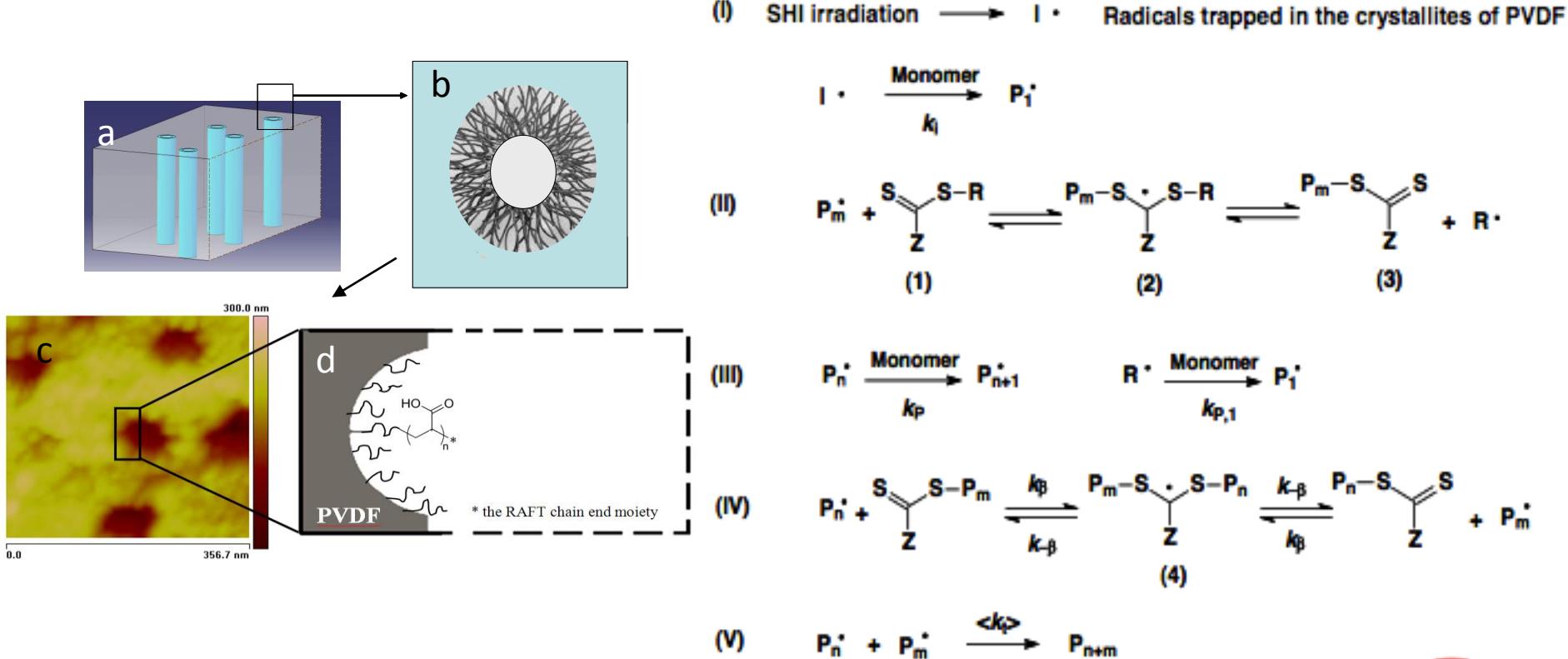
Images CLSM of PVDF-g-PAA membranes modified with ethylenediamine prior to radiografting.

Images are xz-plan (cross-section) re-building of xy-plan series. **Red:** Fluorescein isothiocyanate reacts with amine functions, i.e. oxydation **green:** Alexa Fluor R hydrazide reacts with carboxylic acids, i.e. poly(acrylic acid).

Cuscito, O. ; Clochard, M. C. ; Esnouf, S. ; Betz, N. ; Lairez, D. "Nanoporous PVDF membranes with selectively functionalized pores" NIM B-Beam Interactions With Materials And Atoms 2007, 265, 309-313.

# Controlled radical polymerization inside nanopores

Radiation induced RAFT mechanism



Contents lists available at SciVerse ScienceDirect

Journal of Membrane Science

journal homepage: [www.elsevier.com/locate/memsci](http://www.elsevier.com/locate/memsci)

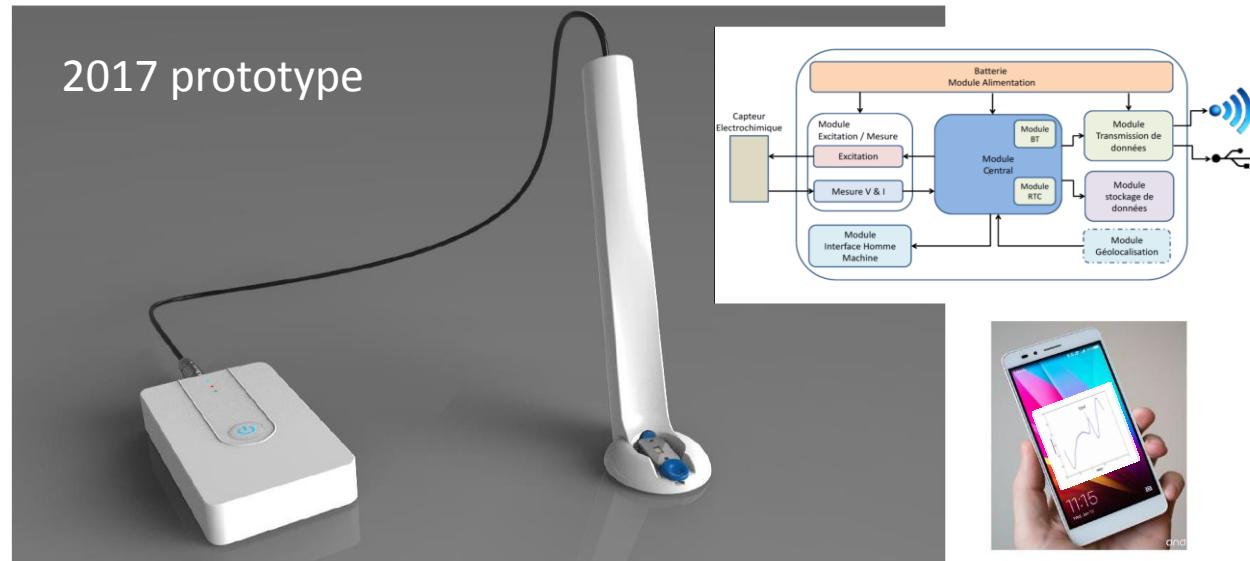


HACETTEPE  
ÜNİVERSİTESİ

# Technological transfer to industry of radiografted track-etched membranes:

## Early warning sensors for monitoring toxic metal ions

*CAPTOT Technology*

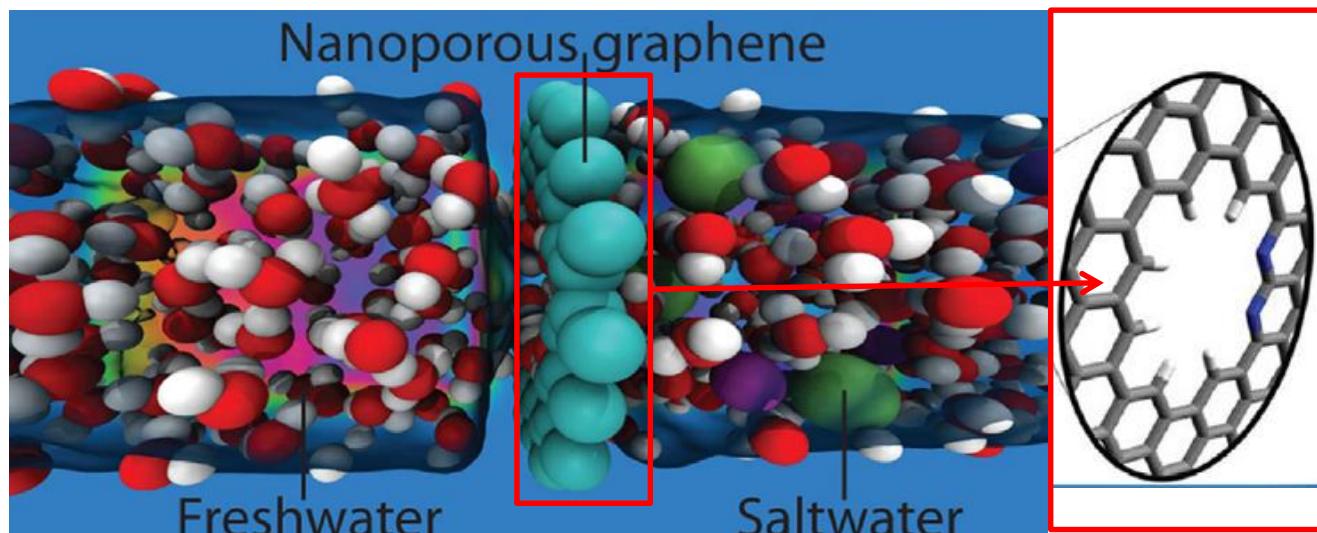


*Travis Wade receiving the award of « Salon Pollutec » ex-project ECOSISTEM*

# Perspectives with GSI-FAIR swift heavy ion beam facility

water desalination using nanoporous graphene

Simulations results



D. Cohen-Tanugi, J.C. Grossman, Nano Lett. 12 (2012) 3602.

Practical problem:  
how to handle such a thin and fragile nanoporous 2D membrane?

# Fabrication on hybrid membranes based on nanoporous graphene: A collaborative work

Materials Letters 184 (2016) 47–51



Contents lists available at ScienceDirect

Materials Letters

journal homepage: [www.elsevier.com/locate/matlet](http://www.elsevier.com/locate/matlet)



## Large area fabrication of self-standing nanoporous graphene-on-PMMA substrate



M.-C. Clochard<sup>a</sup>, G. Melilli<sup>a</sup>, G. Rizza<sup>a</sup>, B. Madon<sup>a</sup>, M. Alves<sup>a</sup>, J.-E. Wegrowe<sup>a</sup>,  
 M.-E. Toimil-Molares<sup>b</sup>, M. Christian<sup>c,d</sup>, L. Ortolani<sup>c</sup>, R. Rizzoli<sup>c</sup>, V. Morandi<sup>c</sup>, V. Palermo<sup>d</sup>,  
 S. Bianco<sup>e</sup>, F. Pirri<sup>e</sup>, M. Sangermano<sup>e,\*</sup>

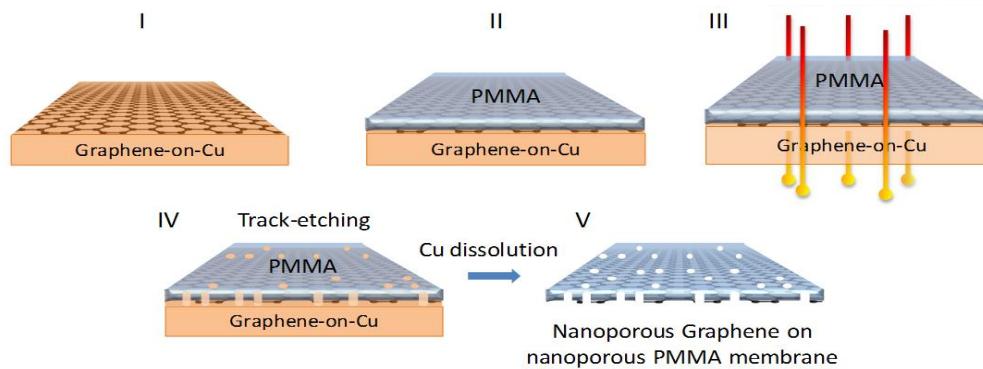
<sup>a</sup> Laboratoire des Solides Irradiés, CNRS, CEA-DRF-IRAMIS, Ecole Polytechnique, Université Paris-Saclay, Palaiseau Cedex, 91128 France

<sup>b</sup> Materials Research Department, GSI Helmholtz Centre for Heavy Ion Research, Planckstr. 1, Darmstadt, 64291 Germany

<sup>c</sup> CNR-IMM Sezione di Bologna, via Gobetti 101, Bologna, 40129 Italy

<sup>d</sup> CNR-ISOF, via Gobetti 101, Bologna, 40129 Italy

<sup>e</sup> Politecnico di Torino, Dipartimento di Scienza Applicata e Tecnologia, Corso Duca degli Abruzzi 24, Torino, 10129 Italy

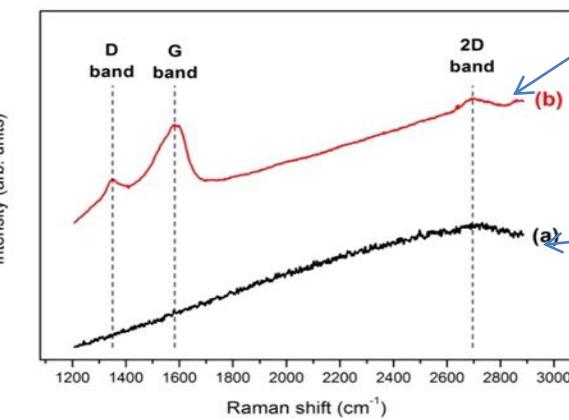
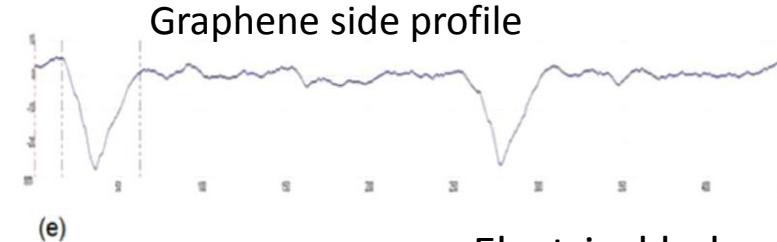
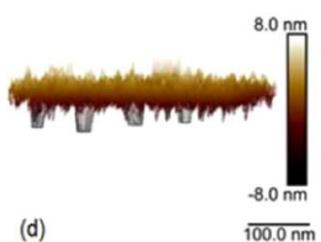
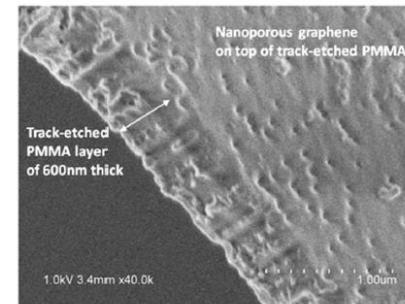
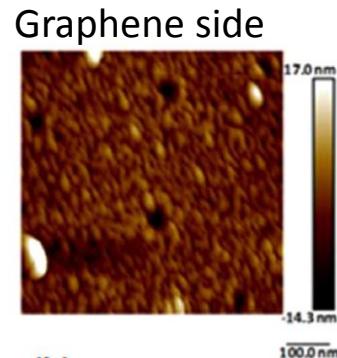
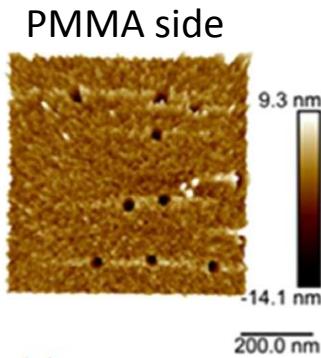


Irradiation platform

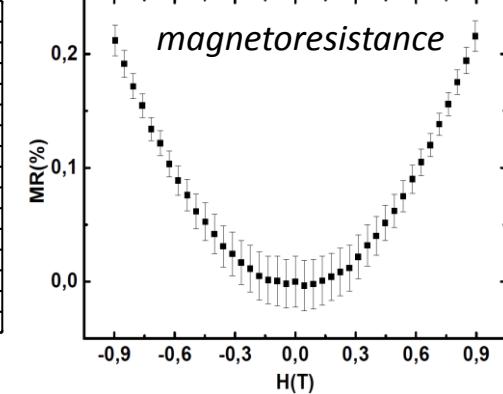
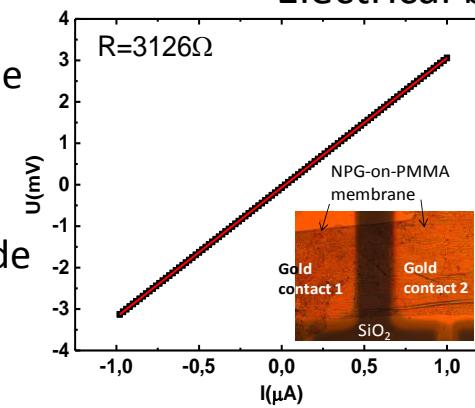
**GSI FAIR**  
GSI Helmholtzzentrum für Schwerionenforschung



# Characterization of nanoporous graphene-on-PMMA substrate



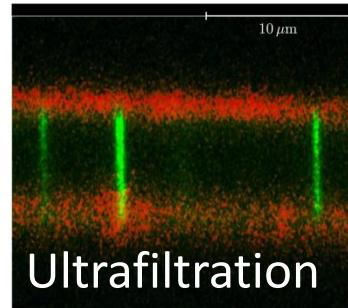
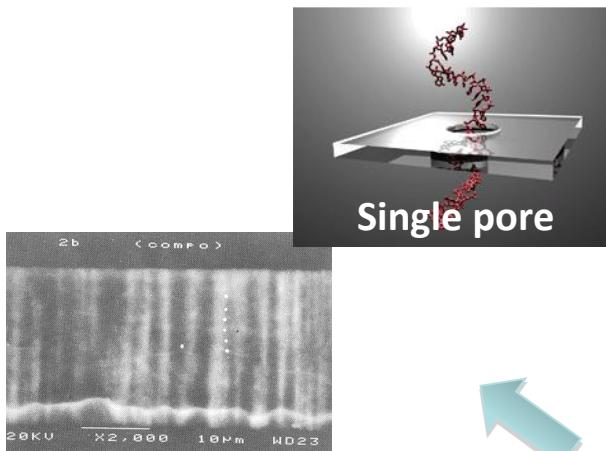
Graphene side  
PMMA side



... still lot of work to come up to a filtration system but feasibility is done !

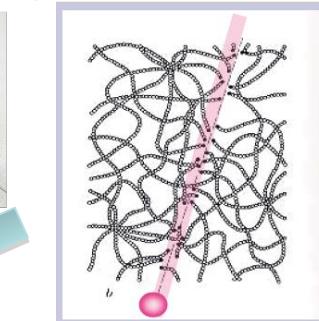
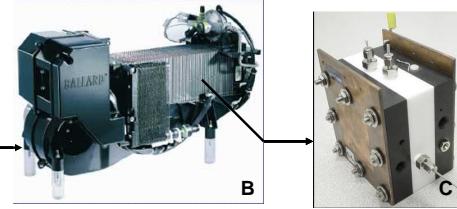
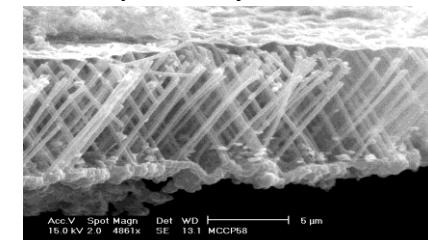
# In summary... Ion track polymer membrane, a versatile tool for research and applications

Proton  
conductive  
channels

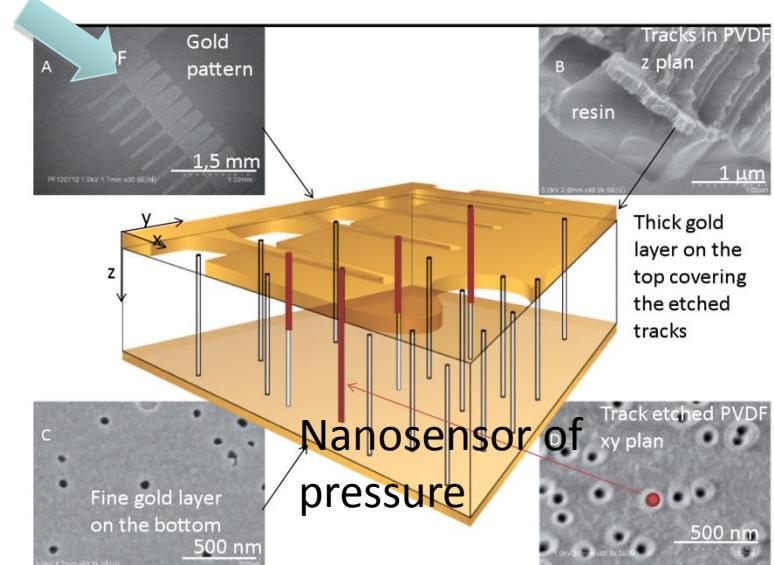
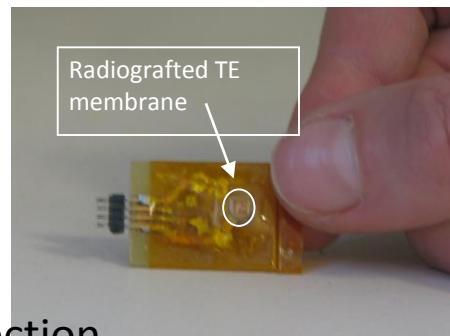


Bi-functional membranes

Template synthesis



Fuel Cell



Sensor for mercury trace detection

**THANK YOU FOR YOUR ATTENTION!**

# Thanks to

