Nanostructured sensors

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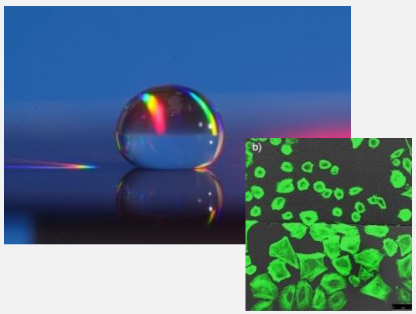
Section Head Nanoscale Technology

Why nanostructures?

Adhesion & wettability

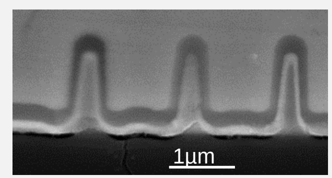


- Superhydrophobicity
- Anti-icing
- Dry-adhesion
- Friction
- Cell-substrates interactions

Optics

- Anti-reflective properties
- Structural colours
- Plasmonic

Photovoltaics



- Light trapping structures

Sensors

- Higher sensitivity
- Faster responsiveness
- Lower drift

CSEM objective and strategy

- Develop processes and manufacturing chains for the large volume fabrication of submicro-/nano- structured surfaces, films, components with enhanced performances or unique properties.

Origination of Micro-/Nano-structures and

Self- Assembly eg. Nanosphere lithography
Sol-gel processes

→

Upscaling or Replication

Dry etching
Hot embossing
UV nanoimprint
Injection Molding
Slot Die Coating

→

Surface functionalization

Molecular vapor deposition (SAMs, metal oxide thin films)
Dye or Enzyme Encapsultation

→

Characterization & Integration

Performance evaluation

Demo: Nanostructured functional components

csem

Outline

- Manufacturing of plastic nanostructured biodiagnostic platform
  - *Origination of low-cost, large scale nanostructures*
  - *Upscaling or replication of nanostructures by injection molding*
  - *Demonstration of improved performances (signal homogeneity, sensitivity)*

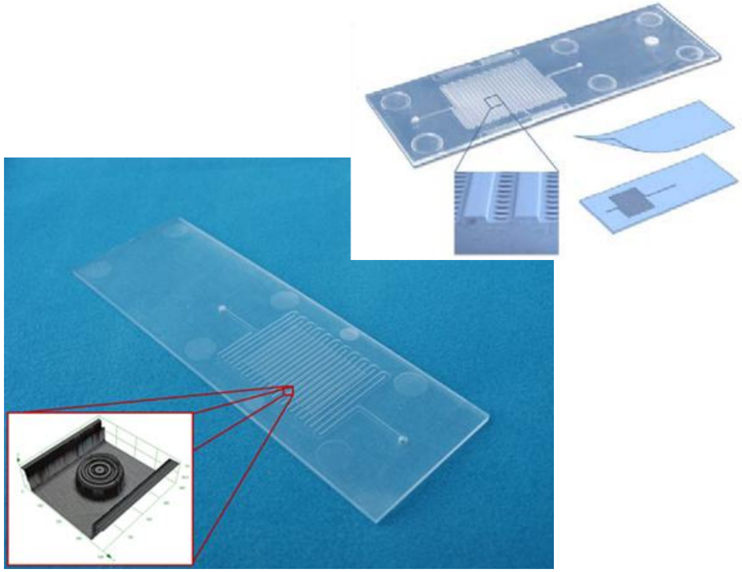
- Manufacturing of disposable patch & film for gas sensing
  - *Fabrication of functional mesoporous sol-gel film*
  - *Integration for Life Sciences*
  - *Pressure Sensitive Painting for Aeronautics*
  - *Air quality monitoring application*

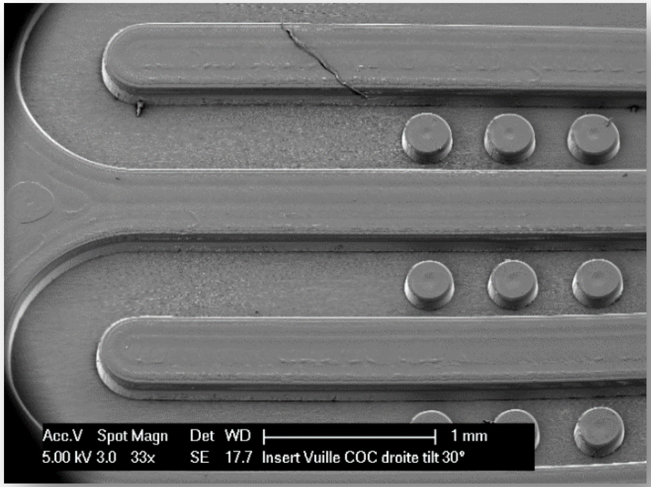
Nanostructured biodiagnostic platform

- Objectives:

Improve sensitivity of injection-molding bio-diagnostic platform with nanostructuration

  - Control of the wettability of detection spots
  - Improve signal quality and homogeneity

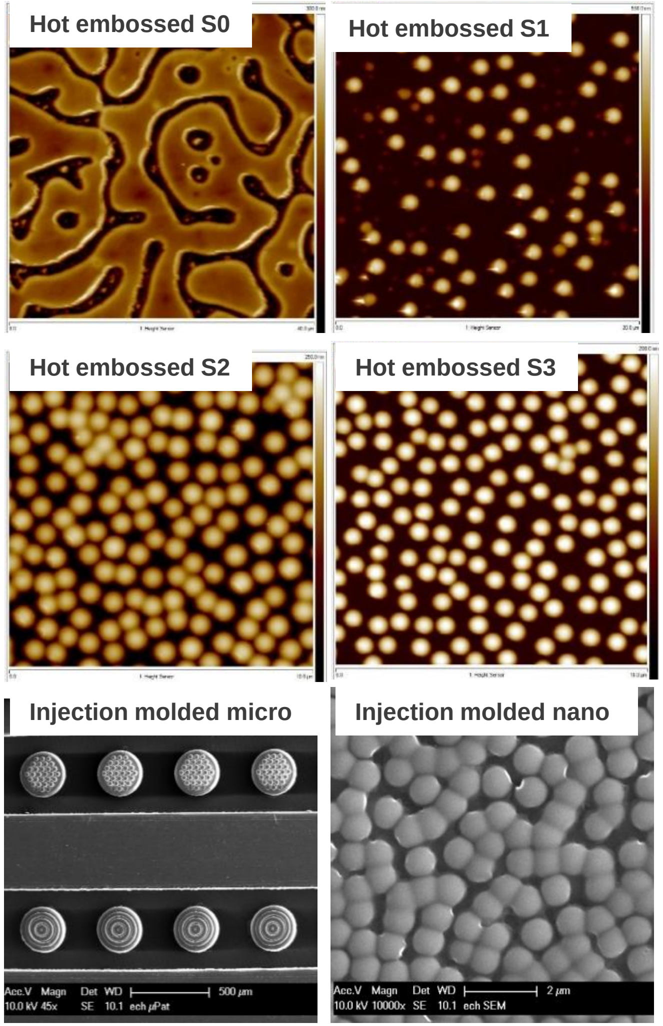




- Tooling: fabrication of nanostructures on a mold insert presenting microchannels and micropins
- Replication : optimization of the replication process for nanostructured micromolds

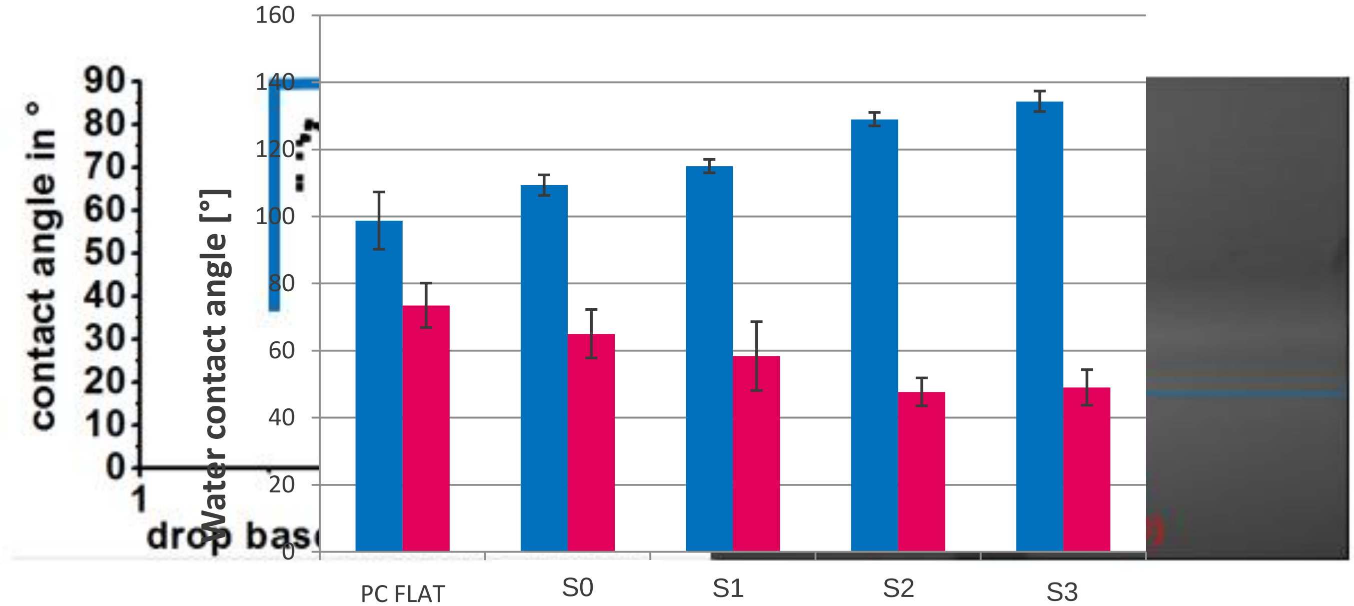
Micro- and nano-structures tested

- Origination of nanostructures by beads and polymer self-assembly
- Replication into plastic, fabrication of nanostructured biodiagnostic platform:
    - Hot embossing and Injection molding: PC parts with four different structures
- Characterization:
    - Influence of structuring on wettability
    - Biodiagnostic platform : fluorescence immunoassay

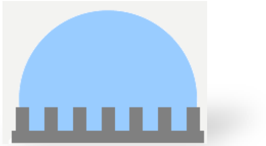


Influence of structuring on wettability

- Dynamic contact angles of water measured on the four types of hot embossed structures and, as a control, flat PC

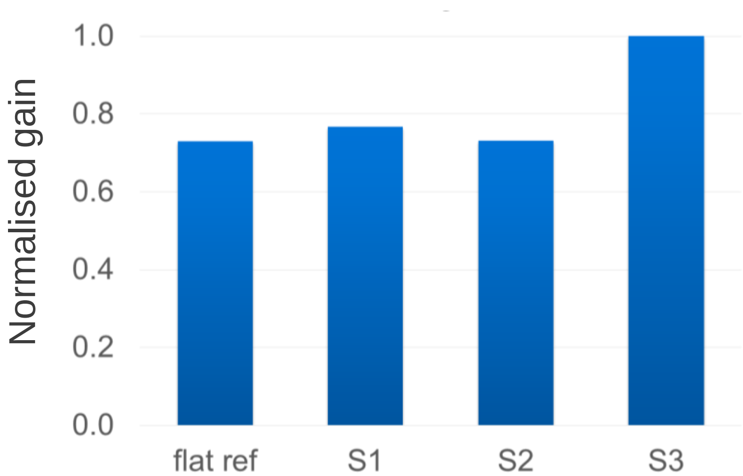


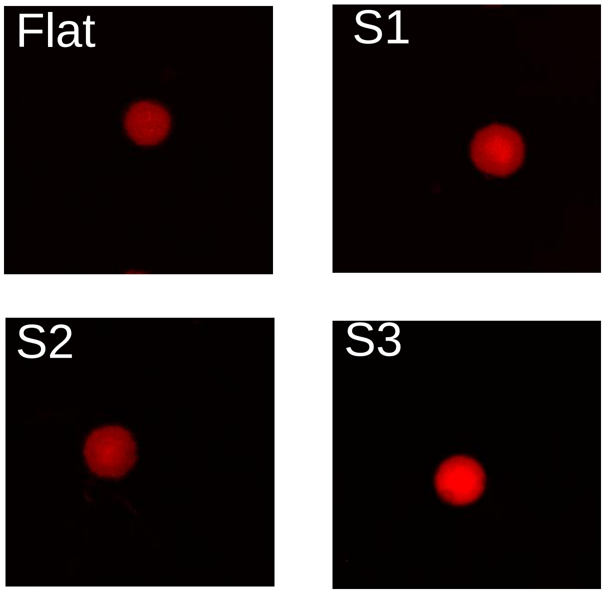
- Advancing water contact angle and contact angle hysteresis significantly increased
- Wetting mode : Wenzel type (sticky drops)



Tests using a model immunoassay

- In these tests, the antibody used for detection is inkjet-printed on the spots of the bio-diagnostic platform.
- The fluorescent spots were imaged using a confocal microscope





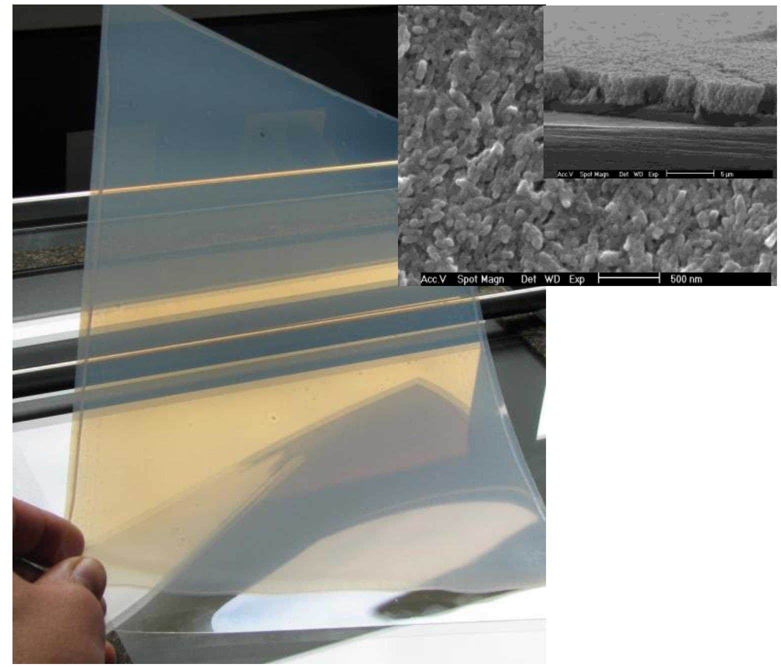
- **Results:**
- Better spot homogeneity: no coffee-ring effect after spotting
- 30% increase in fluorescence for structure S3 (increase in specific surface, different roughness, possible scattering of the emitted light)

Manufacturing of functional mesoporous films

- Objective:

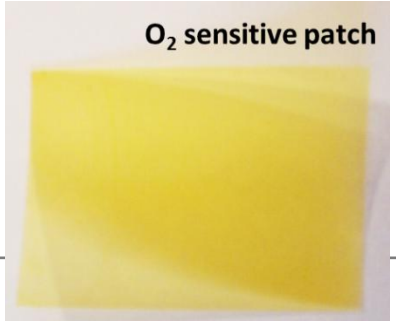
Develop disposable sensitive film enabling the optical detection of dissolved analytes or gases

  - Low cost manufacturing process
  - Higher performance: shorter response time, higher sensitivity

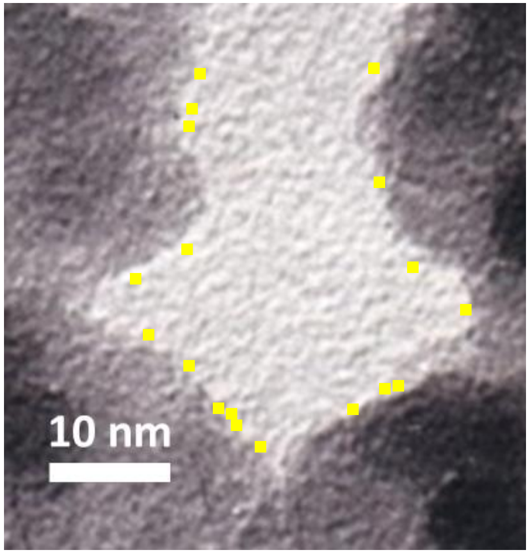


- Manufacturing: Optimize and upscale sol-gel coating
- Highly controlled range of porosity and chemical composition

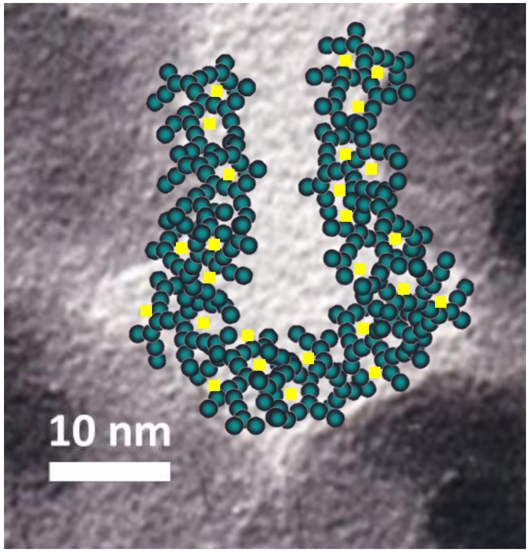
New chemically sensitive optical patches



- State-of-the-art: sensitive molecules embedded into a matrix (polymeric, inorganic)
- Encapsulation of active species into a secondary microporous matrix

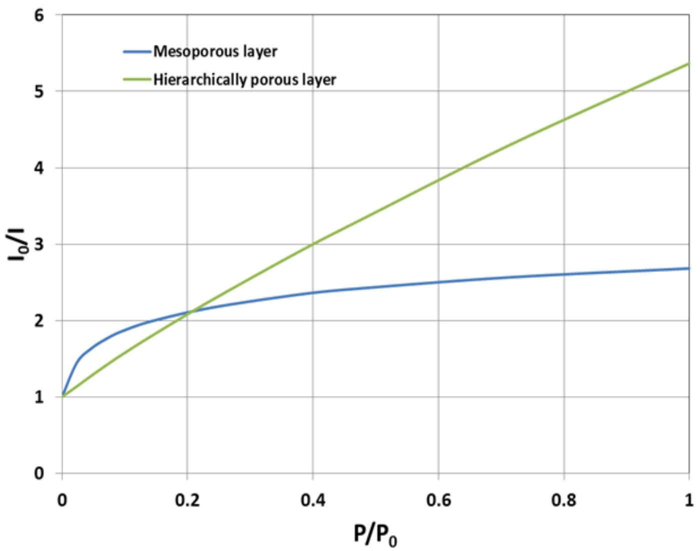


Mesoporous



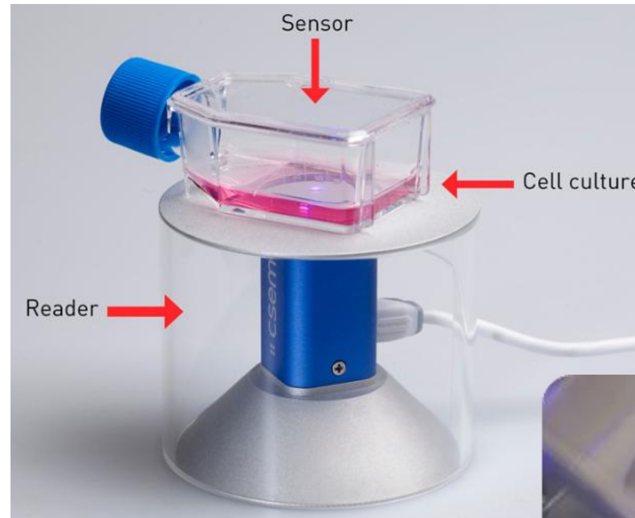
Hierarchically porous

Advantages:



CSEM Patent pending

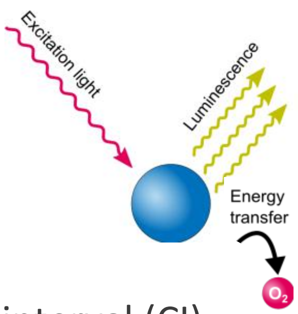
Demox

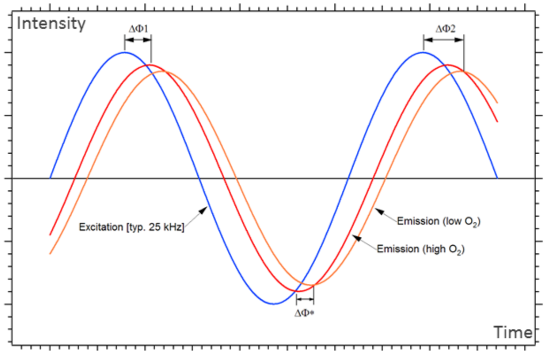


- Determine oygen concentration in cell and tissue culture
- Bio-compatible low cost sensor (disposable SG patch)
- Customizable readers equipped with integrated optics and electronics
- CSEM provides complete solution
- Bio-Innovation Prize awarded to CSEM by the Fondation Eclosion

O2 sensor performances

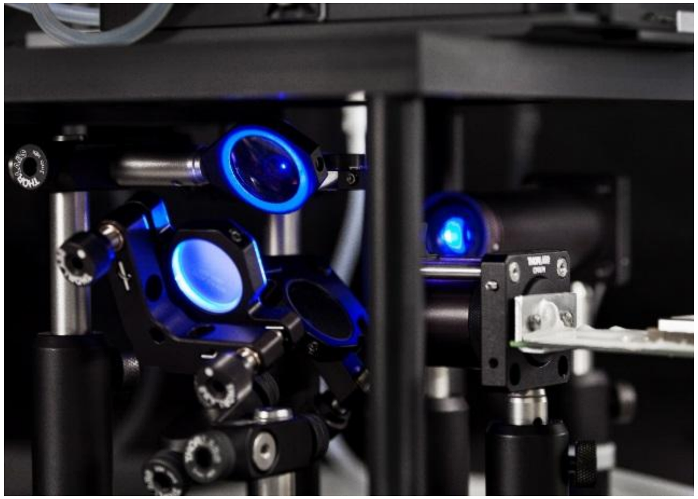
- Frequency-domain lifetime fluorimetry





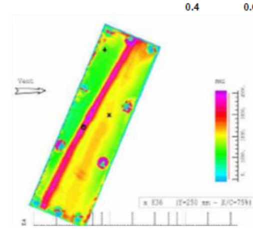
- SPECIFICATIONS accuracy and confidence interval (CI)
- Single point calibration in ambient air
- 0-21% O_2 (stable environment)

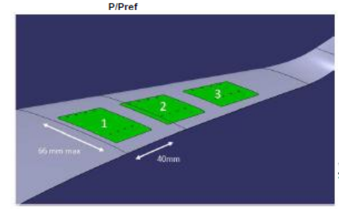
O_2 sensing in gas phase at 23/37°C and 70/90% humidity	
Accuracy	0.1% at 2% O_2
	0.2% at 21% O_2
Precision - 95% confidence interval	±0.3% at 2% O_2
	±0.3% at 21% O_2



Reference fluorimeter

Sensitive mesoporous layers for aeronautic



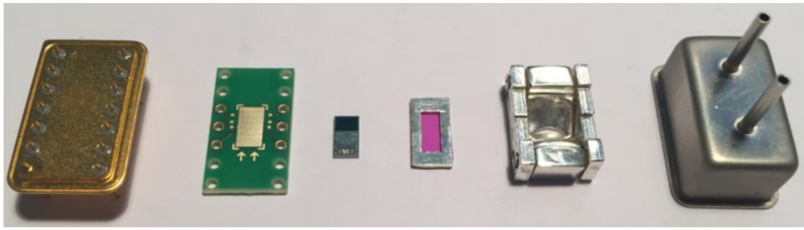


- Pressure-Sensitive Paintings (PSP) for aero-dynamic testing in wind tunnel: meso-porous sol-gel coatings are used to measure fast pressure variations observed in an unsteady aerodynamic flow

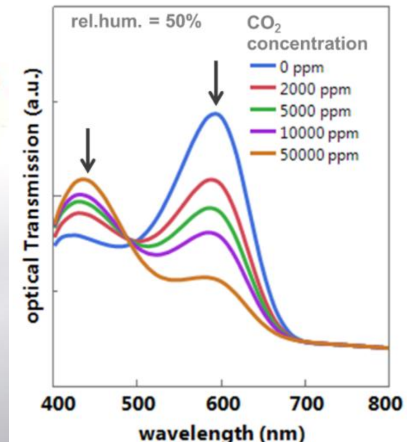
- Higher sensibility when compared to standard PSP, better performances in luminescence (10x) and responsiveness ($F_{acq.}$ up to 10KHz vs $F_{acq.}$< 1KHz for std PSP).

- Technology patented, will be transfered to ONERA (2017-18) for commercialization – CCIFS Innovation Trophy awarded to CSEM

CO_2 sensor for air quality monitoring, prototype fabricated



socket | PCB | MORES Chip | sensitive layer and frame | reflector module | housing with gas in- and outlet



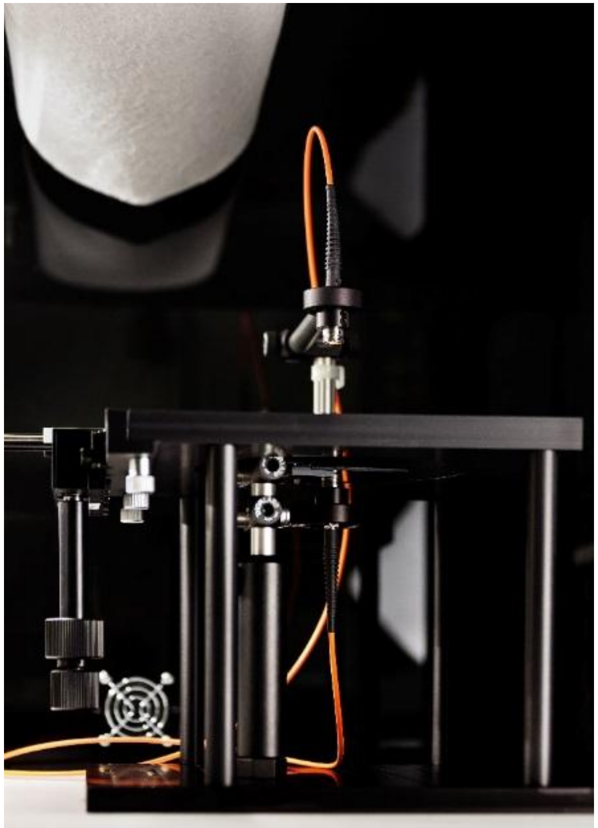
- Highly sensitive CO_2 sensing foil based on patent pending fabrication process
- Sensing patch easy to replace
- Miniature optical reader with reflector system needs low power

CO_2 sensor performances

- Absorbance

- SPECIFICATIONS accuracy and confidence interval (CI)
- Single point calibration in ambient air
- 0-15% CO_2 (stable environment) – phenol red

CO_2 sensing in gas phase at 23°C and 70% humidity	
Accuracy	*0.2% at 3% CO_2*
	0.2% at 12% CO_2
Precision - 95% confidence interval	*±0.4% at 3% CO_2*
	±1% at 12% CO_2



Reference spectrometer

Conclusions

- Process chains for the fabrication of nanostructures surfaces and components have been developed and patented:
  - nanostructured plastic chip by injection molding
  - Mesoporous films by sol-gel process

- Functional nanostructured sensors have been fabricated for different applications
  - High performance biodiagnostic platform
  - Optical sensor for O_2 monitoring in cell culture device
  - Pressure sensitive painting for aeronautics
  - Optical sensor for CO_2 monitoring (Life Sciences and air quality control)

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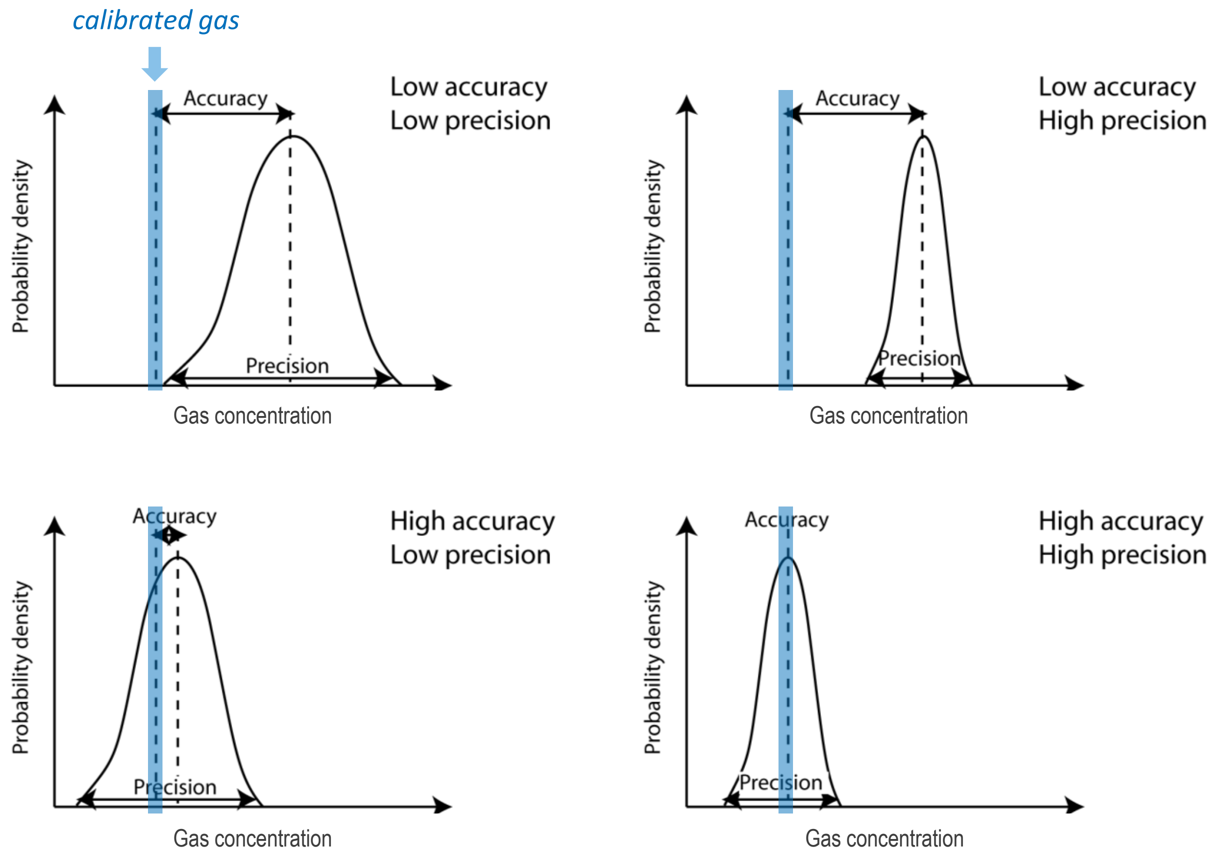
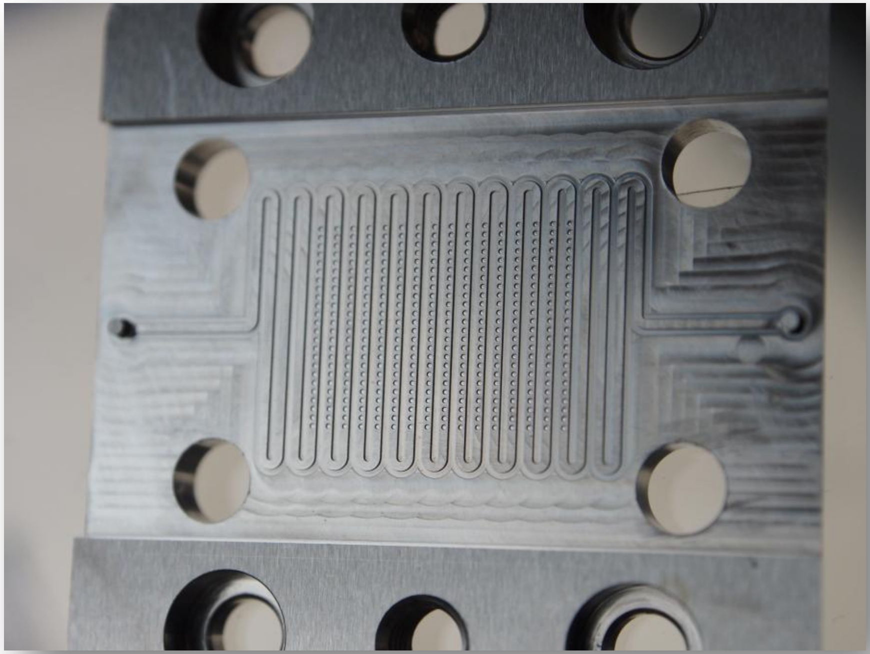
Sensor performances

- Accuracy & Precision



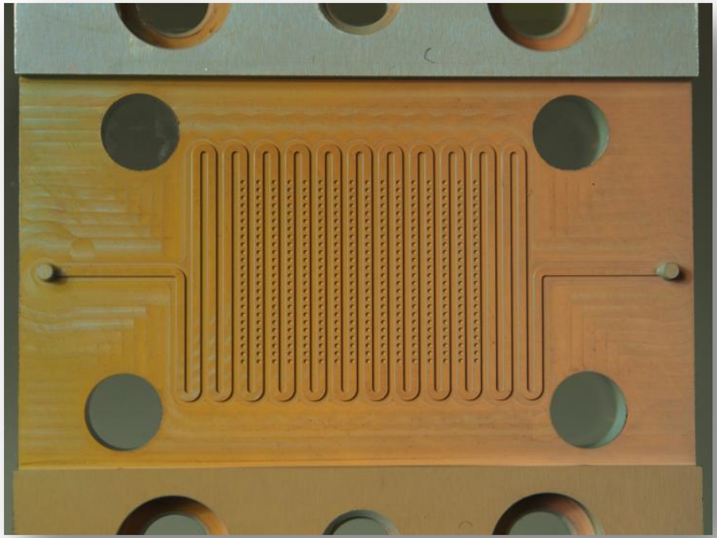
3D mold insert structuring

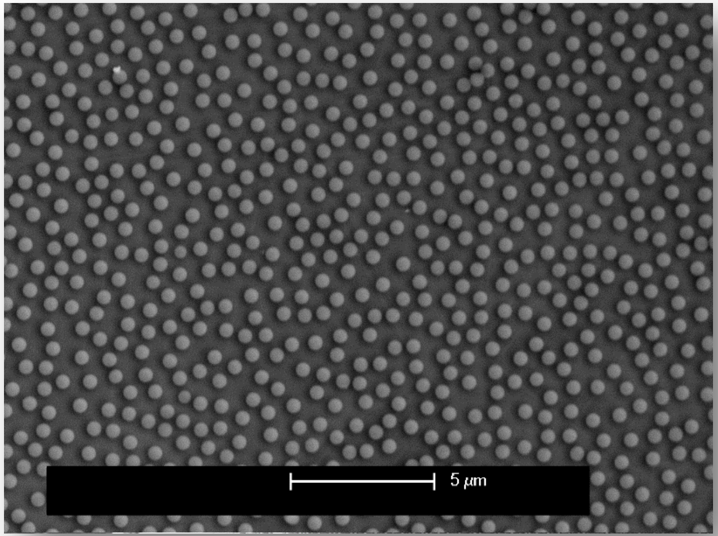


Deposition of particles on the microstructured mold insert

- Objective : deposition of nanoparticles on the mold insert produced by Vuillermoz

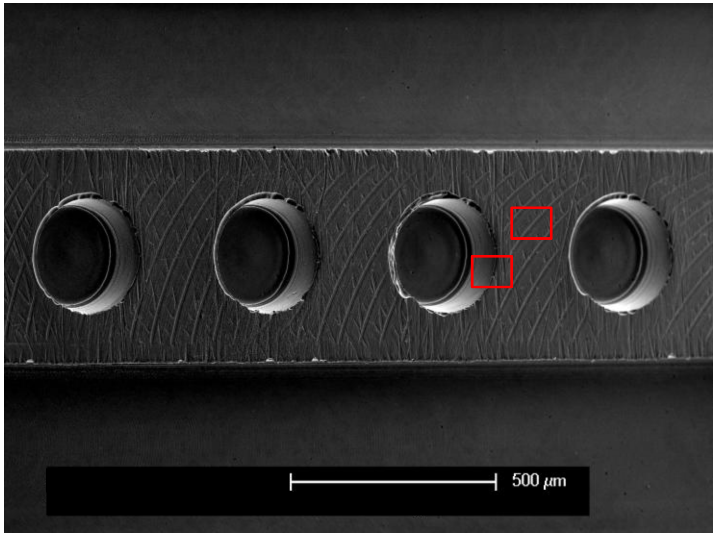
(in the holes made by micromilling (Ø300µm, depth 150µm))

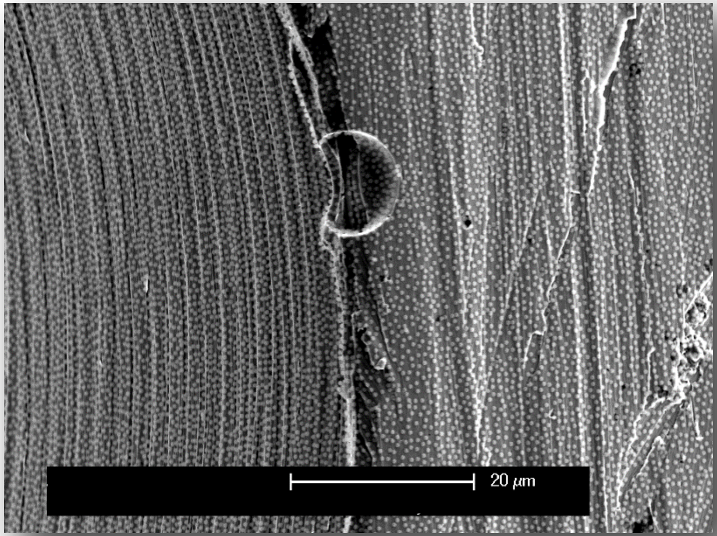




- Successfull deposition at the bottom of the microholes

Deposition of particles on the microstructured mold insert

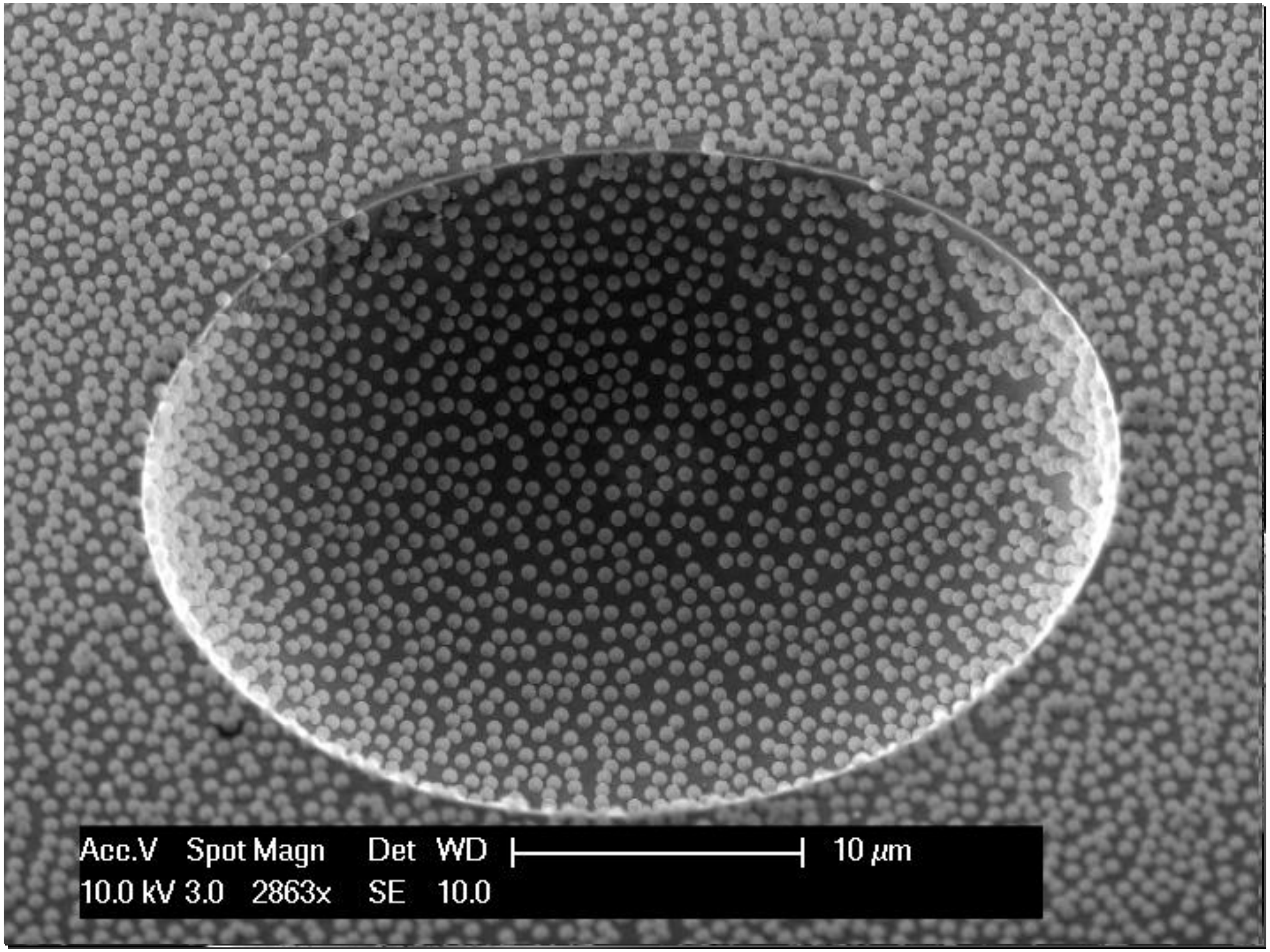




- Deposition on the sidewalls of the microholes
- The background roughness due to the micromilling process does not affect the deposition process

Deposition of particles on freeform parts

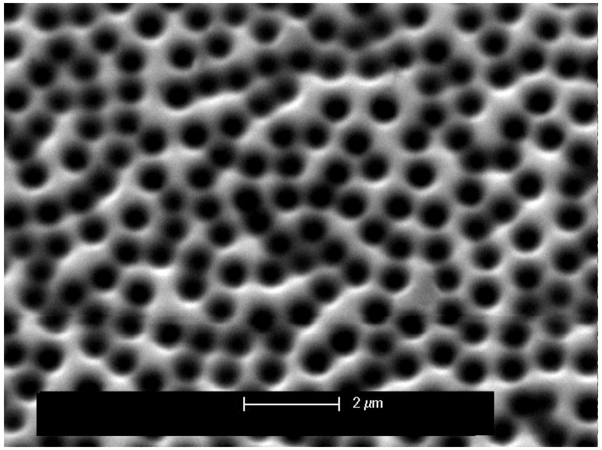
Deposition on a coronary stent

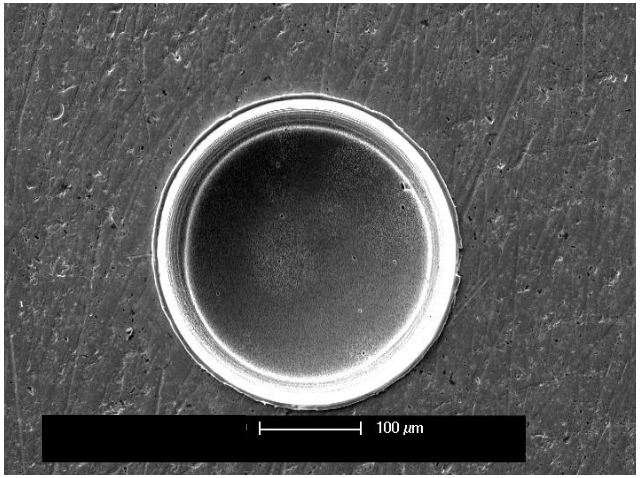


3D mold insert structuring

- Use the process developped for 2D parts onto the 3D mold insert.

- Fabrication of a nanoporous etch mask and electrochemical etching



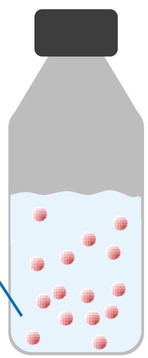


- Nanostructures have been fabricated into the microholes
- Homogeneity to be improved
- Difficulties to characterize the results (AFM not possible)

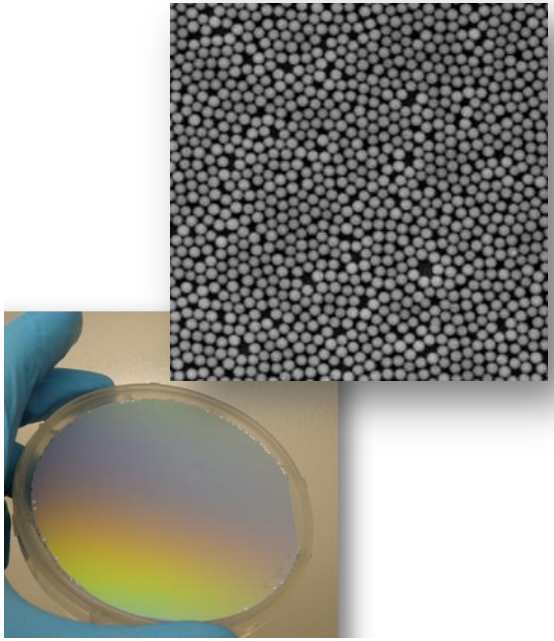
Origination of nanopatterns by self-assembly

- Fabrication of a **formulation** containing micro-nanoparticles or block copolymers and **deposition** of thin films on a substrate

Particles or
polymers
+ solvent
+additives



Material costs: 20€/100g



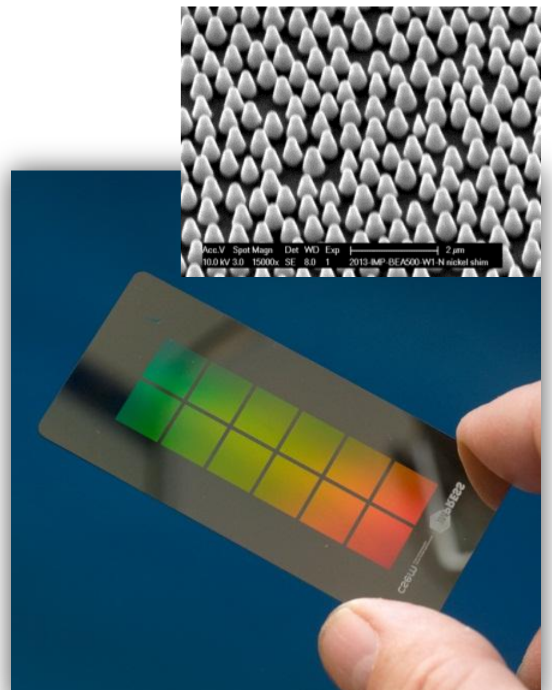
Formulation/Dispersion

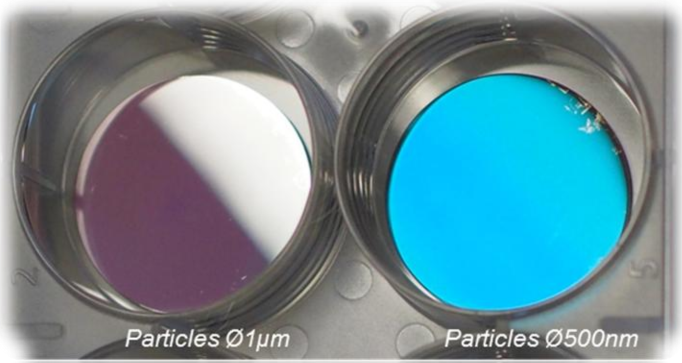
Deposition

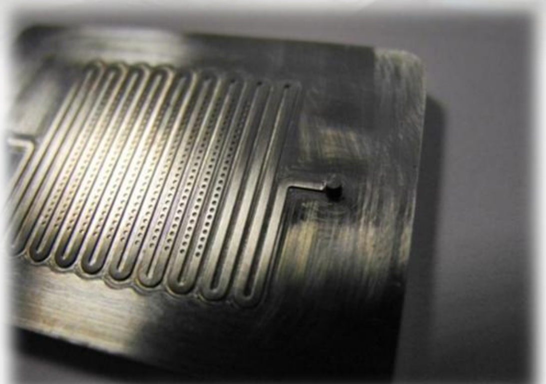
Characterization

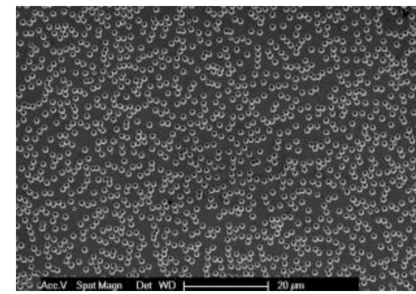
Random low-cost nanostructures transfered in replication tool

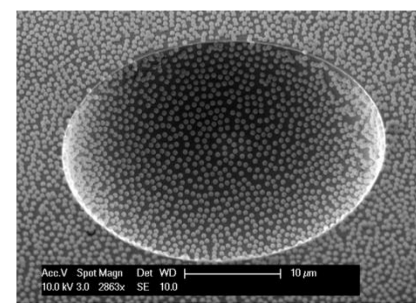
- Self-Assembled structures transferred in nickel or hard steel replication tools
- 2 and 3D nanostructured inserts and mold





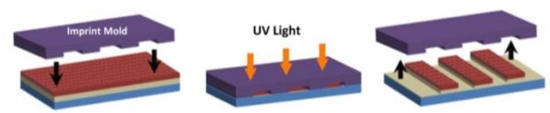




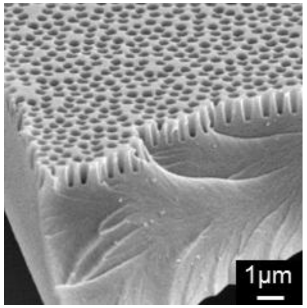


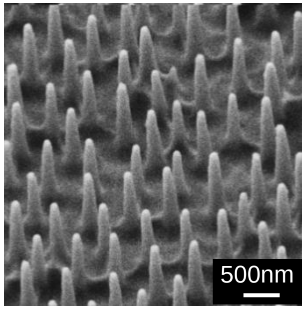
Replication

UV Nanoimprint



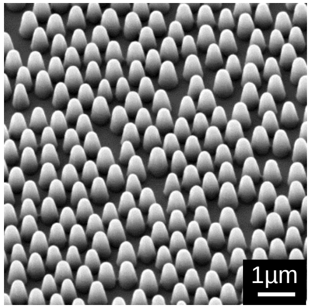
- *Rapid prototyping*
- *Highest accuracy*
- *UV-curable resins (PUA, solgel)*

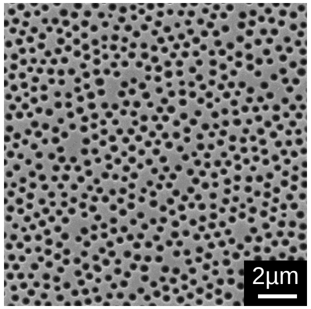




Hot embossing

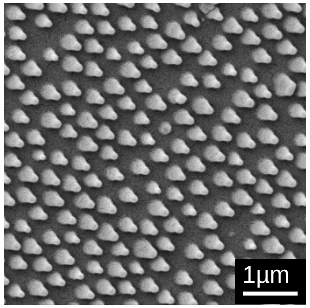
- *Small series production*
- *Thermoplastic & thermosetting materials*



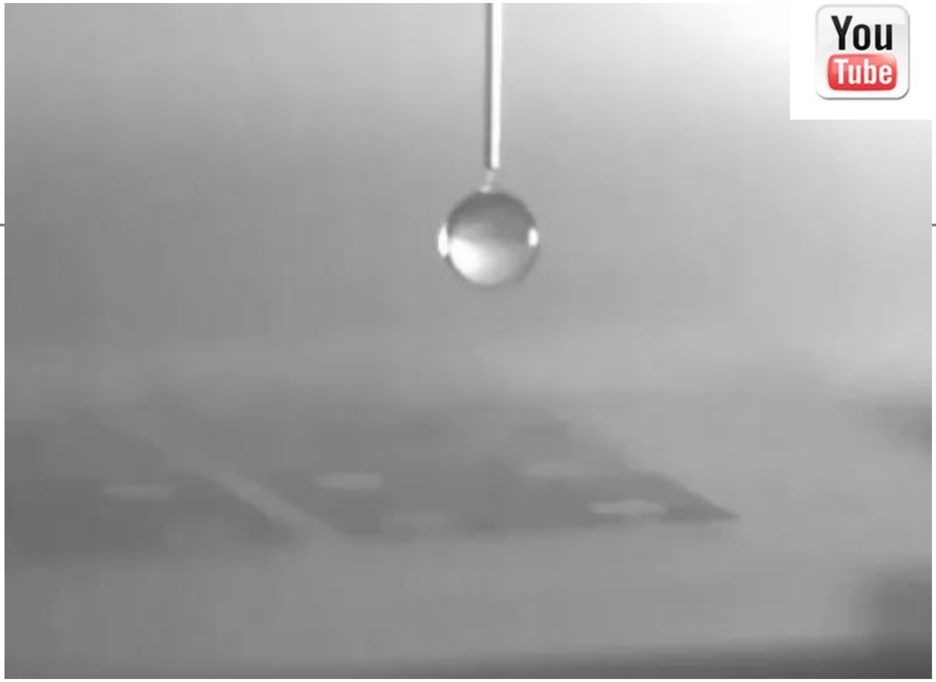


Injection molding

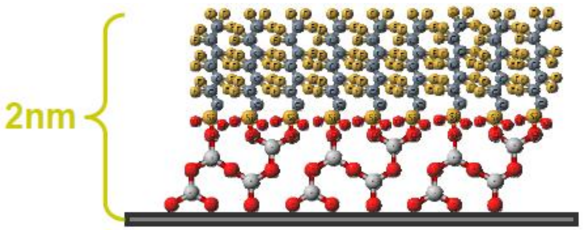
- *High throughput*
- *Large series production*



Superhydrophobic surfaces



- Fabrication of **micro/nanostructured plastic parts** using replication techniques.
- Control **surface chemistry** using MVD™ technology
- Characterization of wettability : dynamic water contact-angles, high speed videos recording of drop impacts

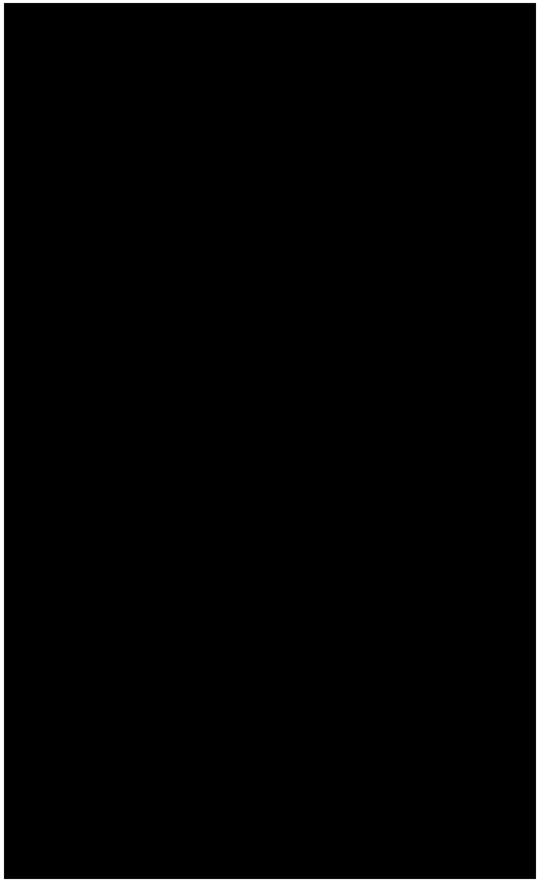


Chemistry: Perfluoro SAM

- Superhydropbobic, self-cleaning surfaces
- Controlled wetting states (Wenzel vs Cassie-baxter)
- Superhydrophilic /hemiwicking surface also possible

Superhydrophobic surfaces

- High speed video records of water drops impacts on superhydrophobic surfaces:



Flat

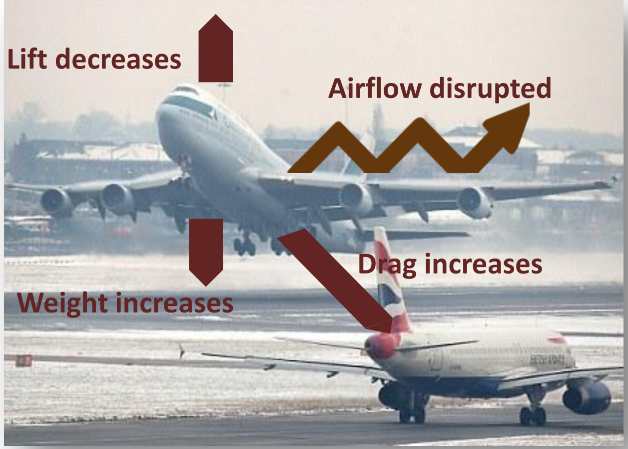
Structure 1

Structure 2

Anti-icing surfaces

- Objective:

Fabrication of superhydrophobic surfaces with enhanced erosion resistance to **improve the performance of electromechanical de-icers** and lower their energy consumption



- Fabrication of **nanostructured surfaces** by means of UV-nanoimprint
- Control **surface chemistry** using MVD™ technology
- Characterization: measurement of **ice-adhesion strength, outdoor icing tests**

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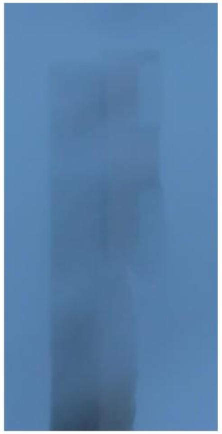
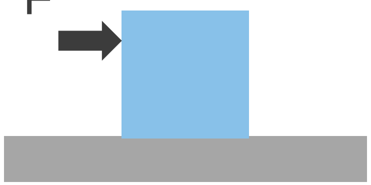
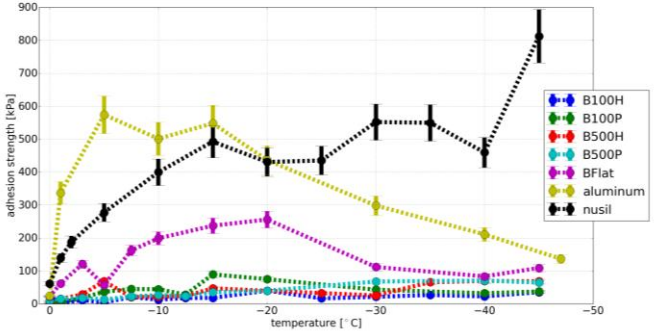
Anti-icing surfaces

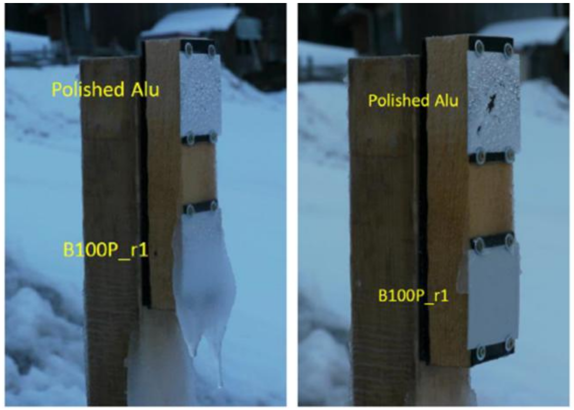
- Both structured/flat samples are iced with snow gun
- Ice easily removed from nanostructured samples by pole shaking
- Ice remained on polished Al surface, event after scratching
- Ice adhesion strength measured by applying shear until the pellet adhesively or cohesively breaks

- Test running (30-60 s duration)





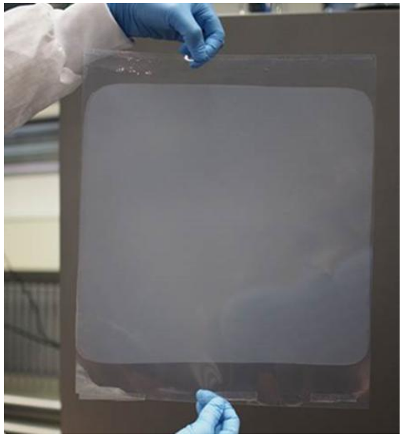


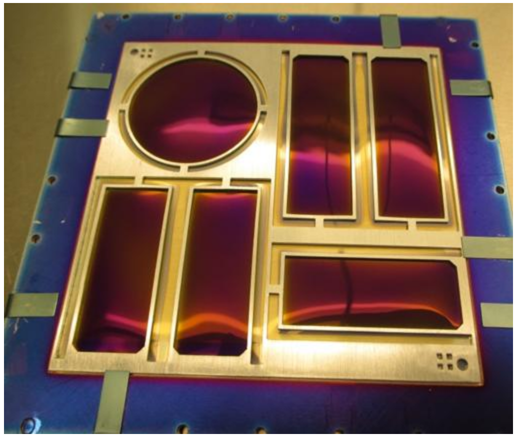


After icing .... + ice gently shed

Application: wearable device

- Objective: Create and integrate PV solution in a wristband
- Fabricate textured surface for the growth of the flexible solar cell that provide excellent light coupling capabilities
- Outstanding PV performance at ultra-low illumination
- Upscaling of the texturation process (30x30 cm^2) successful. UV-NIL on 30-200µm thick polymer foil



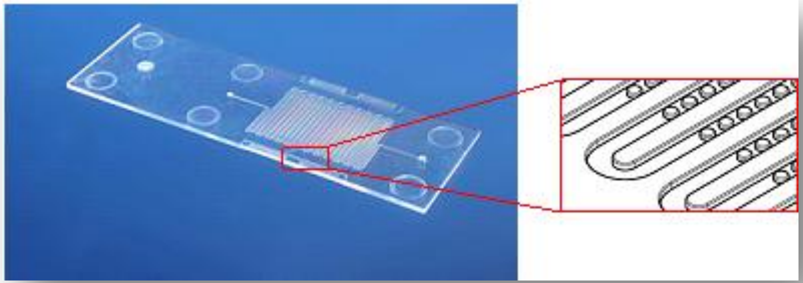


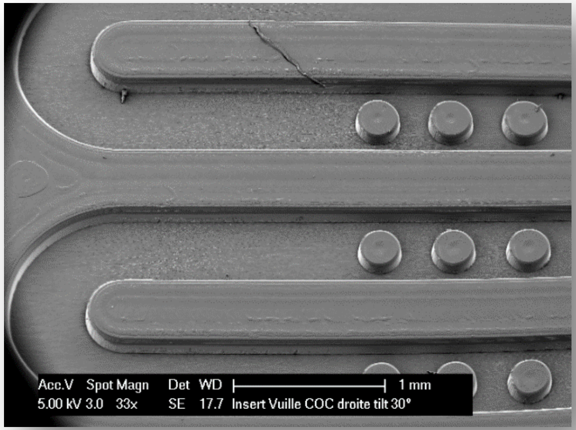
Nanostructured biodiagnostic platform

- Objective :

Injection molding of nanostructured bio-diagnostic platform with improved sensitivity

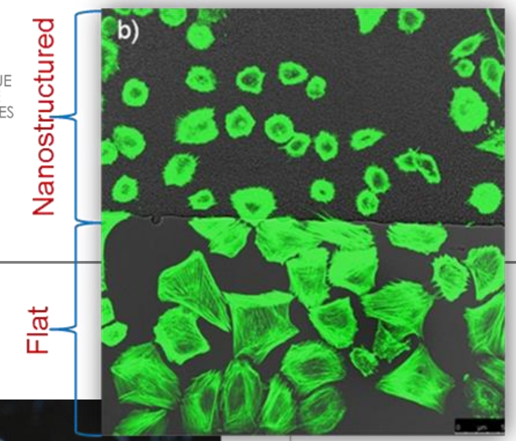
- Control of the wettability of detection spots
- Improve signal quality and homogeneity



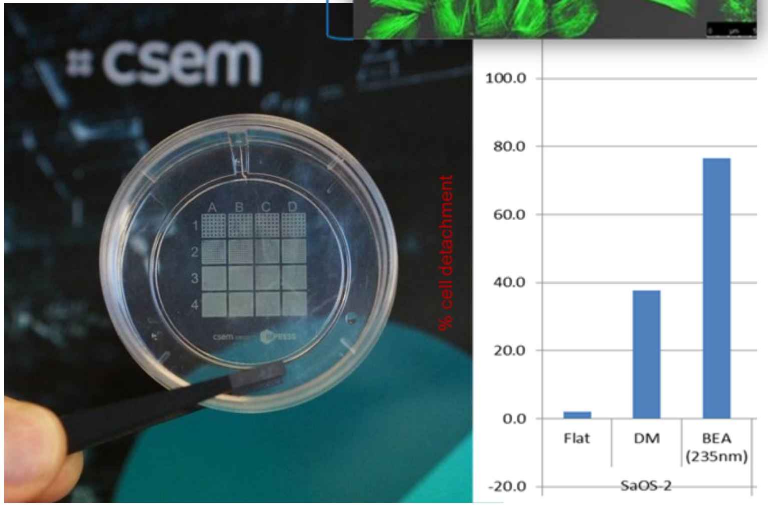


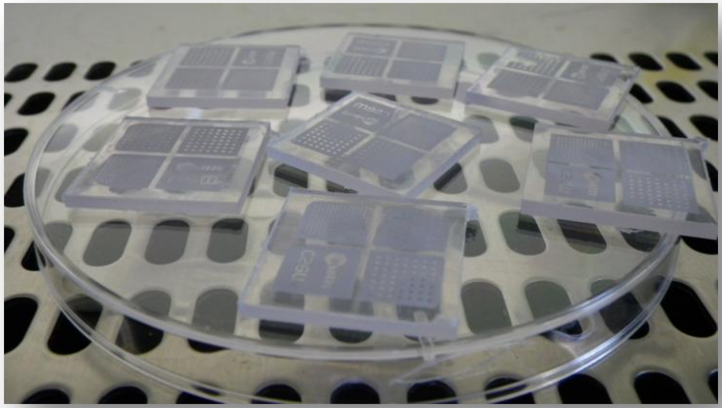
- Tooling: fabrication of nanostructures on a mold insert presenting microchannels and microholes
- Replication : optimization of the replication process for nanostructured micromolds

Biological cell growth



- Grow eukaryotic cells on flat and structured surfaces
- Analyse the morphology of the cells after 3days
- Characterize the adhesion of cells on flat/structured surfaces

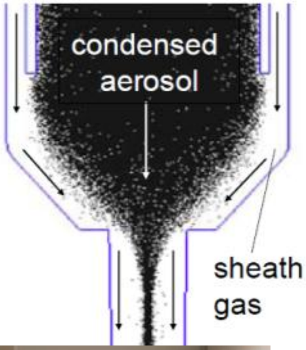




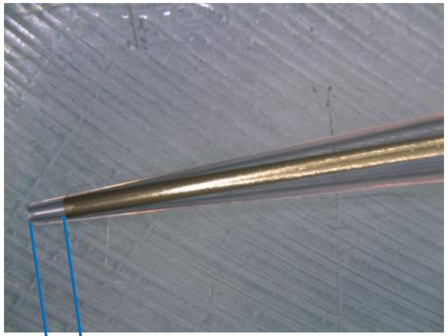
- Control the growth of adherent cells via micro-nanostructuring surfaces.
- Create surfaces with cell-adhesion/cell repellent patterns

Functionalisation via aerosol-jet printing

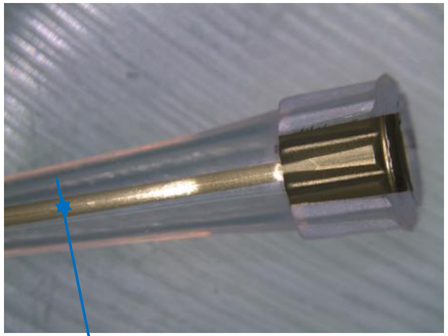
- Aerosol-jet printer system AJ-300
  - Aerodynamic focusing of colloidal suspension
  - Contact-free deposition
  - 3D and flexible substrates
  - Deposited materials incl. metals, polymers, ceramics, dielectrics, biomaterials…



Electrode on pipet tip



2 mm



1 mm

Biofunctionalisation by Aerosol Jet Printing

- Currently optimising deposition parameters for biological samples on various chemistries
- Spots can be done on structured or 3D samples