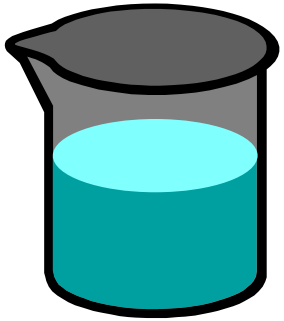
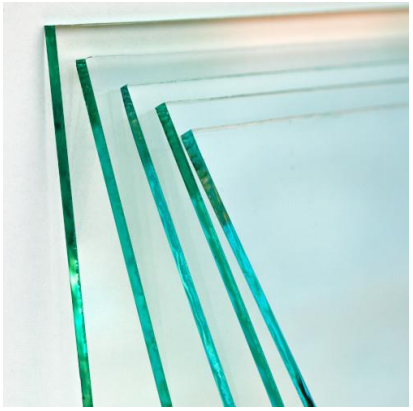
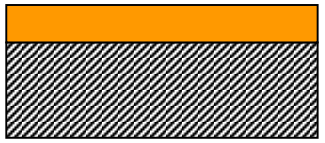
MÉTHODES CHIMIQUE DE FONCTIONNALISATION DES SURFACES DE VERRES PLATS







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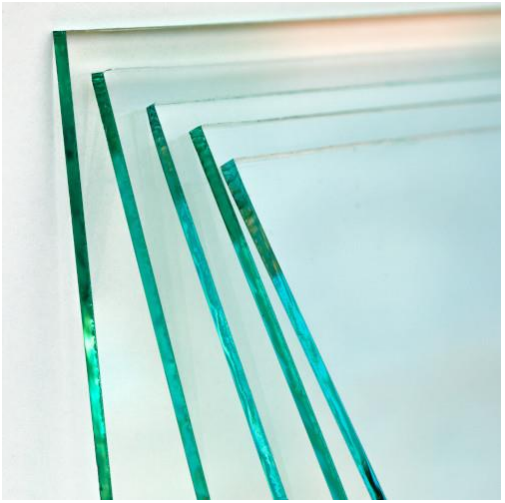
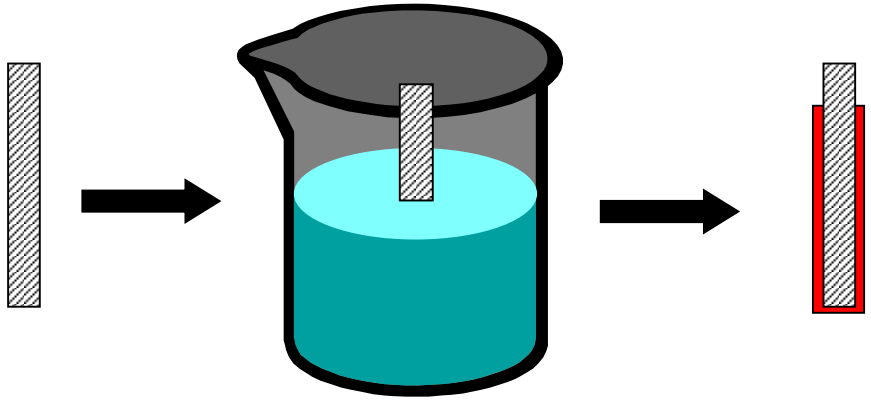
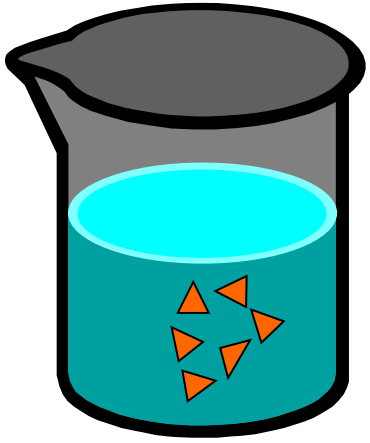
Laboratoire de Physique de la Matière Condensée (LPMC)
Ecole Polytechnique – CNRS – Institut Polytechnique de Paris

Wet coating

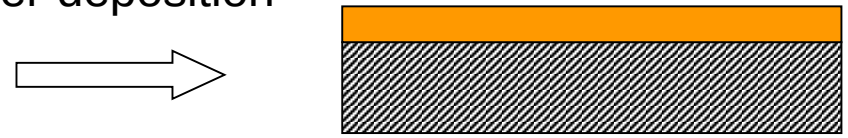


Surface modification through chemical reaction

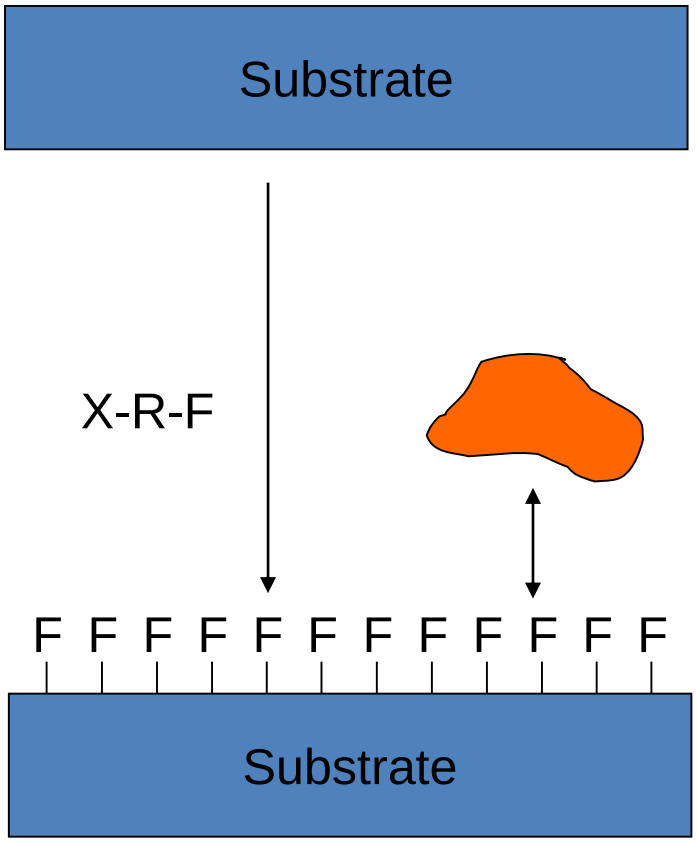




Layer deposition



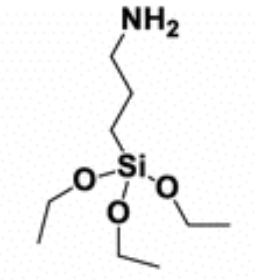
Glass surface modification - Molecular layers

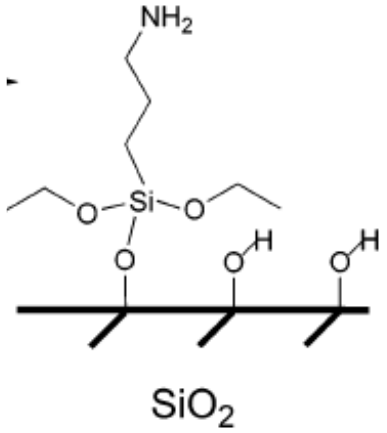


- hydrophylic / Hydrophobic
- Demolding agent
- Adhesion promoters
- Coupling agents to biological species
- catalysis

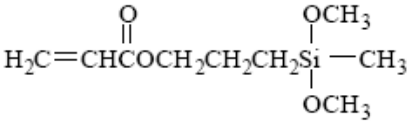
Functionnal organosilanes

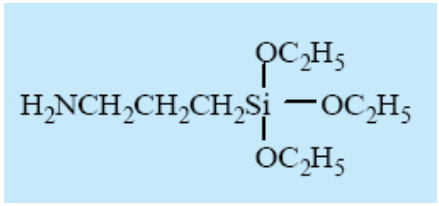
Silanization

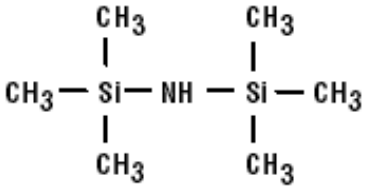


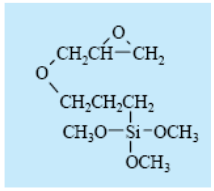


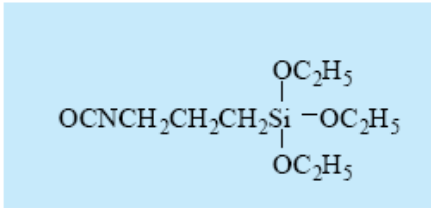
Large variety of functionnal silanes :

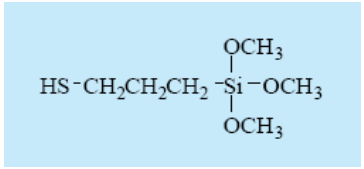




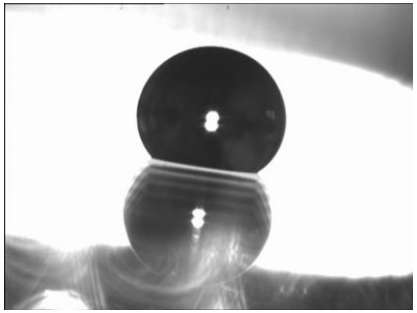


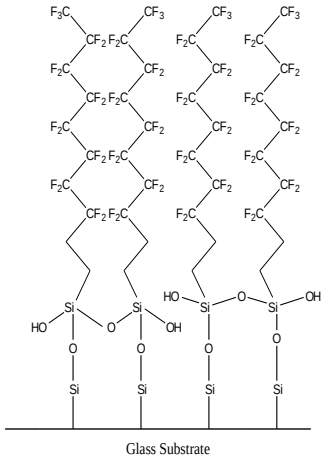




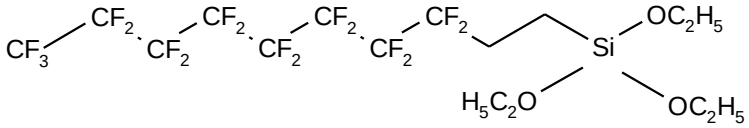


Perflorosilane precursors for hydrophobic windows

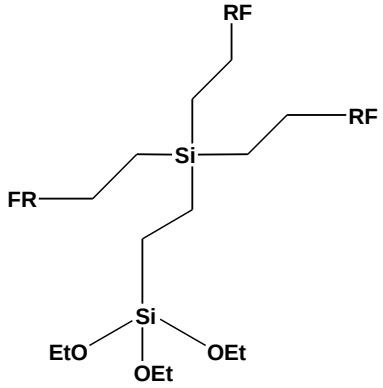


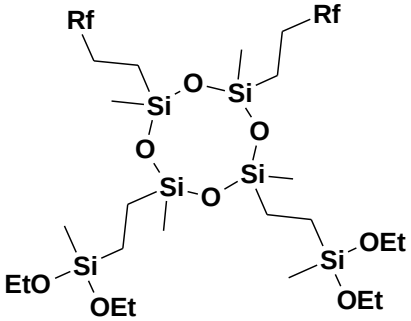


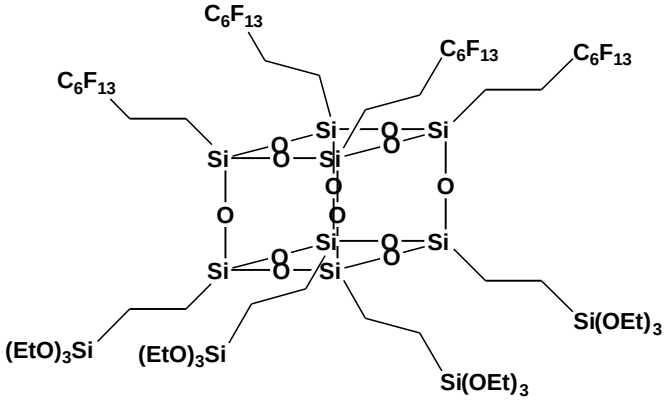
C8 – C16 chains : functionnality and packing



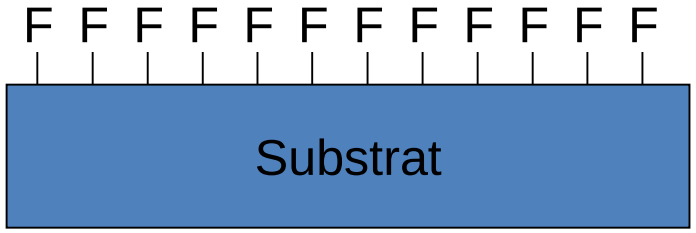
Playing on precursor structure for enhanced functionnality

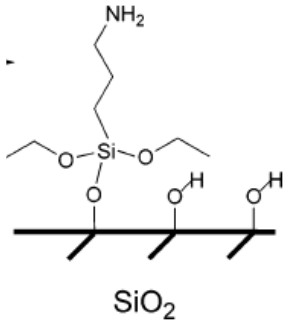






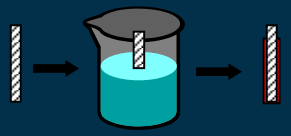
Some important issues





- The structure of the layer is not as ideal as in the scheme above…
- Stability issues toward ageing : UV / Water / mechanical abrasion / dust deposition
- Stability toward glass surface evolution – alcaline lixiviation
- Environnemental issues regarding perfluorinated precursors

Electroless deposition – silver miror



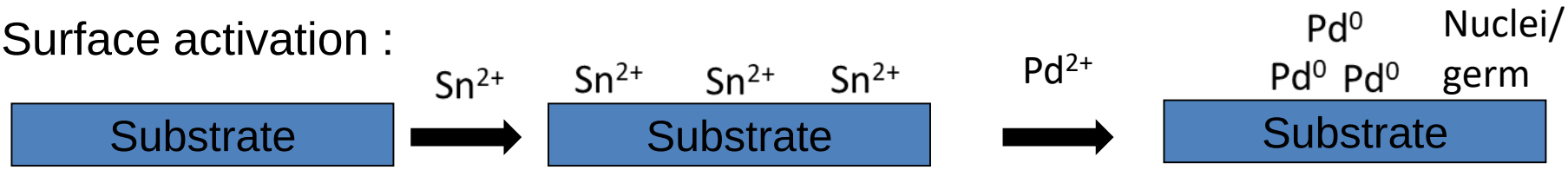
$$RCHO + 2Ag(NH_3)_2^+ + 3OH^- \xrightarrow{H_2O} RCOO^- + 4NH_3 + 2H_2O + 2Ag$$

Metastable reactive solution

Ag+/Ag° single atoms E_{ENH} = -1,8V

Ag/Ag+/Ag° E_{ENH} = O,4V

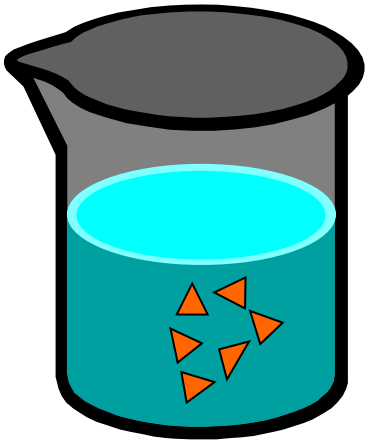
Surface activation :

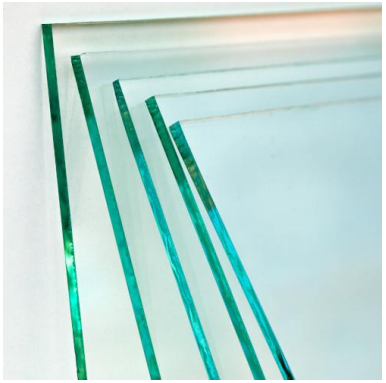


Rem : many other compounds can be electroless deposited : Ni / Au, but also ZnO, CdInGaSe, GaAs…

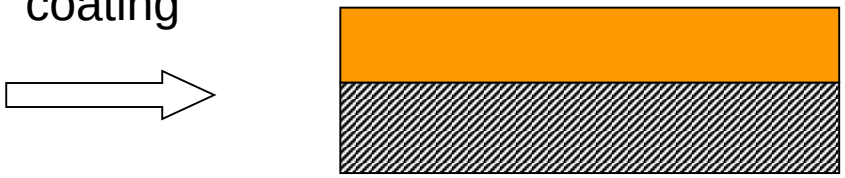
Wet coating of thin films

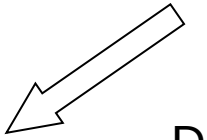
Precursors in solution
partially condensed





coating



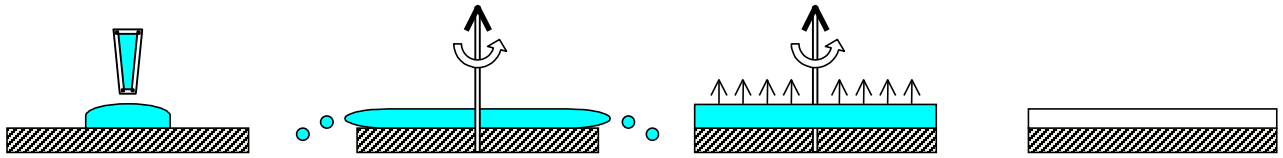


Drying / thermal treatment

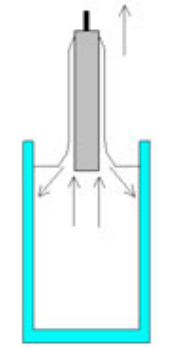
Thickness 50 nm -> few μm

Deposition techniques

Spin-coating

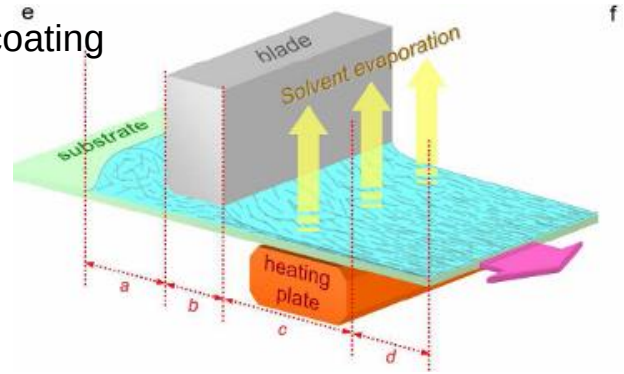


dip coating

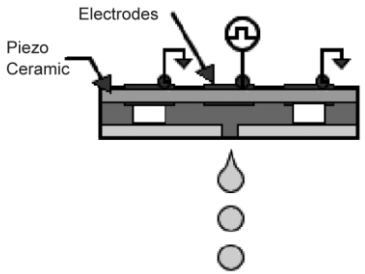


wet layer formation

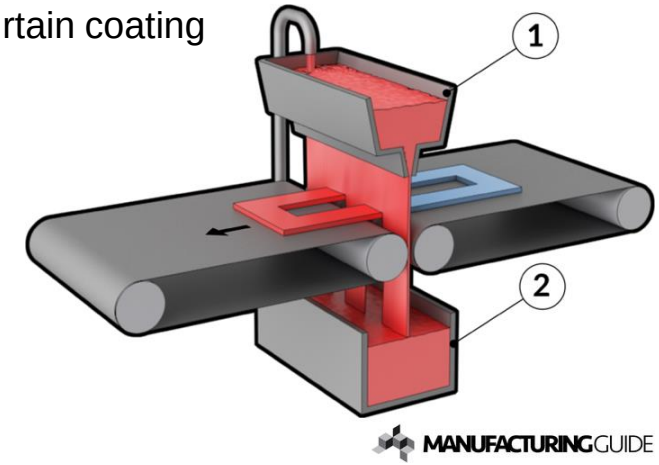
Blade/pool coating



Ink jet

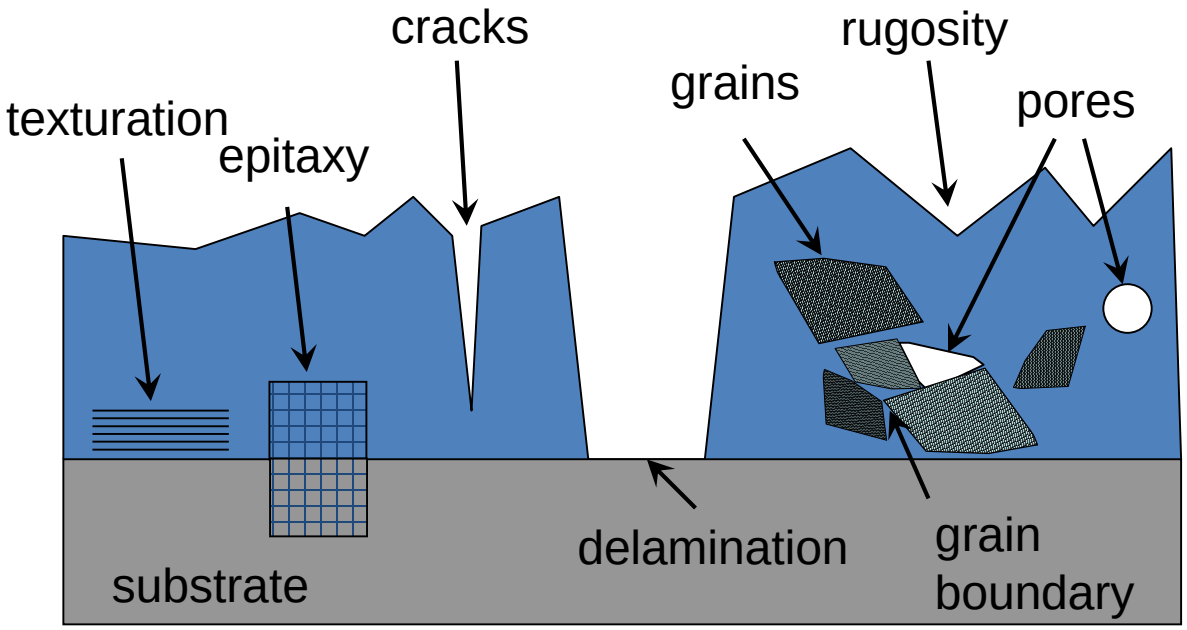


curtain coating



Spray-coating

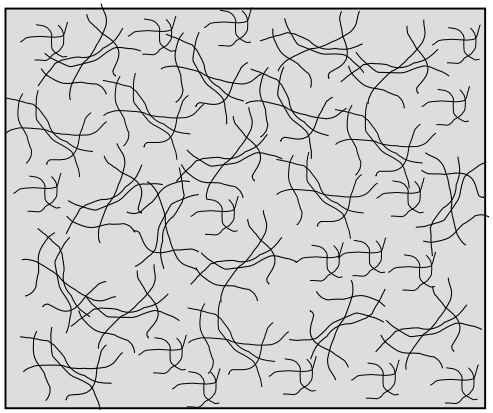
Mains issues related to functionnal coatings

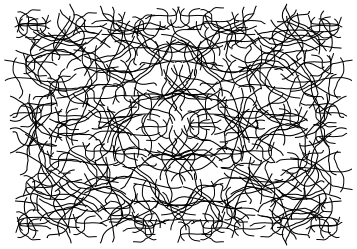


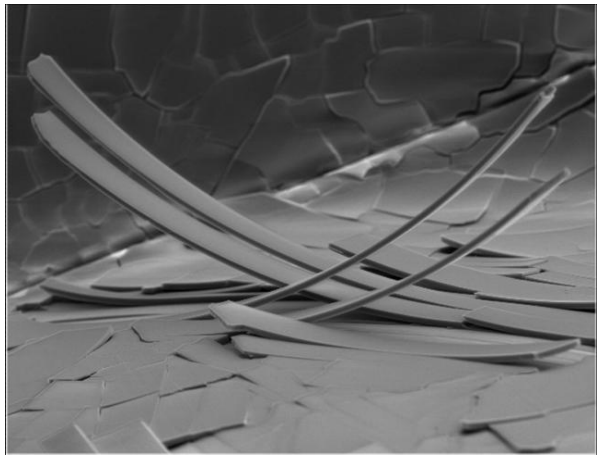
- Thickness, strains, cracks…
- Post-deposition thermal treatments (600°C few min…)
- Hydrolytic properties
- Alcaline diffusion / buffer layer
- Mecanical properties (indentation, Opel, Taber)
- Large scale deposition process

Crack issues…

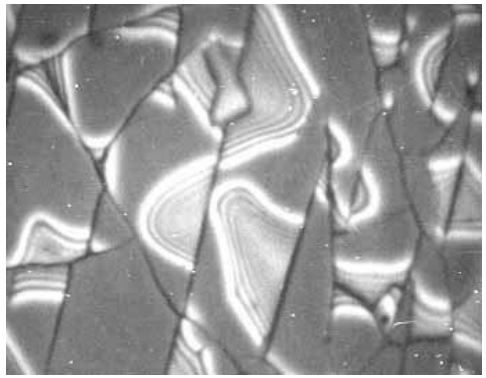
Strains (densification, capillary stresses)





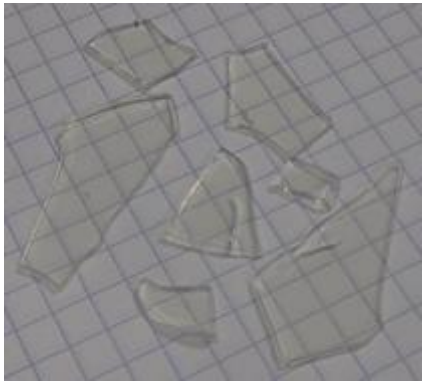


- Critical thickness (few 100 nm – few μm)

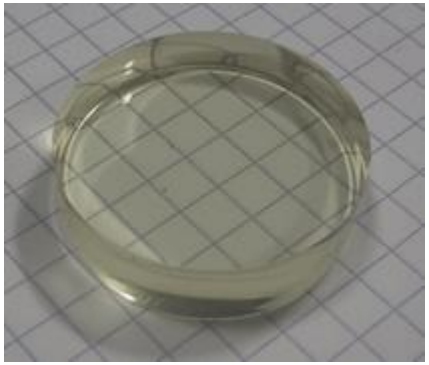


- Hybrid precursors

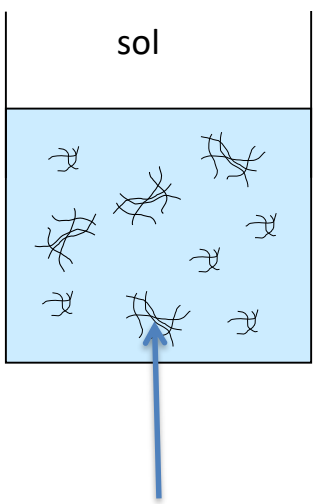
$Si(OC_2H_5)_4$



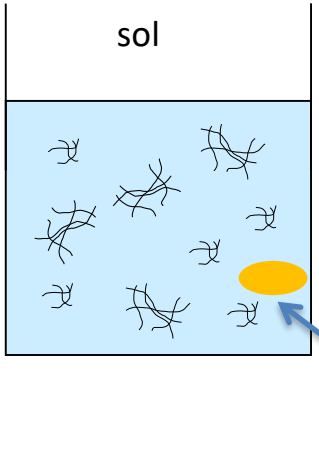
$CH_3\text{-}Si(OC_2H_5)_3$

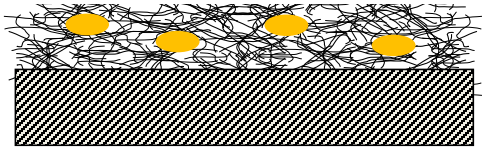


Composite coatings



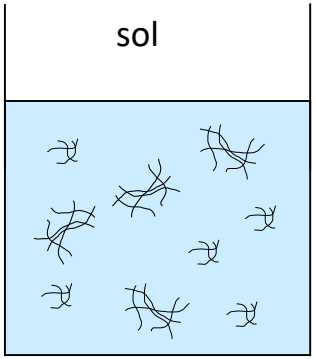
Binder

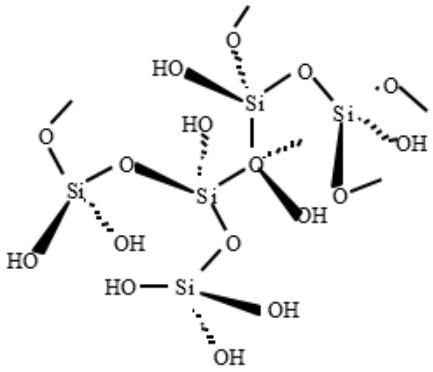




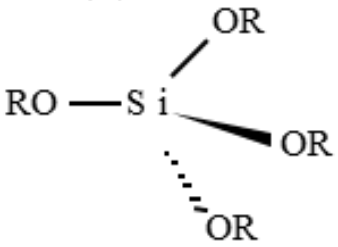
Functionnal system
- Molecule
- Nanoparticles
- Porogen agents

Silicate Binder chemistry

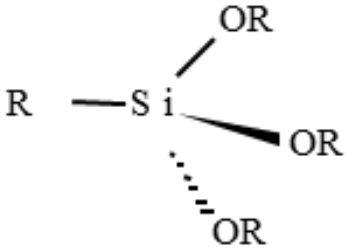




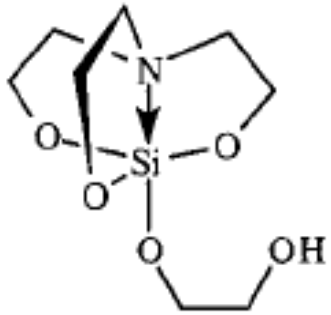
TEOS



Hybrid silanes



silatranes



Alcaline silicates

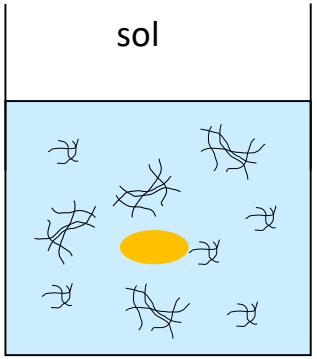
NaxSiyOz

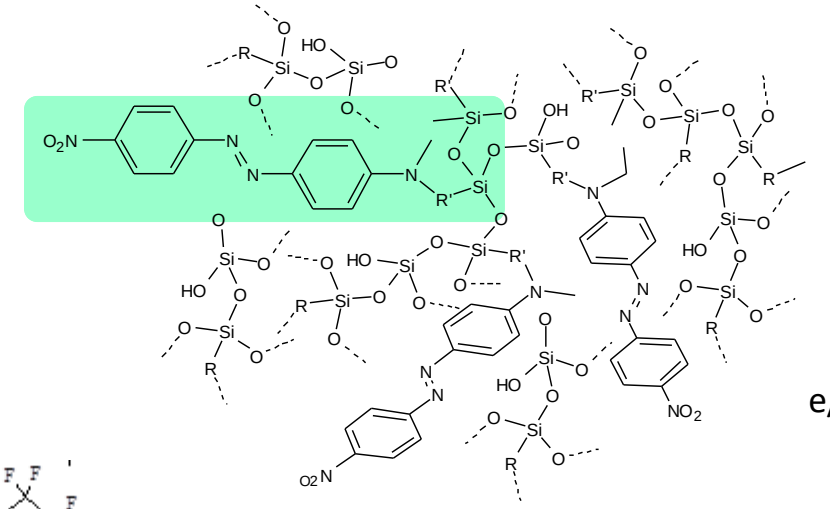
Sol-gel enamel compositions

Colloidal silica / alcaline silicate / Ca(Acetate)

Hybrid organic/inorganic coatings

Appropriate dispersion requires grafting on the silicate finder

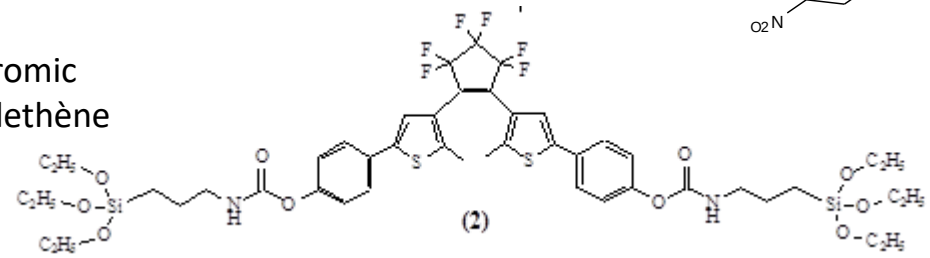


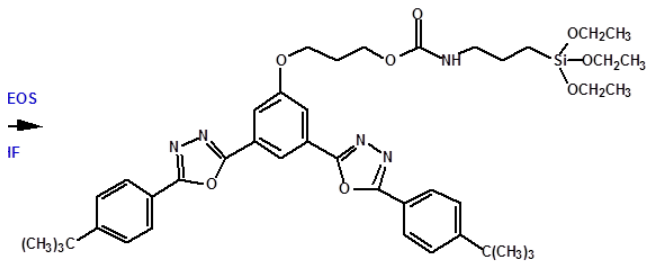


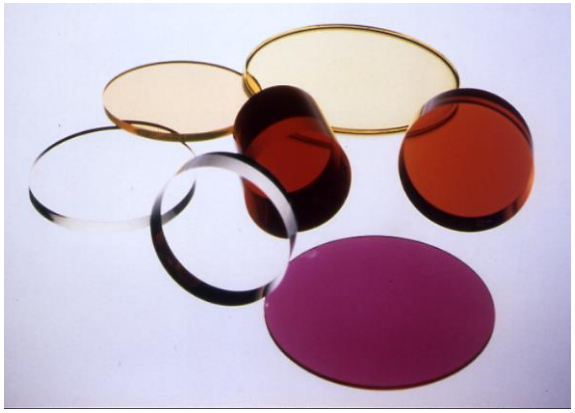
photochromic
Azobenzene derivatives

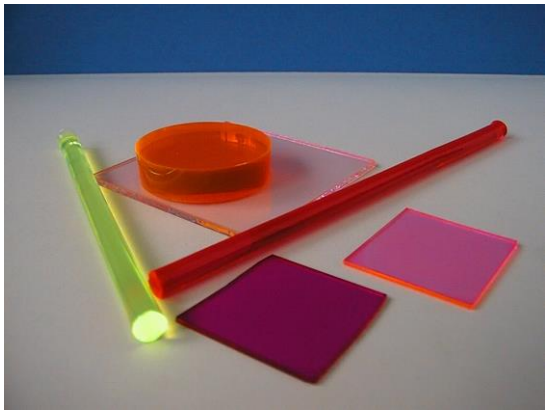
e/h transporter for OLEDs

photochromic
dithyenylethène









JP Boilot
F. Chaput

Composite coatings with nanocristals

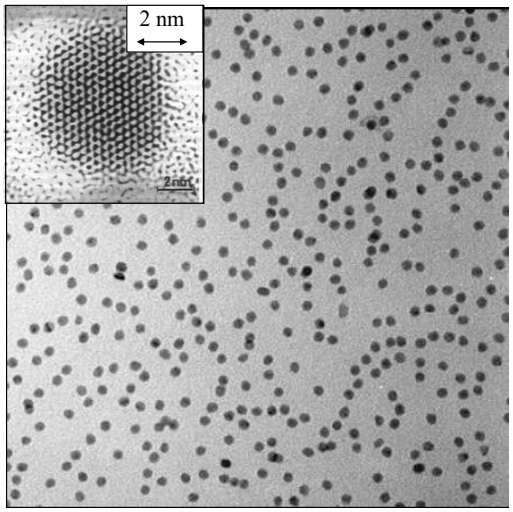
Nanocristals exhibit remarkable properties modulated by size / shape / surface…

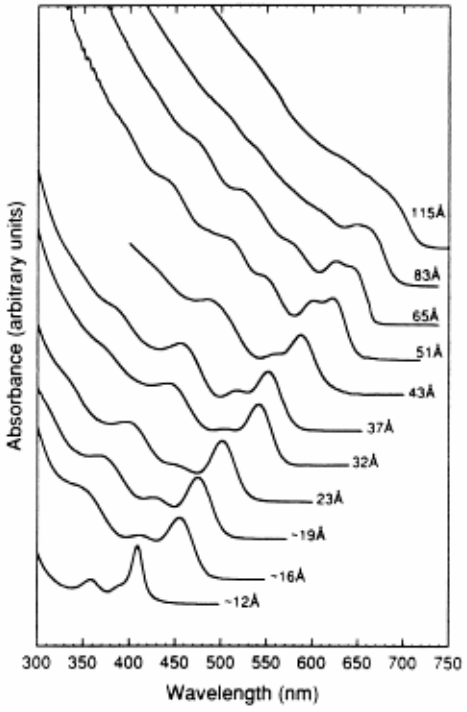
Absorbance / luminescence / (photo)catalysis / transport …

Alexei Ekimov

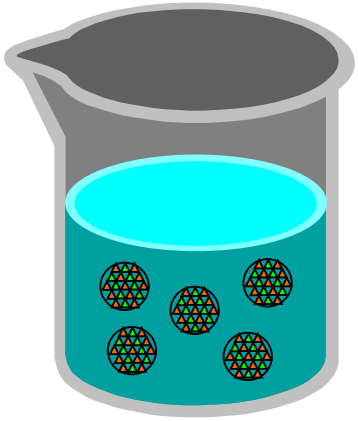
Composite coatings with nanocristals

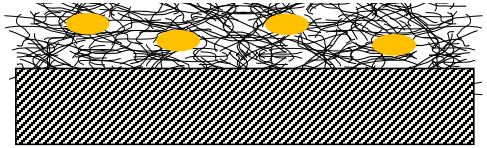
Remarkable ability to control nanocrystals size/shape/dispersion





Mougi Bawendi
C. Murray / D. Norris

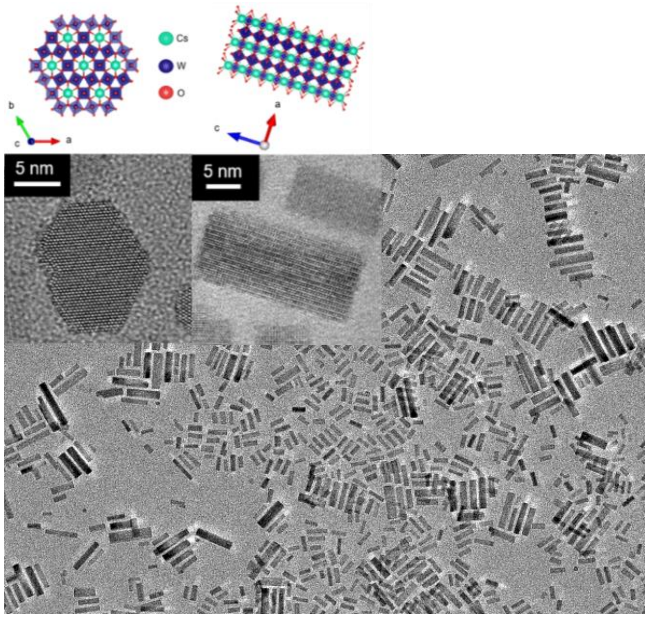




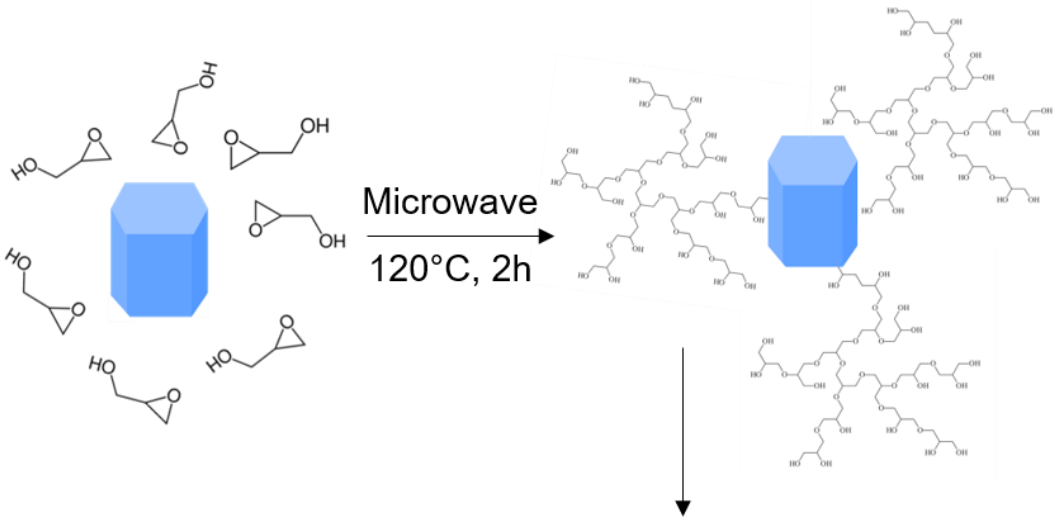
Dispersion issue…

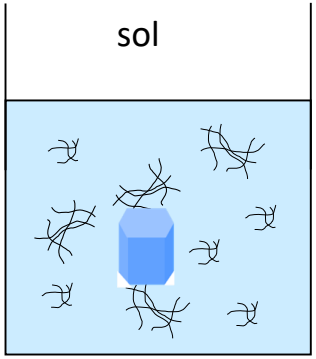
Composite coatings with nanocrystals – plasmonic $Cs_xWO_{3-\delta}$

Highly doped semiconductor exhibiting Near Infra-Red absorption



Dispersion issue : Glycidol functionnalization

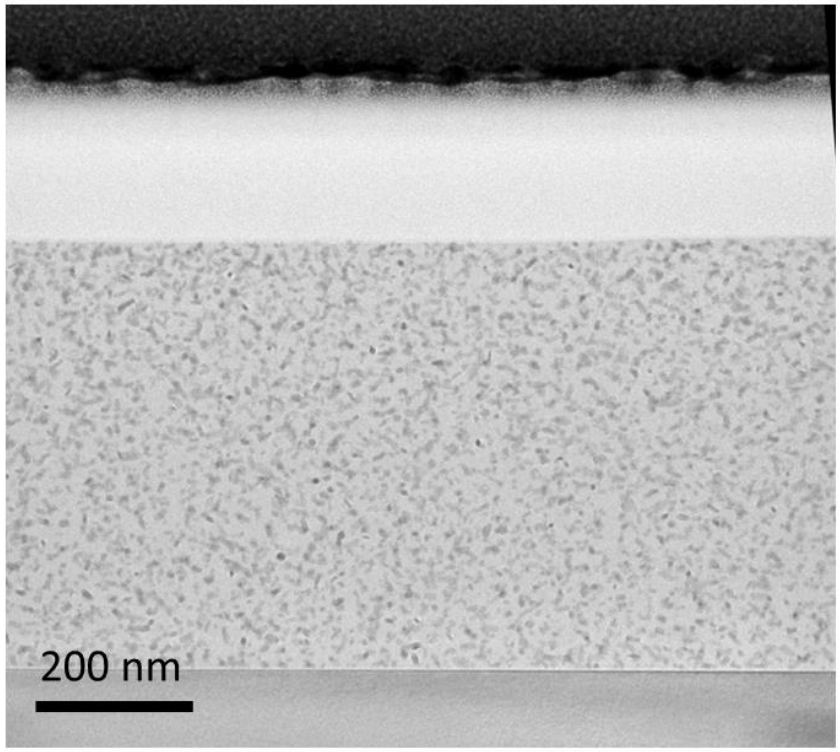


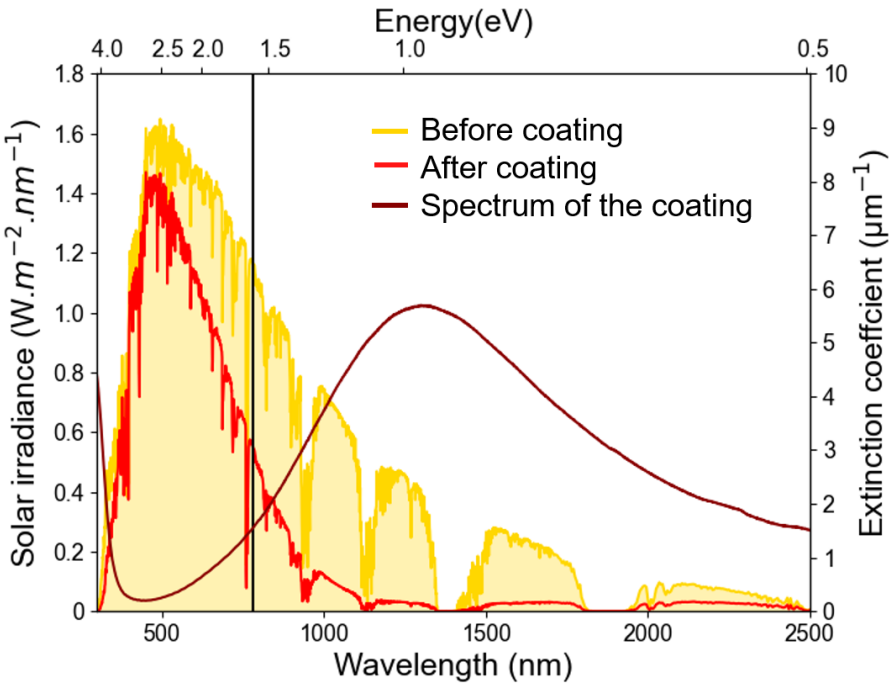


Louise Daugas, PhD – K. Lahlil - JW Kim

Composite coatings for solar NIR screening

TEM cross section of the composite

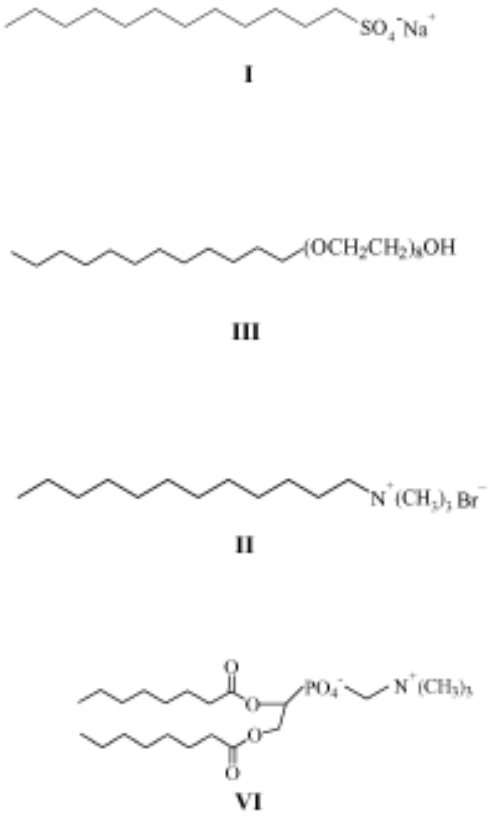


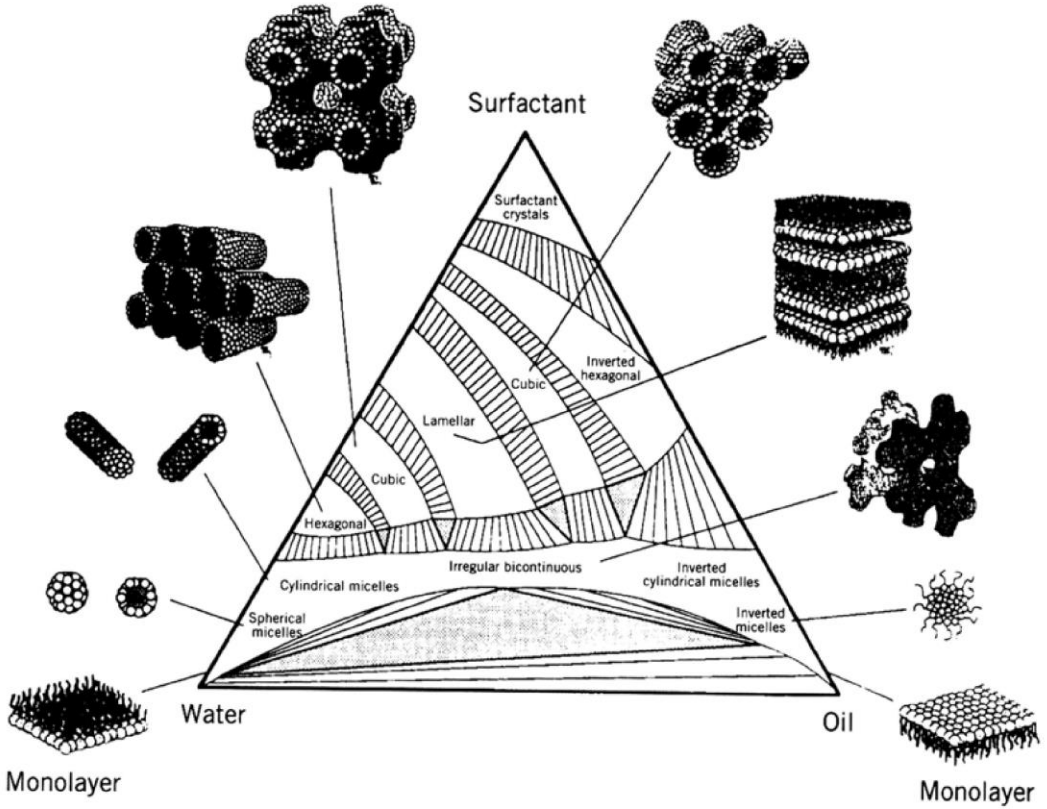


Thickness	T_{vis}	A_{NIR}
5.9 µm	80%	74%

Colloidal micellar assemblies

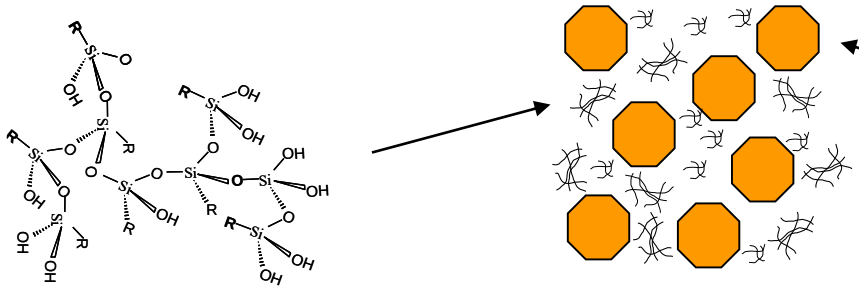
micellar assemblies of surfactants



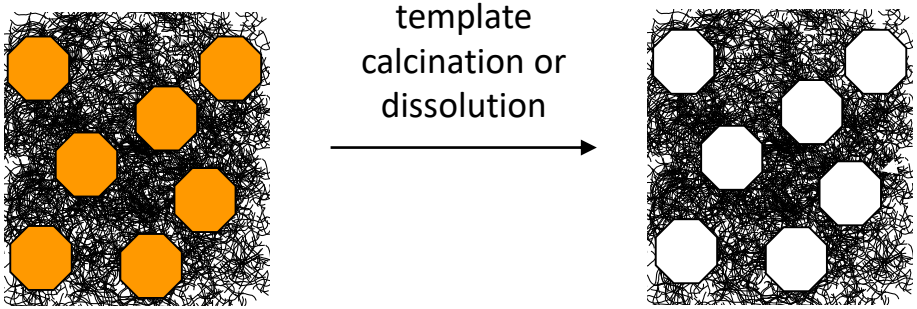


Porous silica coatings

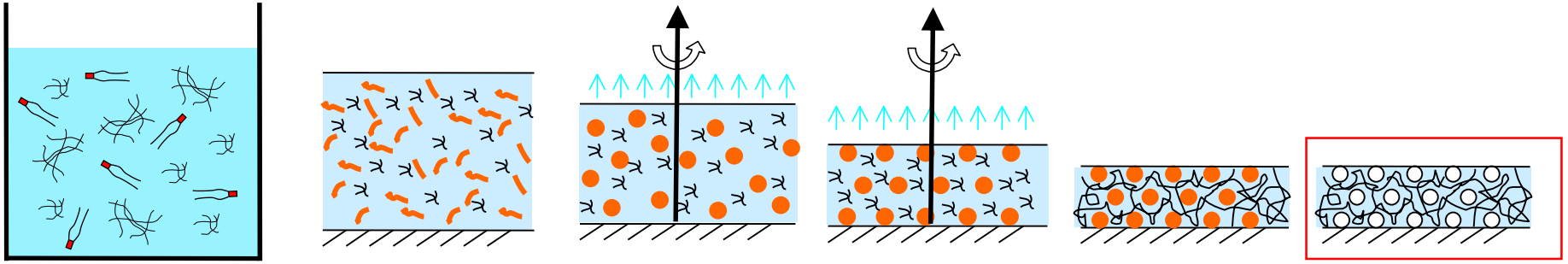
Following Mobile Oil Corp. work on the development of porous silica for catalysis



organic template / porogen agent

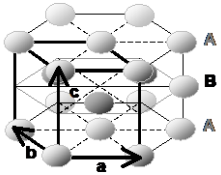


mesopore (2-10 nm)

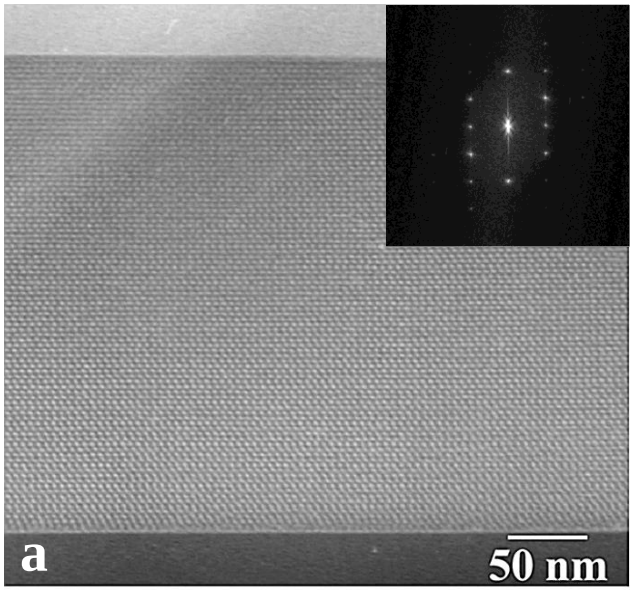


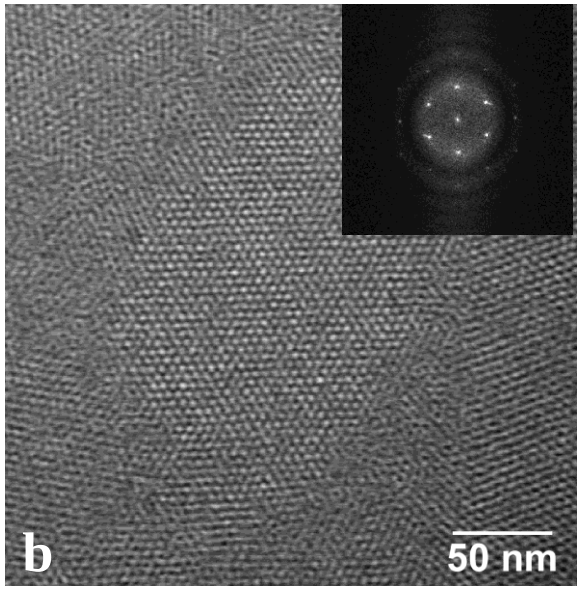
Catherine Jacquiod, Sophie Besson, Muriel Matheron

Organized mesopore 3D arrays

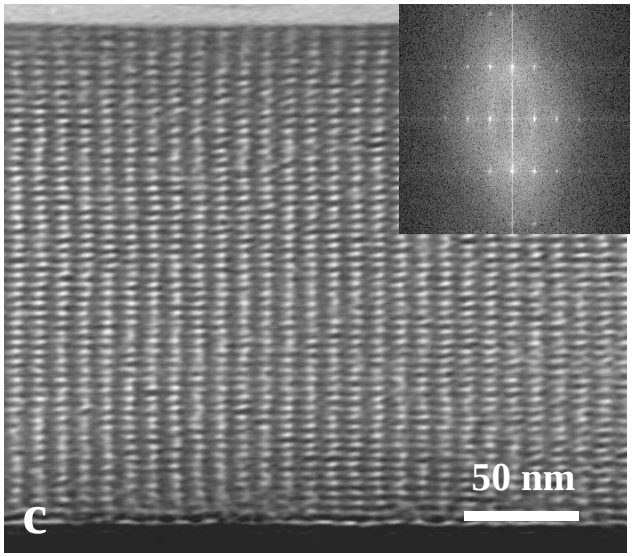


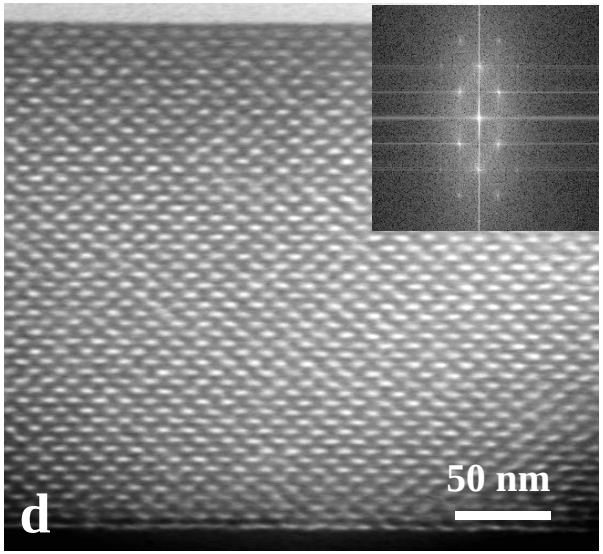
a=5.6 nm
c=6.2 nm



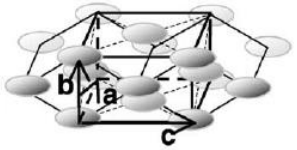


CTAB





Copolymère



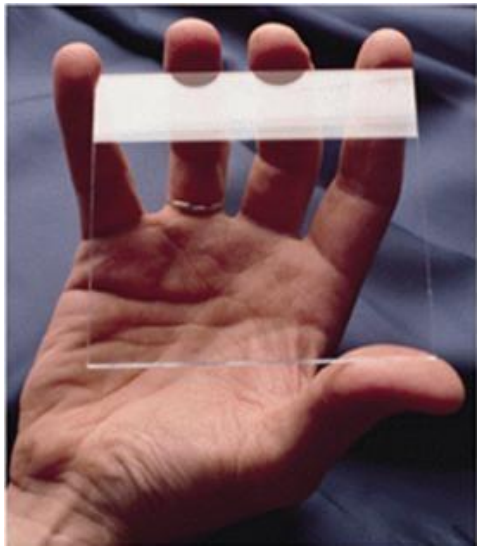
a=16 nm
b=10 nm
c=23 nm

Sophie Besson (PhD-SGR), Catherine Jacquiod

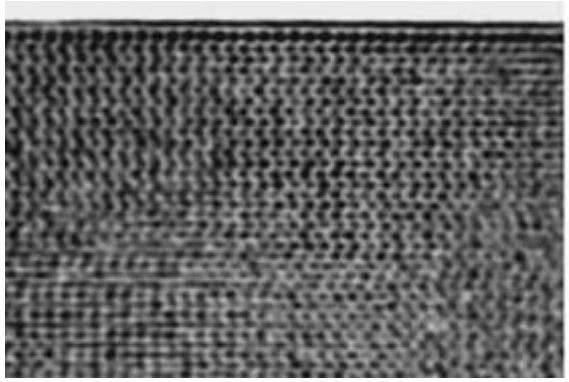
SAINT-GOBAIN

Functionnal coatings from mesoporous silica layers

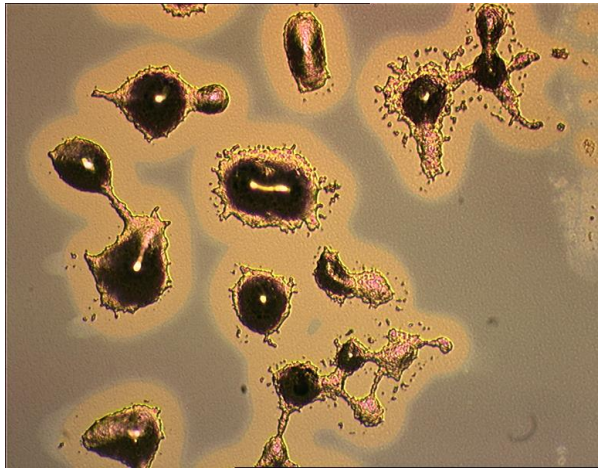
AR coatings



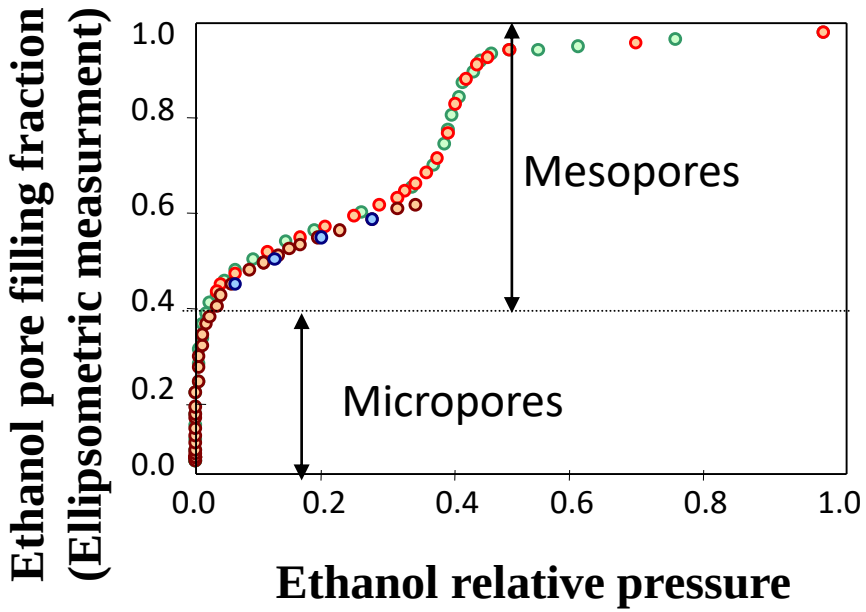
Host for organized arrays of NP

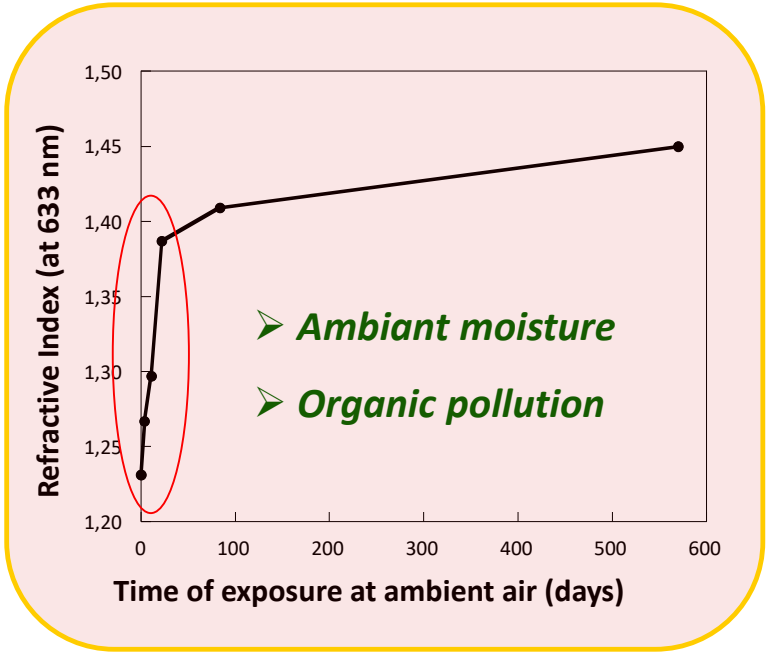


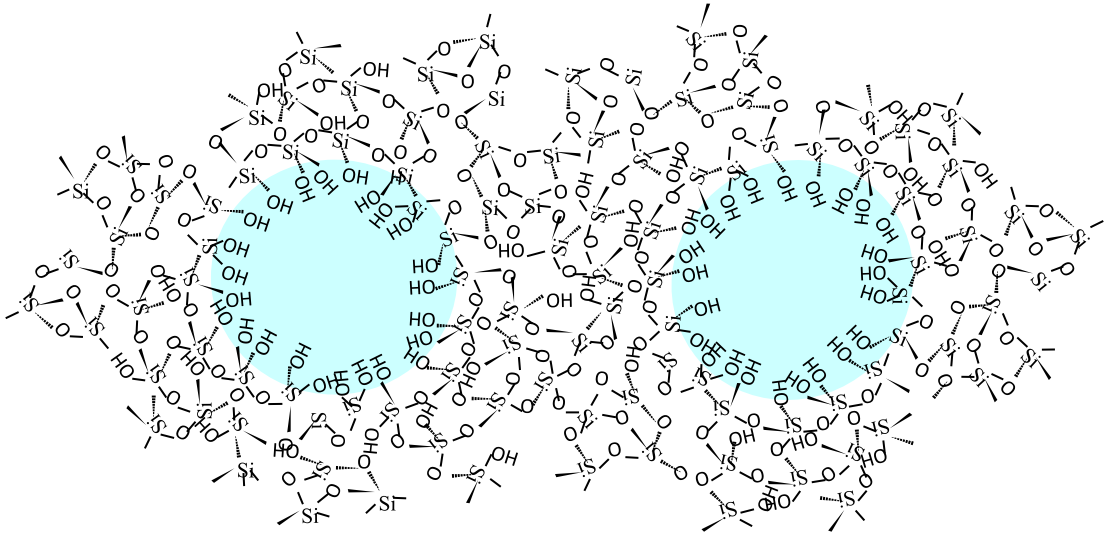
Reservoir for active molecules (photochromic, hydrophobic)



Capillary condensation and contaminent adsorption



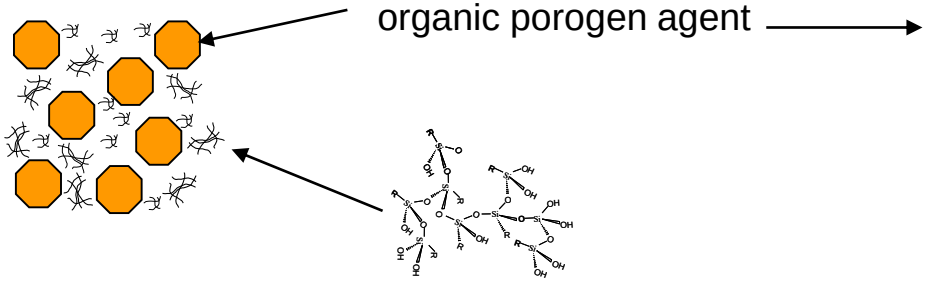


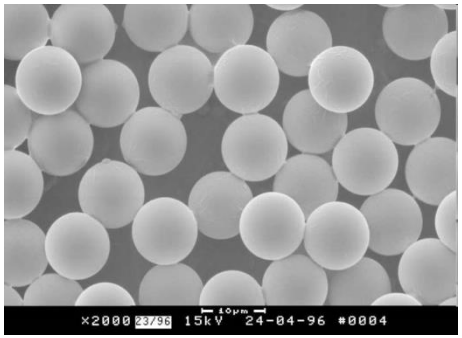


Kelvin law :
Increase pore size!

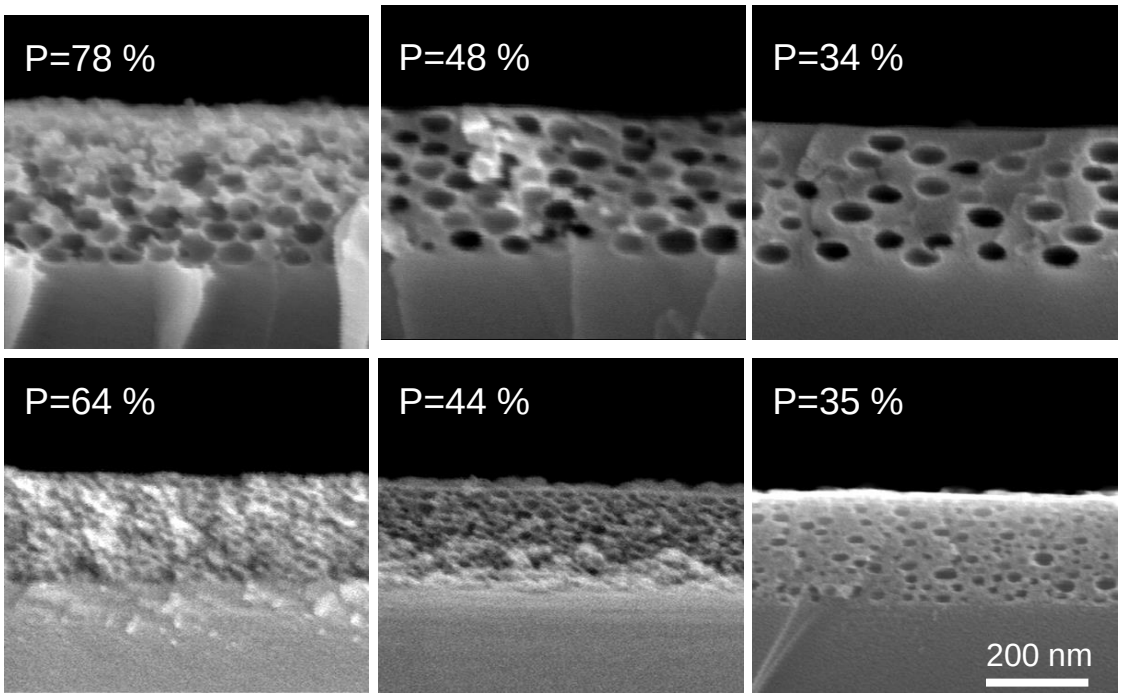
Microporous to macroporous

A. Huignard / S. Besson





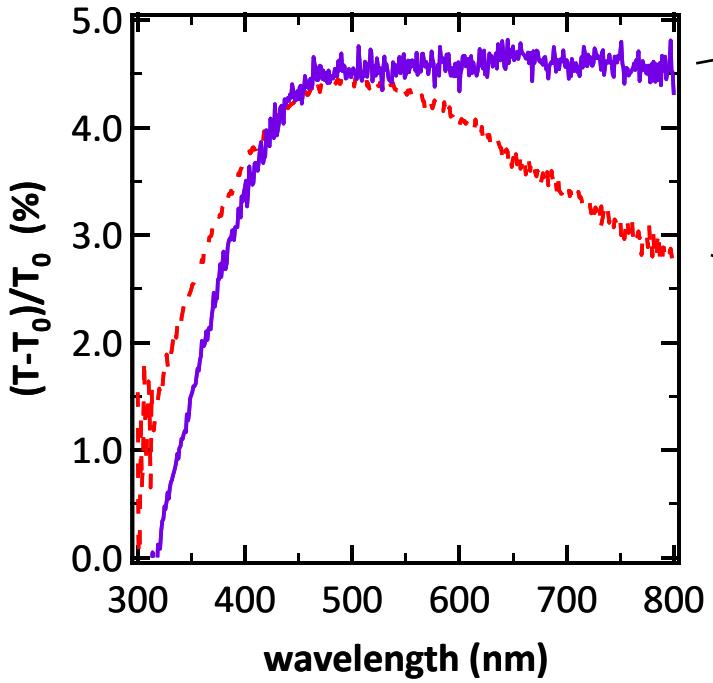
latex spheres
30-100 nm

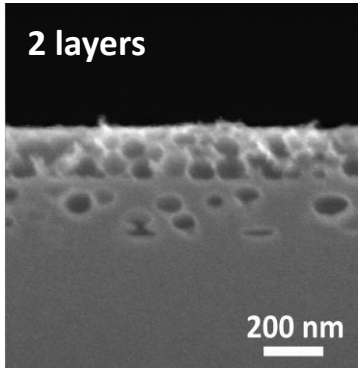


Adjustable porosity
Dense silica walls

High stability toward ageing

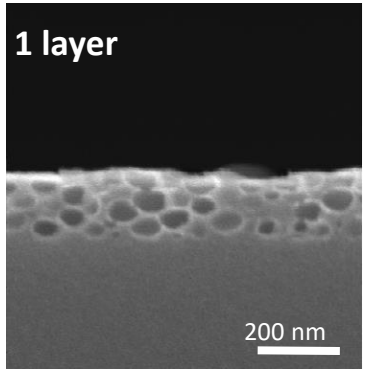
AR coatings for photovoltaics





n = 1.12

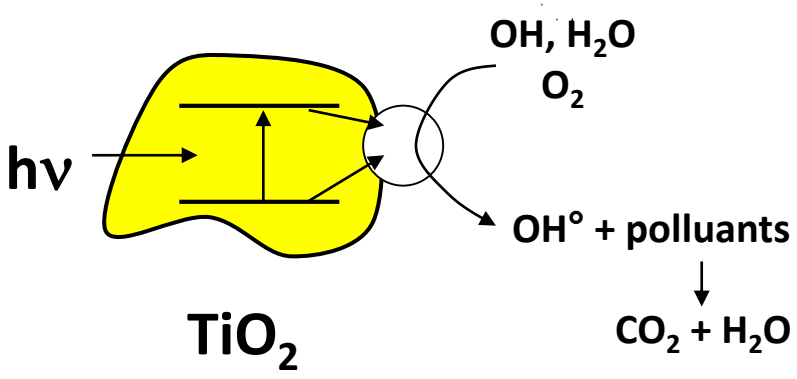
n = 1.34

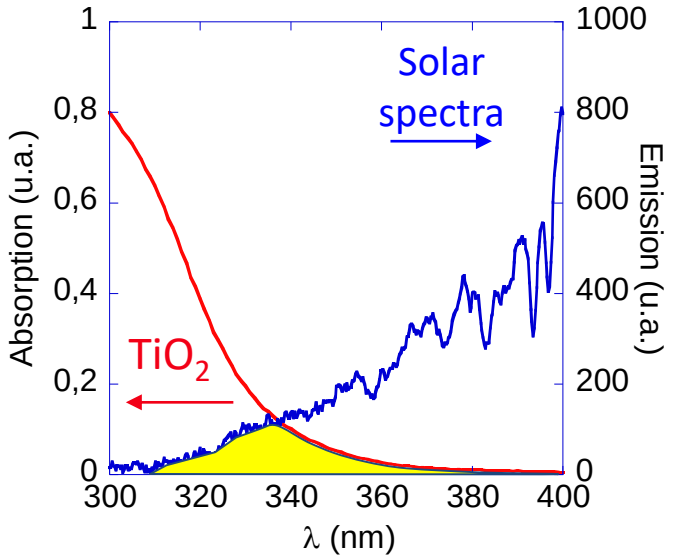


n = 1.23

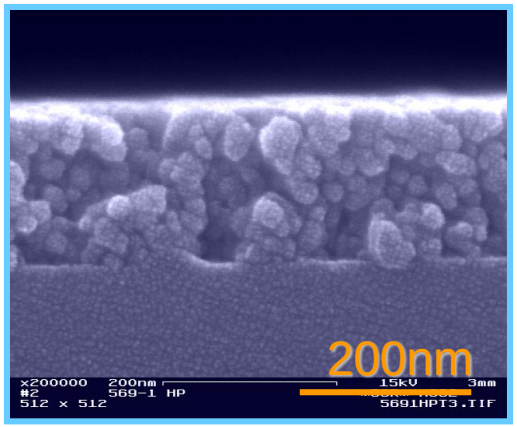
SGG commercial product

Photocatalytic coatings





SAINT-GOBAIN

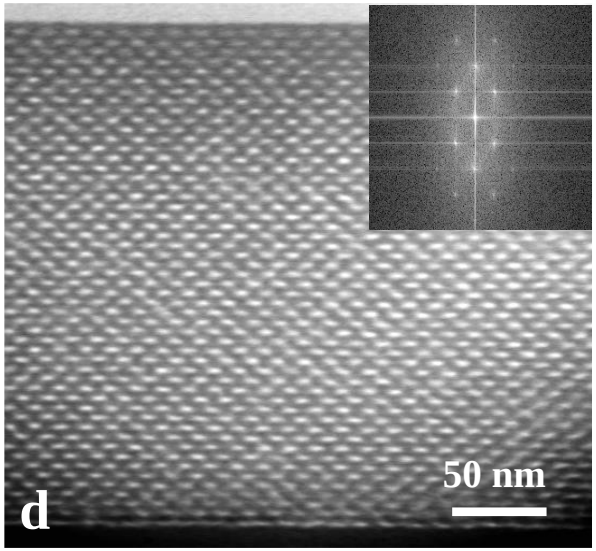


SGG Bioclean :

Photocatalysis and hydrophylicity

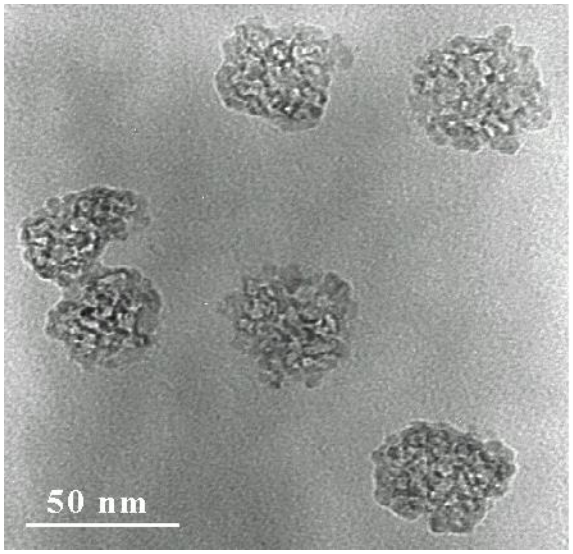
- Enhanced performance : optimized microstructure and visible light activation

Highly porous photocatalytic coating

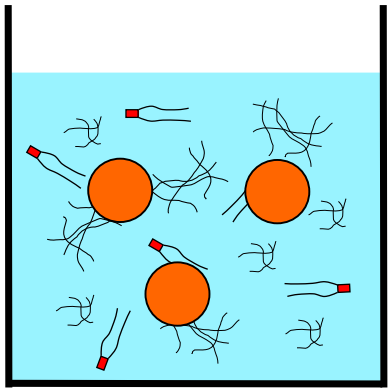


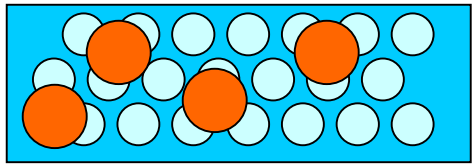
Mesoporous silica

+

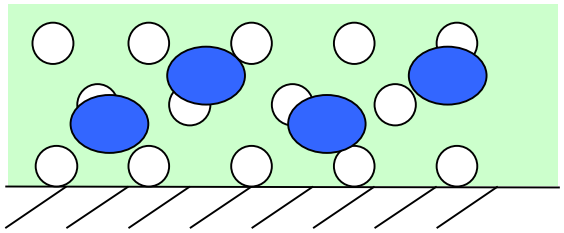


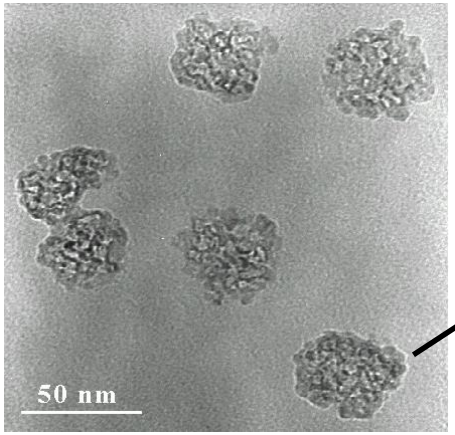
TiO_2 preformed colloidal particles (commercial)

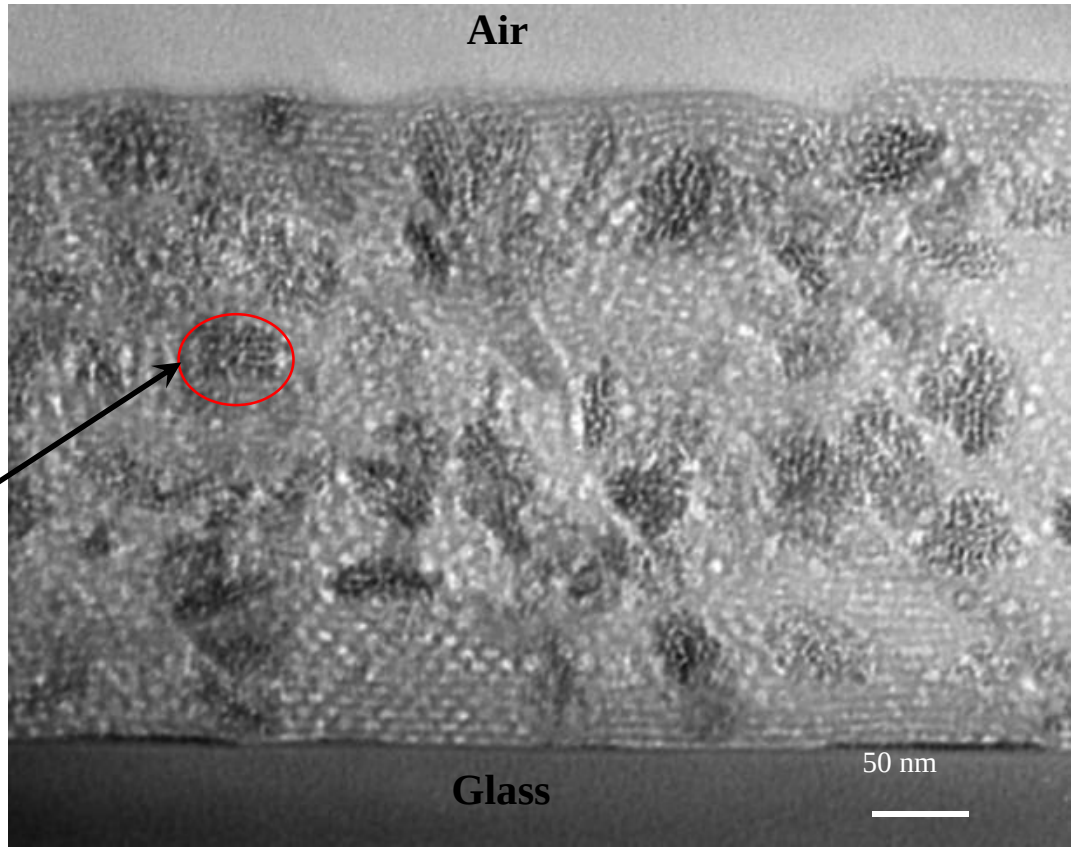




Enhanced performance





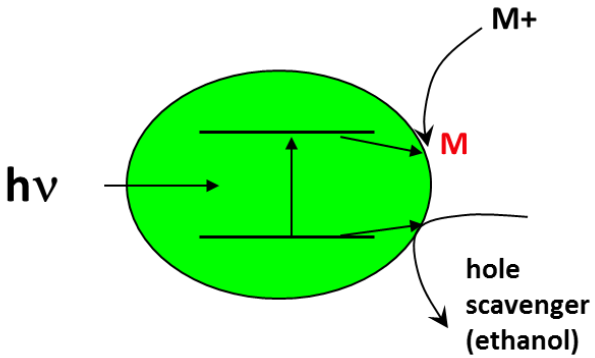


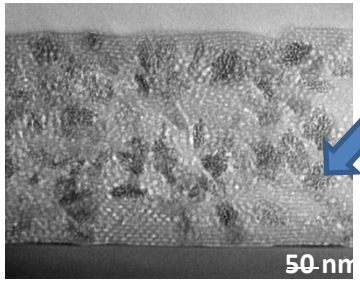
- x10 improvement of photocatalytic quantum yield
- Applications under low UV conditions
- Visible activation through N doping

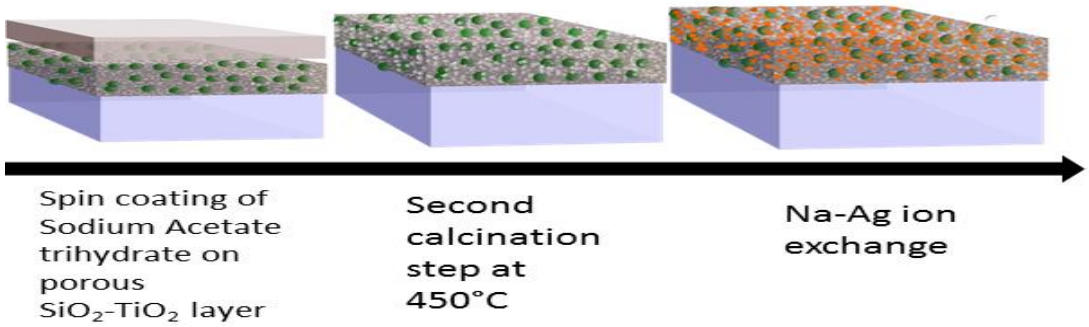
Clarisse Durand, Morgan Gohin, Emmanuelle Allain – Sophie Besson - Léthicia Guéneau – Nicolas Chemin

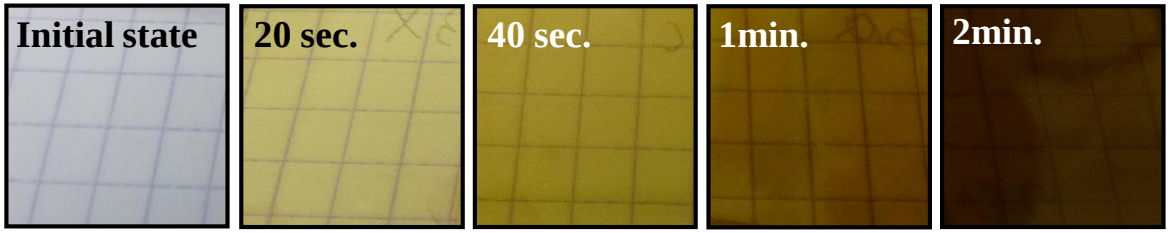
SAINT-GOBAIN

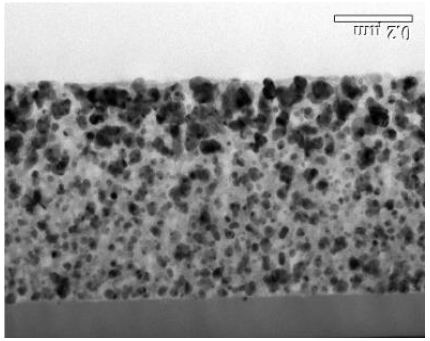
Photocatalytic reduction toward metal/dielectric nanocomposites





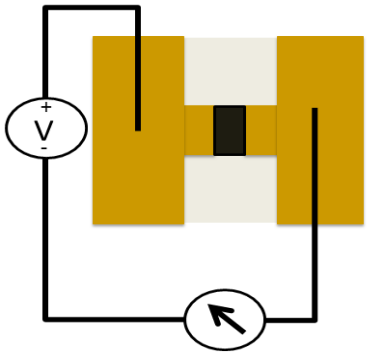


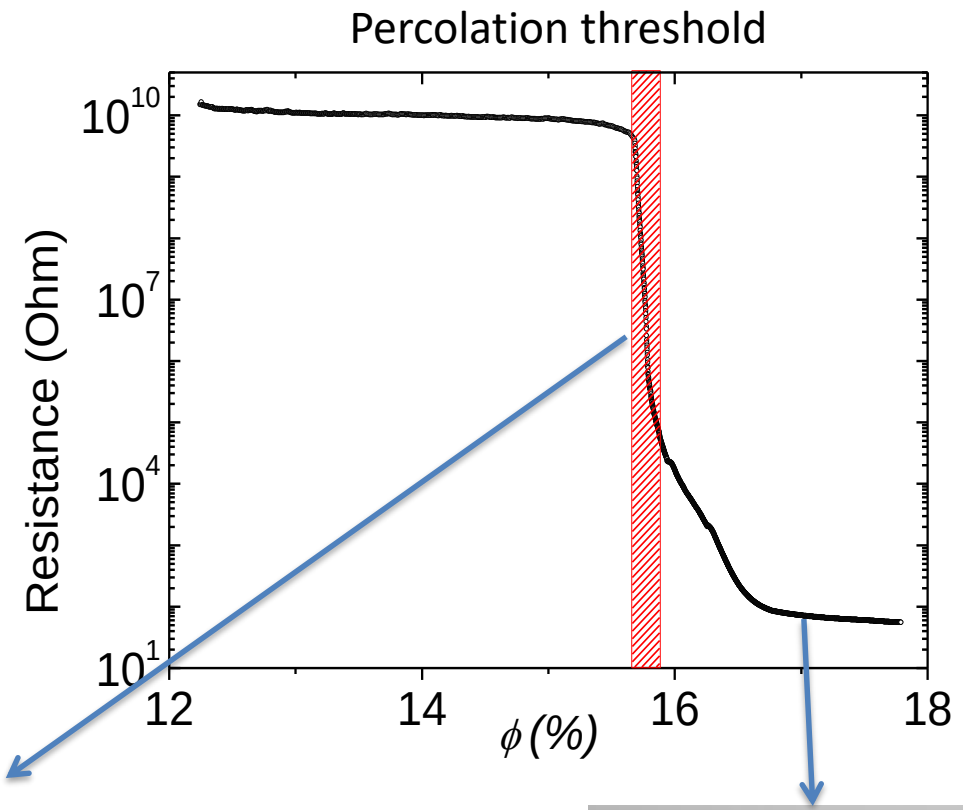




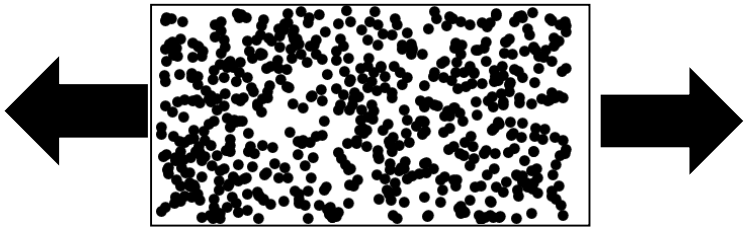
T. Das Gupta, J. Corde (CNRS PhD)

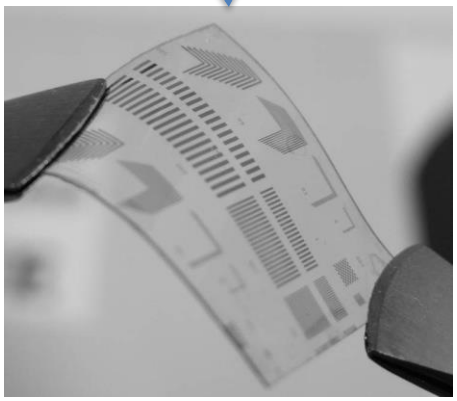
Tunable metal loading - Insulator to metal transition





Piezoresistive device

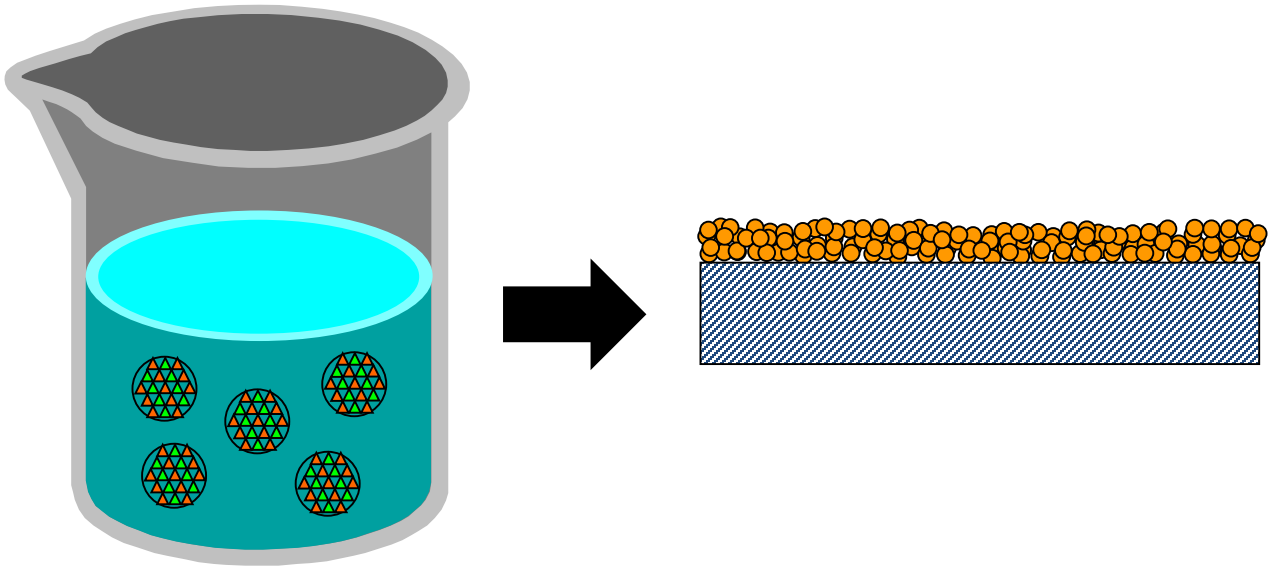




Patterned electrodes

Joëlle Corde, T. Das Gupta (CNRS PhD)

Coatings from nanoparticles



TiO_2

Silica

Gold

Silver

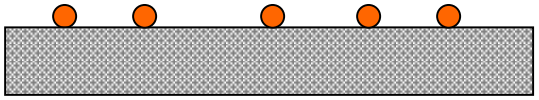
Diamond

YVO_4:Eu

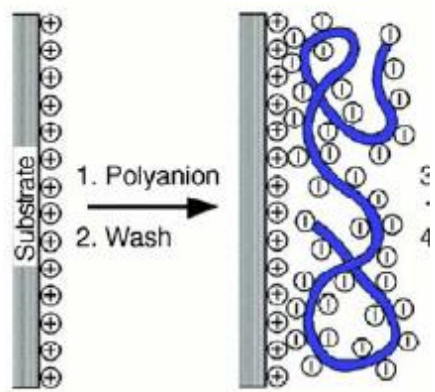
LaPO4

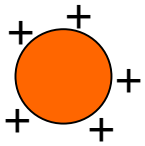
YAG:Ce

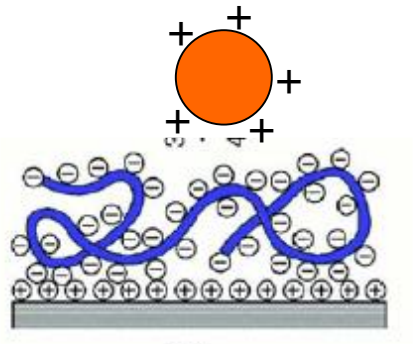
Particles grafting on surfaces

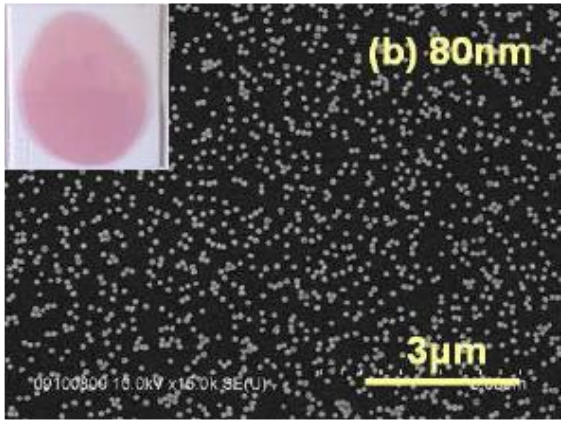


Electrostatic grafting :









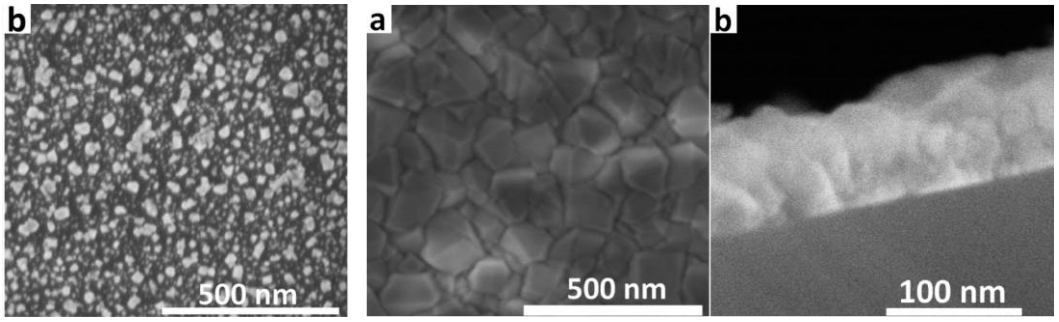
SAINT-GOBAIN

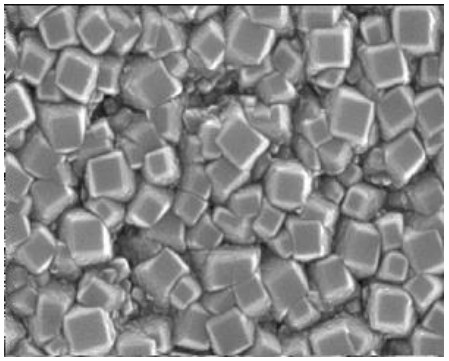
Gold particles for plamon exaltation in luminescent coatings

- very simple to achieve with good density control (random)

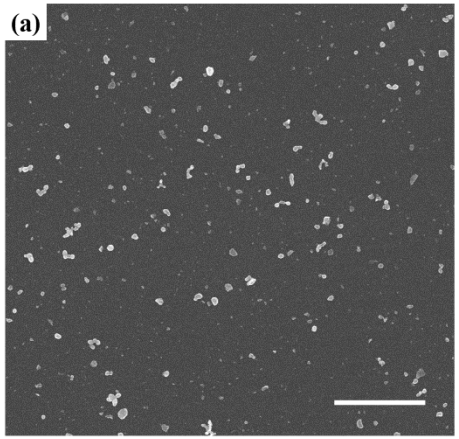
Liquid deposition of NP and CVD growth

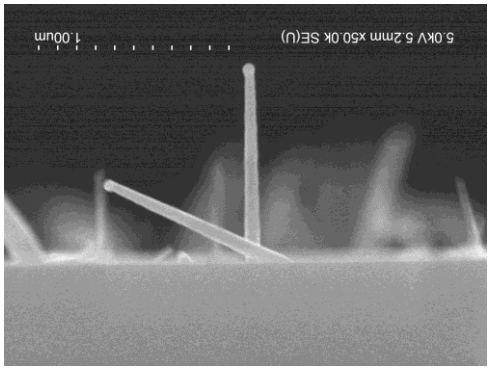
Diamond nanoparticles as seeds for CVD diamond films

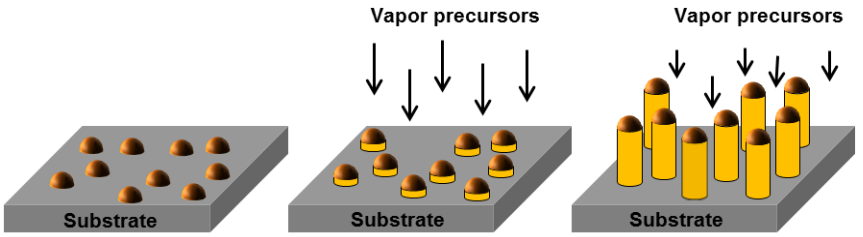




SnO_2 catalyst for PECVD growth of Si nanowires







L. Dai (CNRS – LPICM)

Rare earth doped nanoparticles

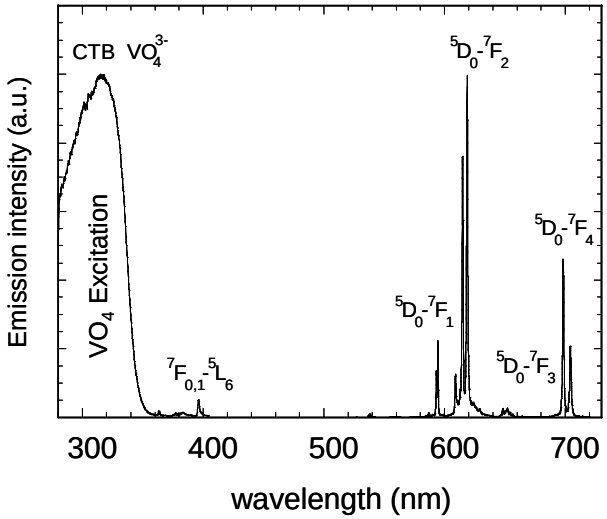
$YVO_4:Eu^{3+}$

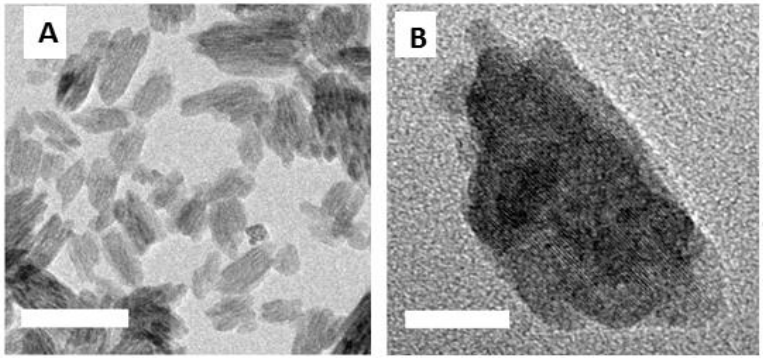
$LaPO_4:Ce^{3+}$

$LaPO_4:Eu^{3+}$

$LaPO_4:Ce^{3+},Tb^{3+}$

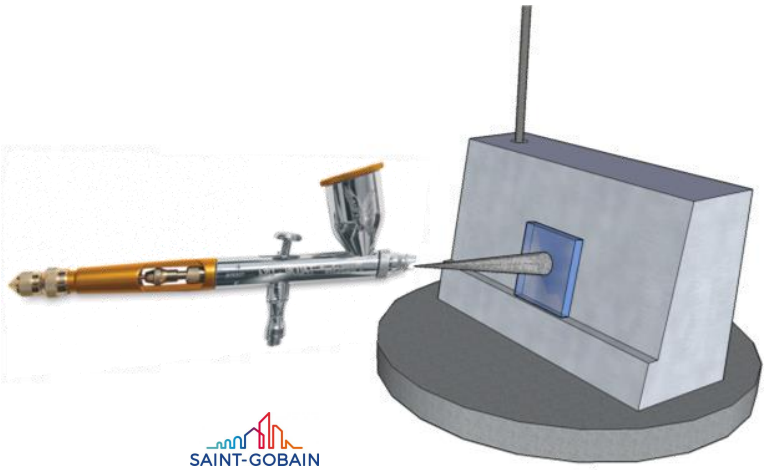
$Y_3Al_5O_{12}:Ce^{3+}$

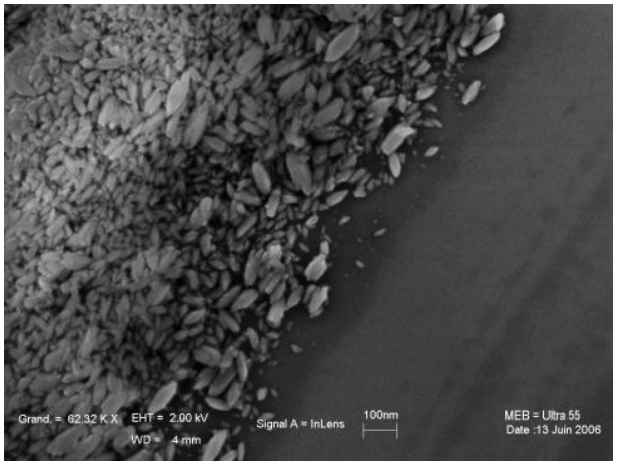


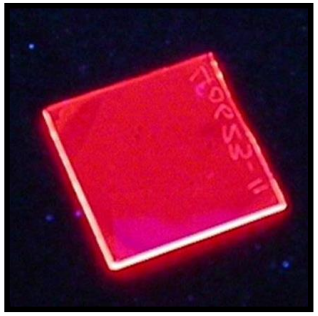


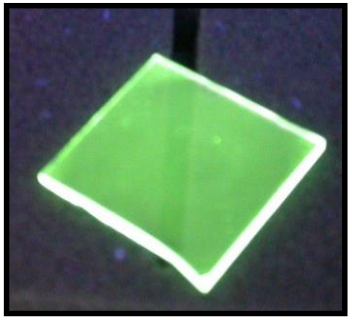
A. Huignard (CNRS PhD), G. Mialon (CNRS PhD), L. Devys (CNRS PhD)

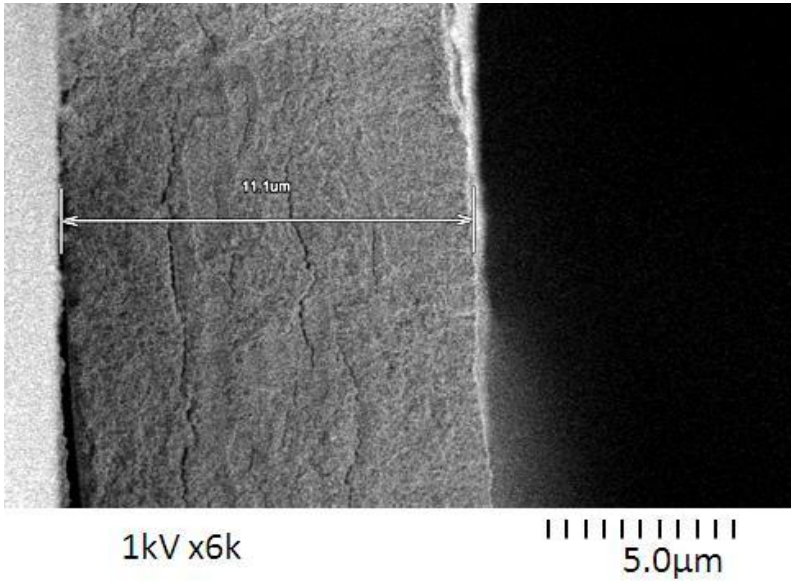
Spray deposition of luminescent thin films





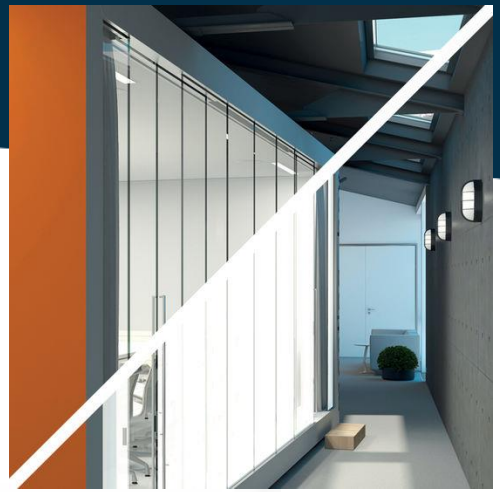




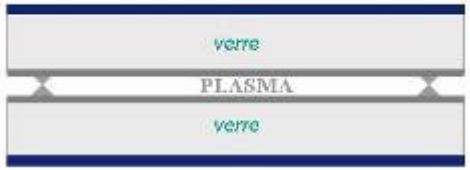


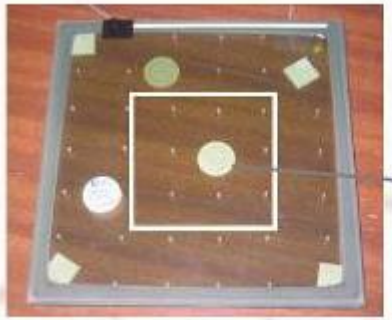
Arnaud Huignard – Vincent Rachet - Blaise Fleury (CNRS PhD)

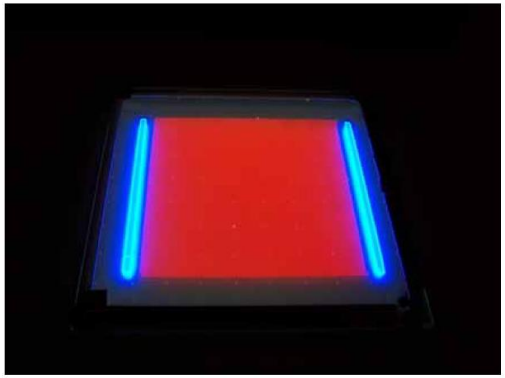
Transparent Planilum – SPOT Project



Lampe plane Planilum®





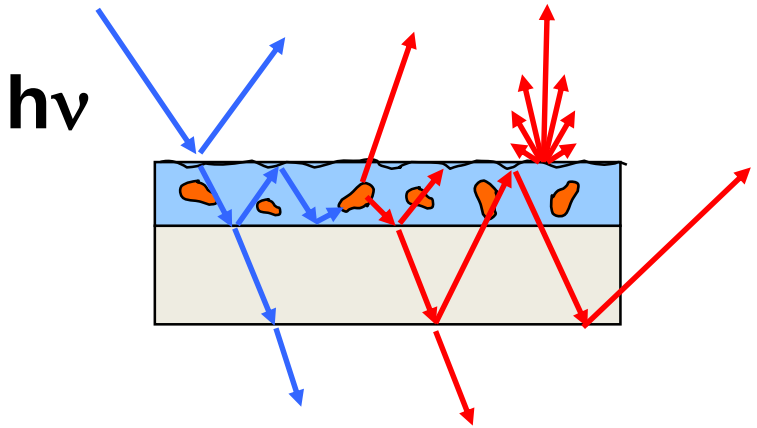


Lampe plane 1 face – env. 3μm
1600 V à 40 kHz
Nanoborate : 06VBF552

Lampe plane 1 face – env. 3 à 4 μm
1600 V 40 kHz

Aranud Huignard, Vincent Rachet (SPOT ANR Project with Rhodia)

Light management in optical coatings

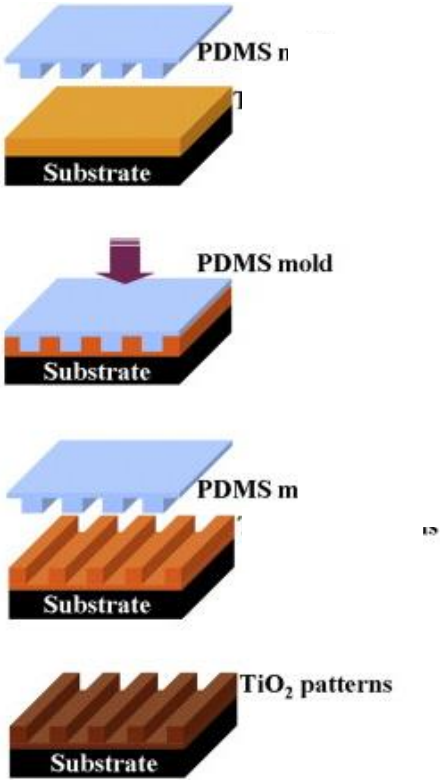


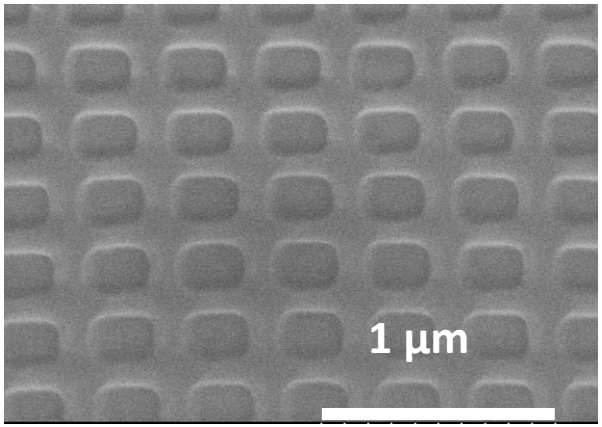
Functionnality optimization :

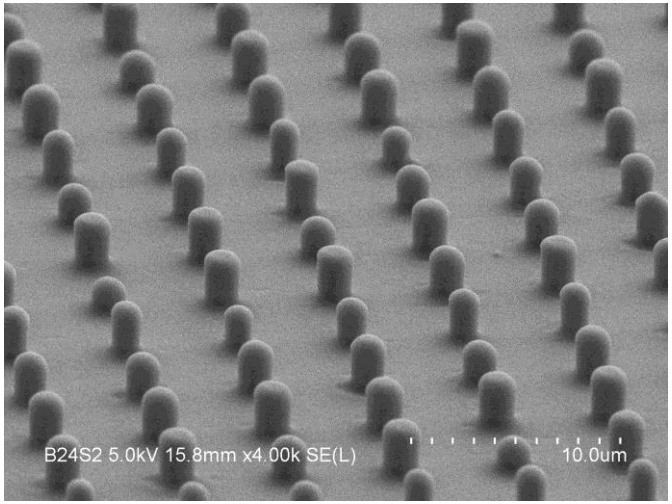
intrinsic nature of the optically active material	**Structure of the active material**	**Global film microstructure**
• absorption cross section • internal quantum yield • photostability	• morphology, size • local microstructure	• **light propagation**

➢ Design of the film dielectric microstructure for optimized light propagation

Structuration through embossing / imprint

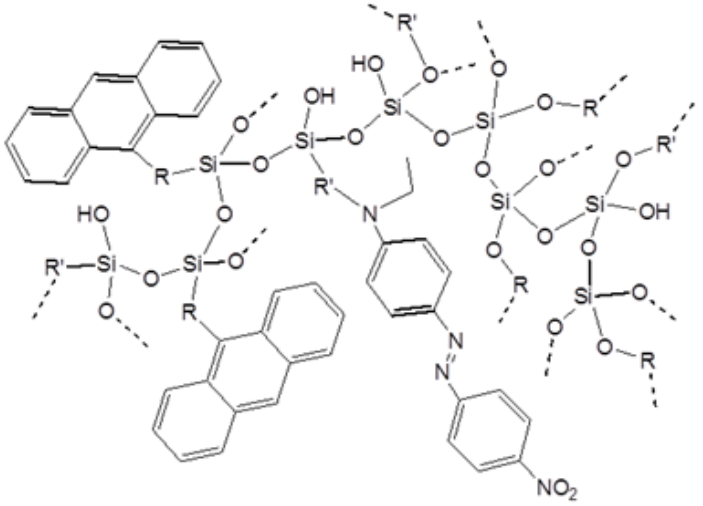


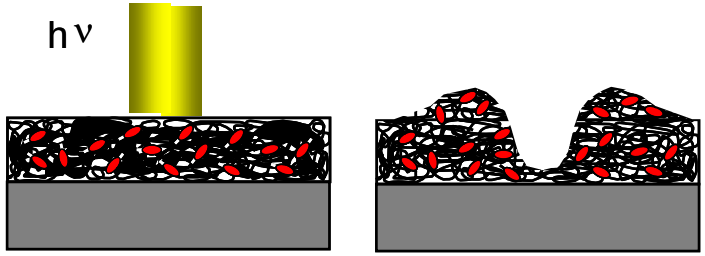


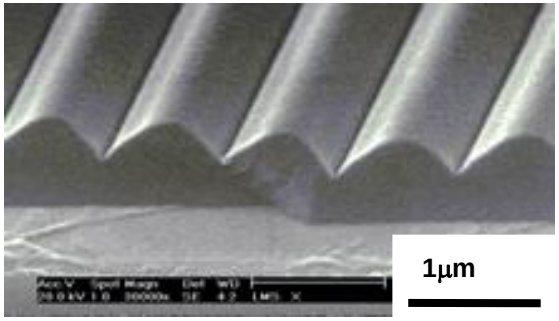


Amélie Revaux (CNRS PhD), Lucie Devys (CNRS PhD), Barbara Brudieu (SGR PhD) + SVI (Alban Letailleur…)

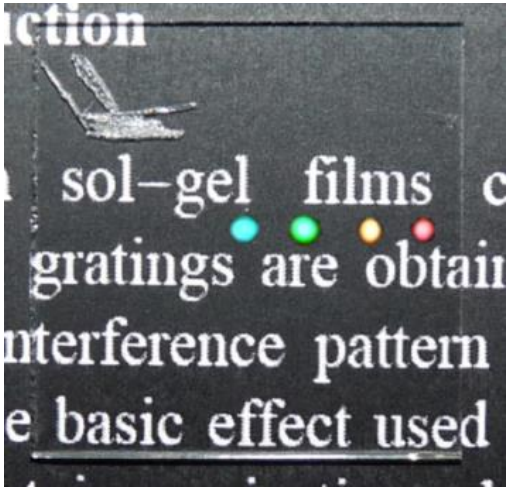
Photostructuration of sol-gel azo-based coatings

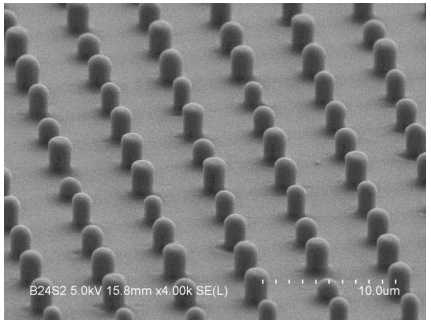


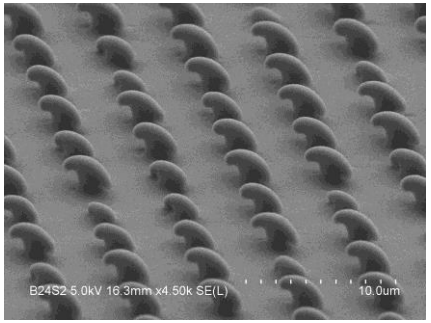




SAINT-GOBAIN

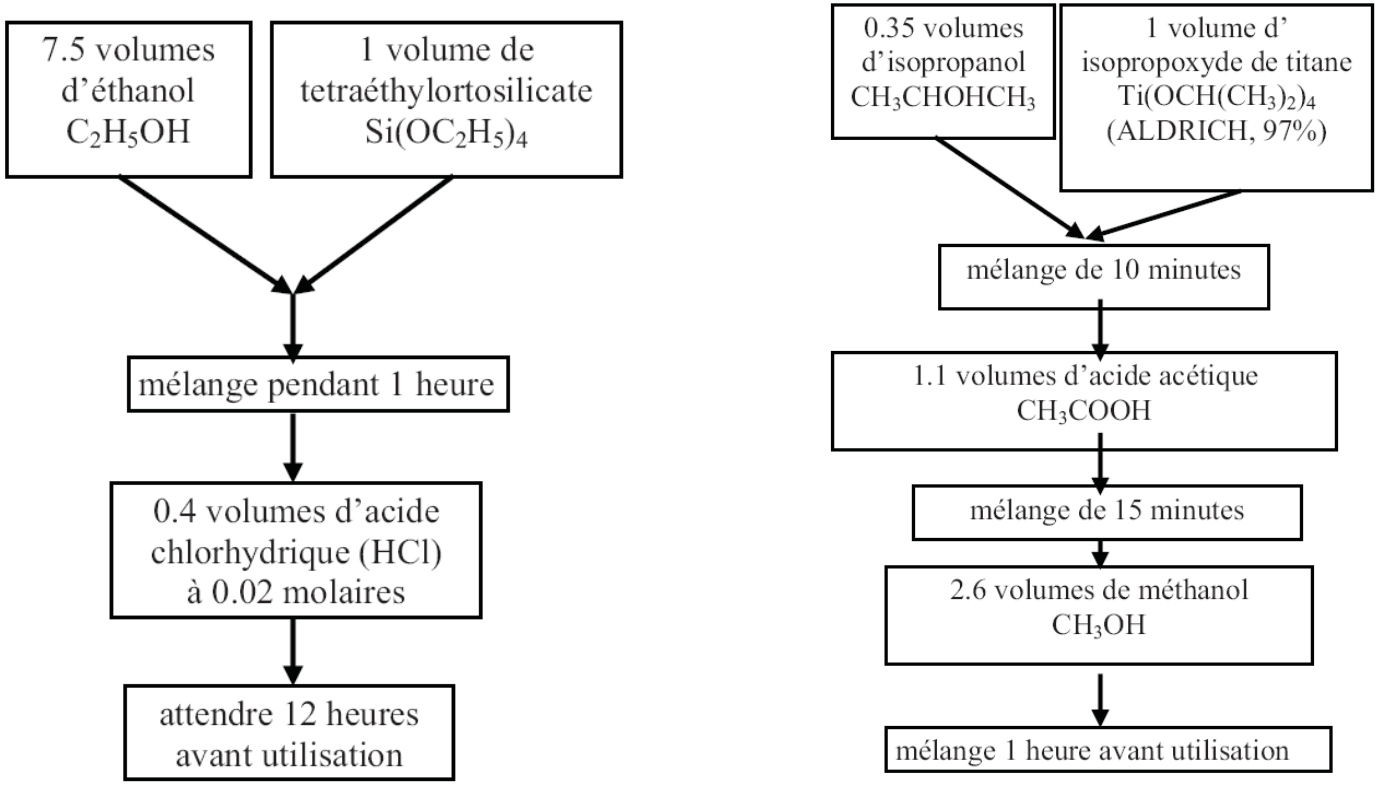




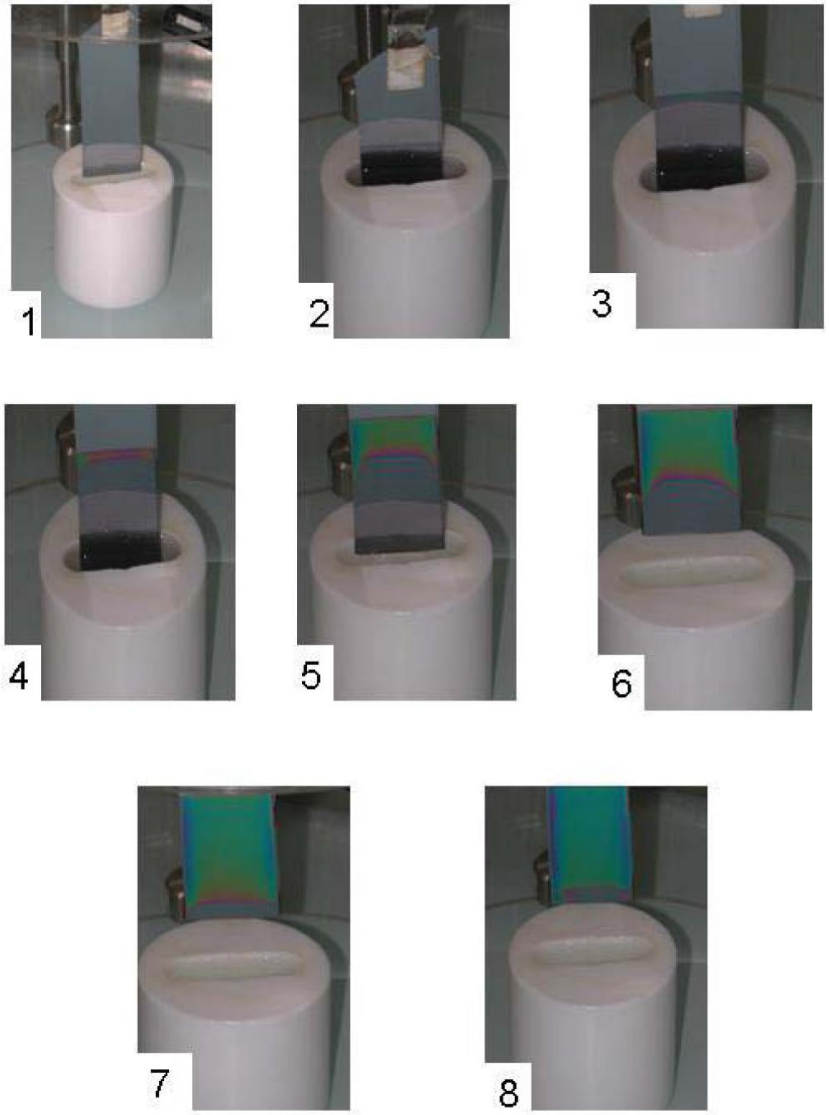


Nicolas Desboeuf (CNRS PhD), Sylvain Chevalier (CNRS PhD)

Bragg mirrors elaboration from sol-gel TiO_2/SiO_2



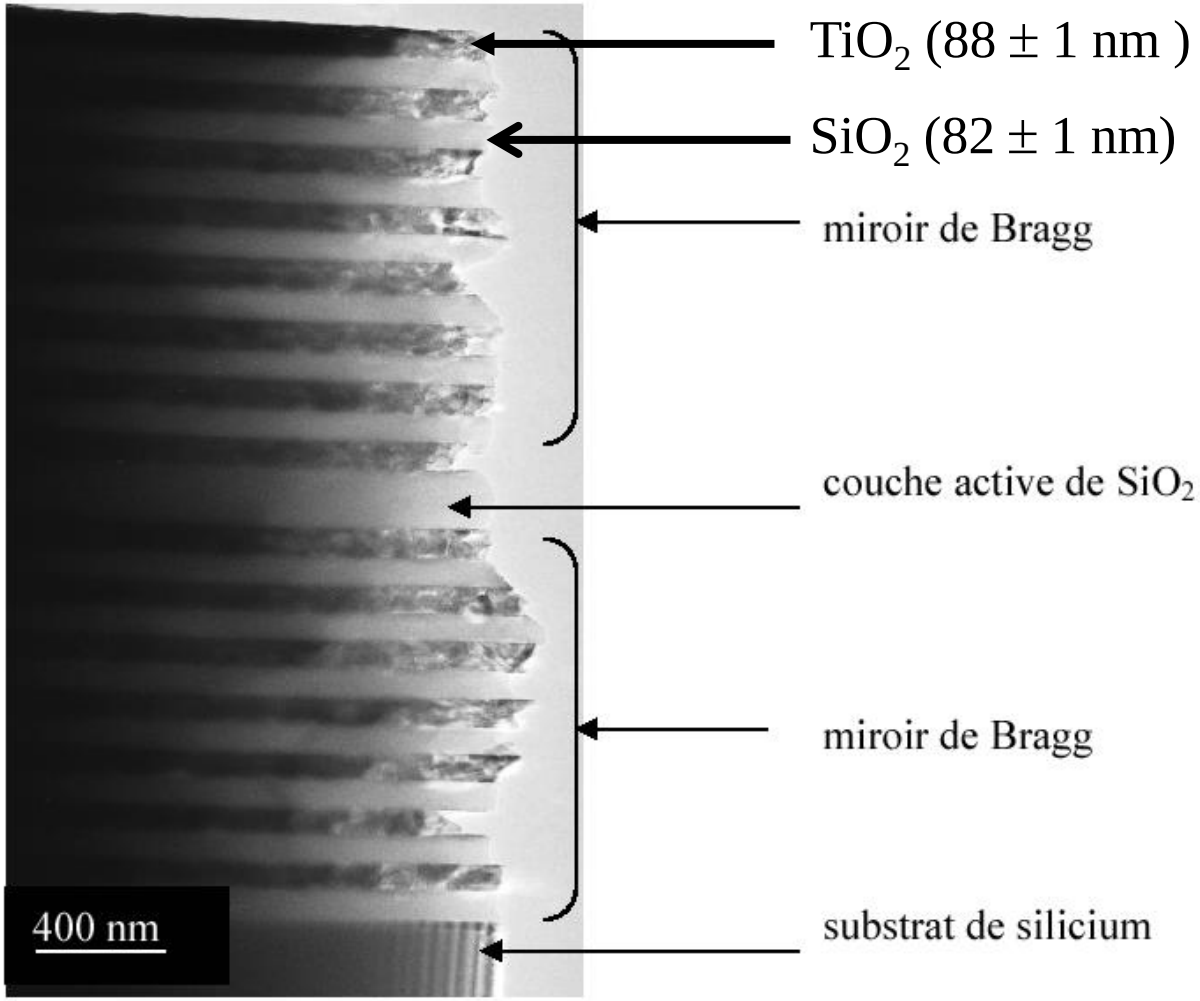
Alternate dip-coating deposition



Compensation des contraintes (900°C - 1 s)

60 couches alternées SiO_2 / TiO_2 sans craquelures ou rugosité importante

Bragg mirros elaboration from sol-gel TiO_2/SiO_2



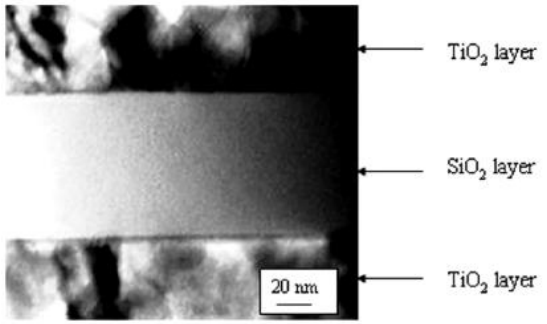


Fig. 4. TEM enlarged image of a cavity shown in Fig. 3. The SiO_2 middle layer is inserted between two TiO_2 layers.

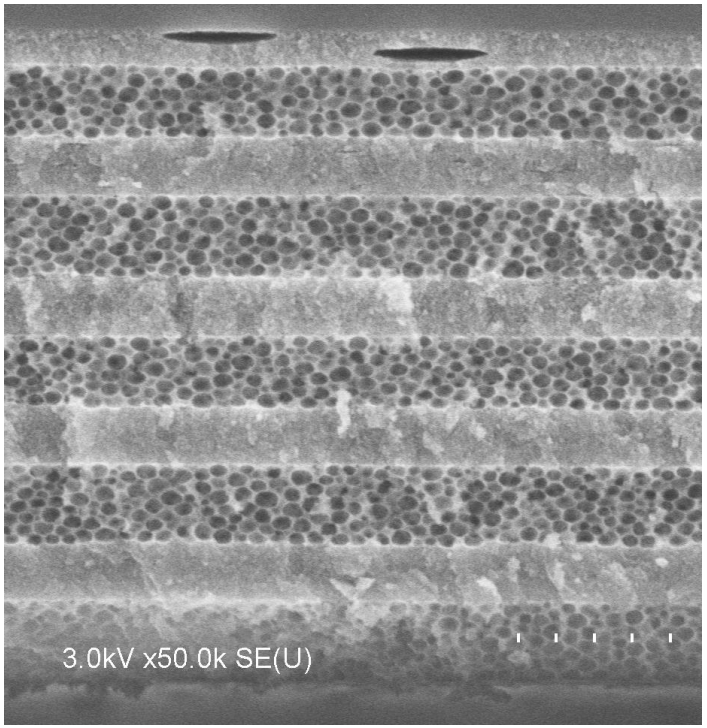
PhD thesis Sébastien Labaste, Lyon

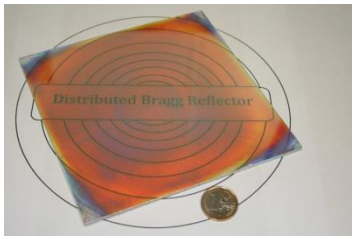
Bragg mirrors

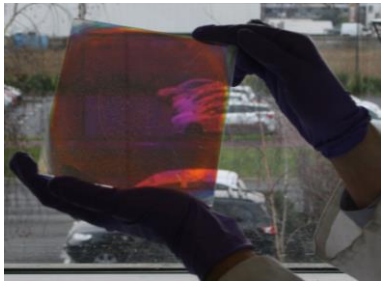
Macroporous silica layers (n=1,24)

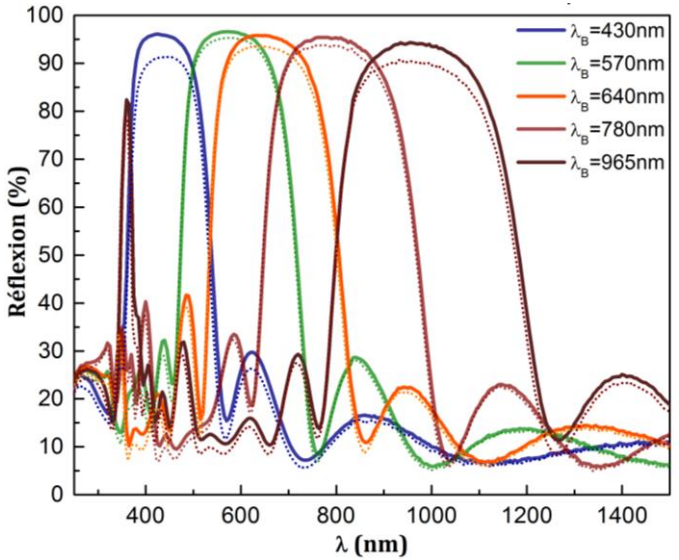
Polymeric TiO_2 (n=2,08)

SAINT-GOBAIN







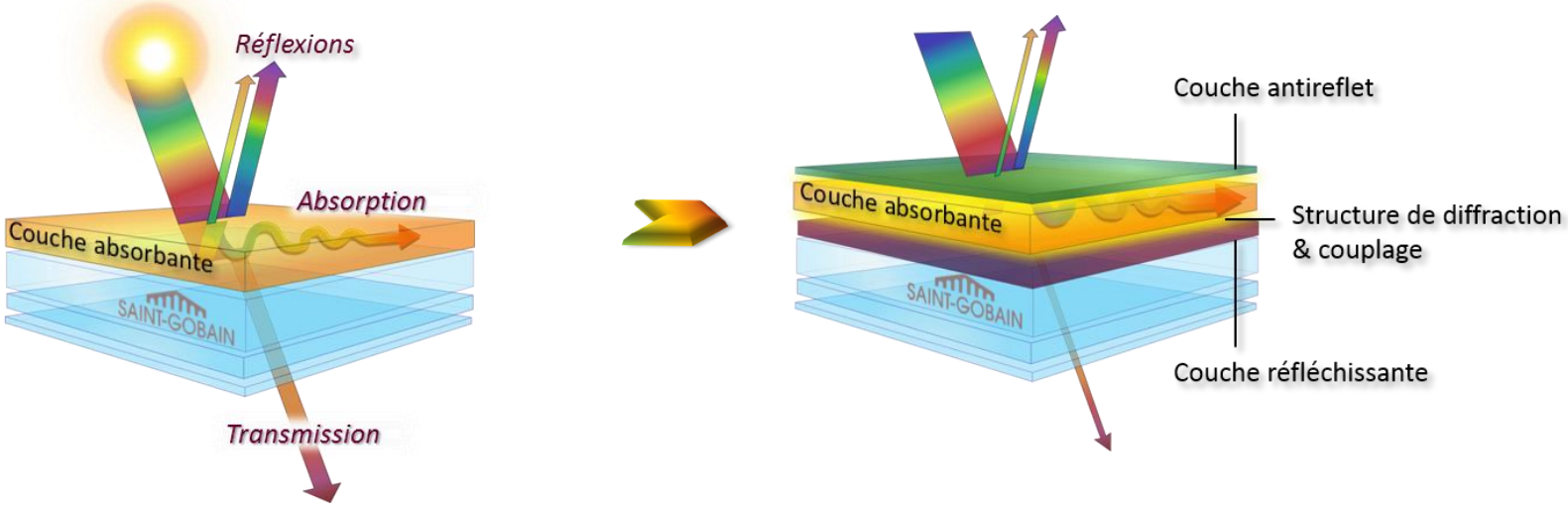


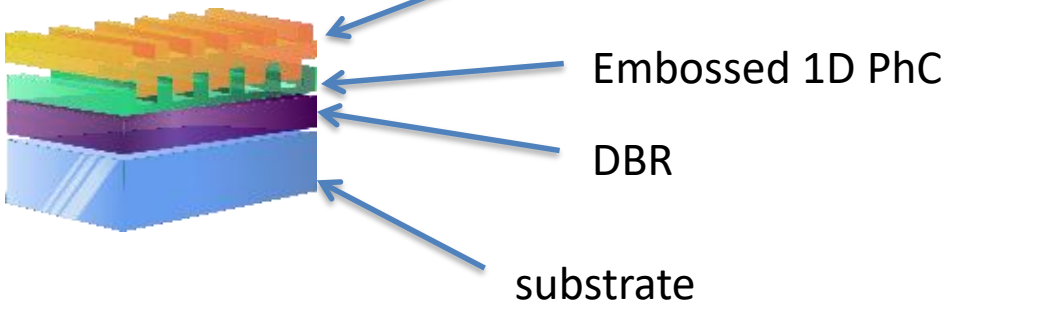
➢ Simple process, tunable properties

Barbara Brudieu (SGR PhD), Fabien Sorin, François Guillemot, Jérémie Teisseire

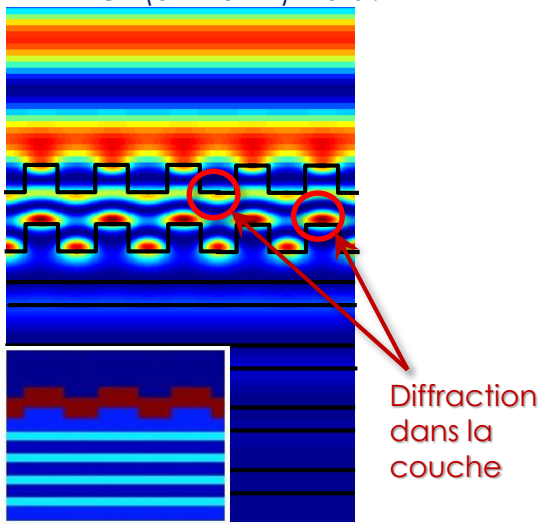
Light trapping in Photovoltaic absorbers

Increase of optical path length in absorbing layers



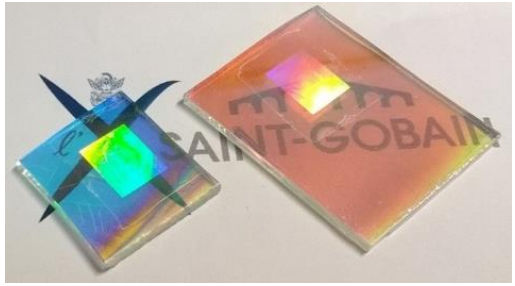


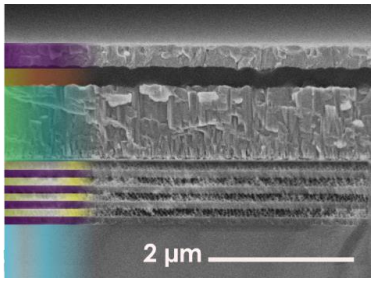
DBR + 1D CP (a=225nm) + a-Si:H

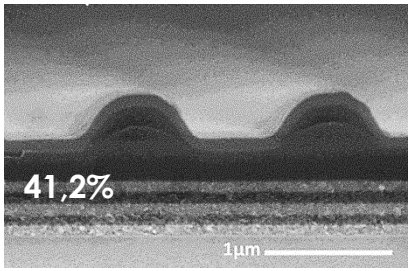


Fabien Sorin, Barbara Brudieu (SGR PhD), Jérémie Teisseire, Iryna Gozhyk

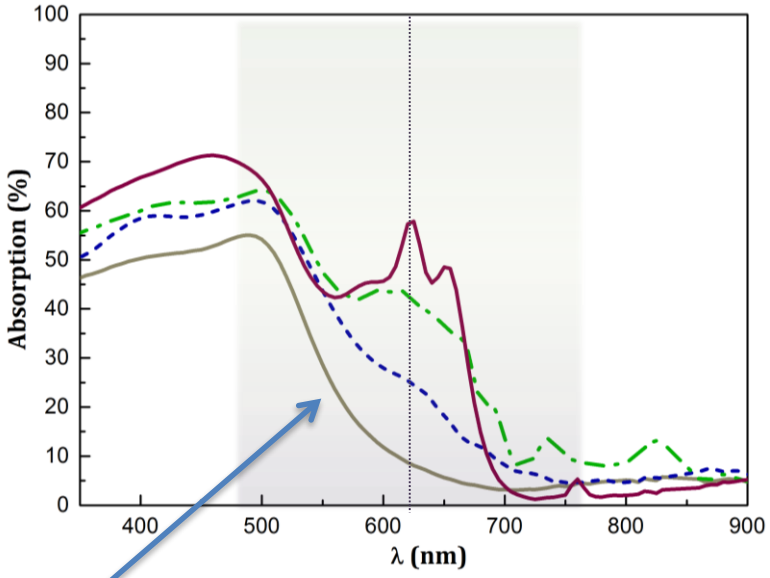
Exalted absorption in a-SiH layers



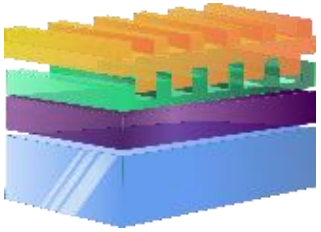


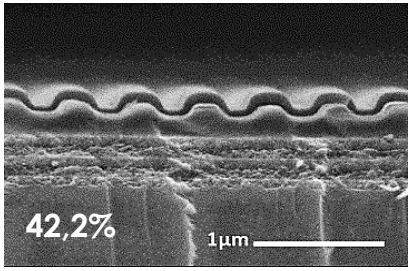


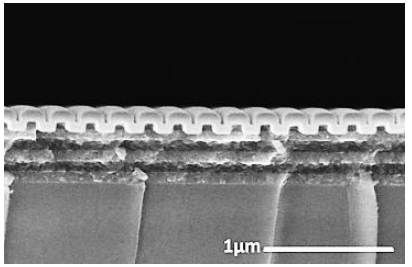
a-Si:H : 100nm

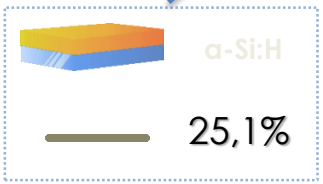


a-Si:H +
DBR + CP









A : P=1500nm — 34,3%

B : P=500nm — 41,2%

D : P=225nm — 42,2%

Barbara Brudieu (SGR PhD), Fabien Sorin, François Guillemot, Jérémie Teisseire, Iryna Gozhyk

Conclusion

- Chemistry and liquid desposition routes offer unique opportunities for innovative products

- Gap between lab and industrial product
  - Academic collaborations
  - hard work of process engineering

- Interactions between wet coatings and PVD (magnetron) or CVD

- Important general issues:

  - Deposition processes, homogeneity over m^2 surfaces
  - Thermal treatments (laser…)
  - Binder silicate chemistry
  - Substrate/coating interactions
  - Strain control in sol-gel thin films

Acnowledgements

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Emmanuelle Alain
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Sylvain Chevalier
Capucine Cleret de Langavan

SGR – SVI

Jérémie Teissère
Iryna Goszhyk
Katia Burov

LPMC group

Jean-Pierre Boilot
Frederic Chaput
Khalid Lahlil
Isabelle Maurin
Simon Delacroix

SAINT-GOBAIN

Essilor

LABORATOIRE PMC

cnrs dépasser les frontières