



**UNIVERSITY OF ROME "LA SAPIENZA"**  
**NANOTECHNOLOGIES ENGINEERING**

**MEMBRANE APPLICATIONS IN  
NANOTECHNOLOGY:  
PRODUCTION OF NANOPARTICLES**

PROF. MARCO STOLLER

DEPARTMENT OF CHEMICAL MATERIALS ENVIRONMENTAL ENGINEERING

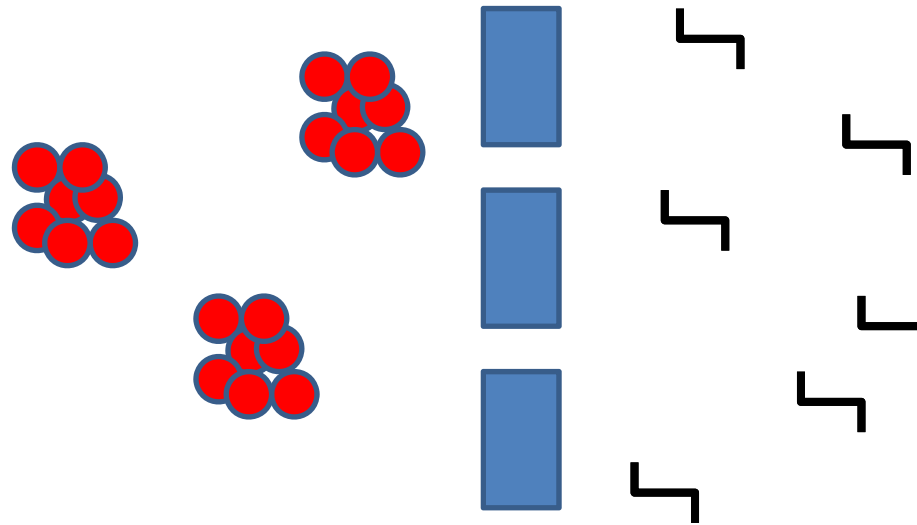
2<sup>ND</sup> FLOOR – ROOM 205

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# PRINCIPLE

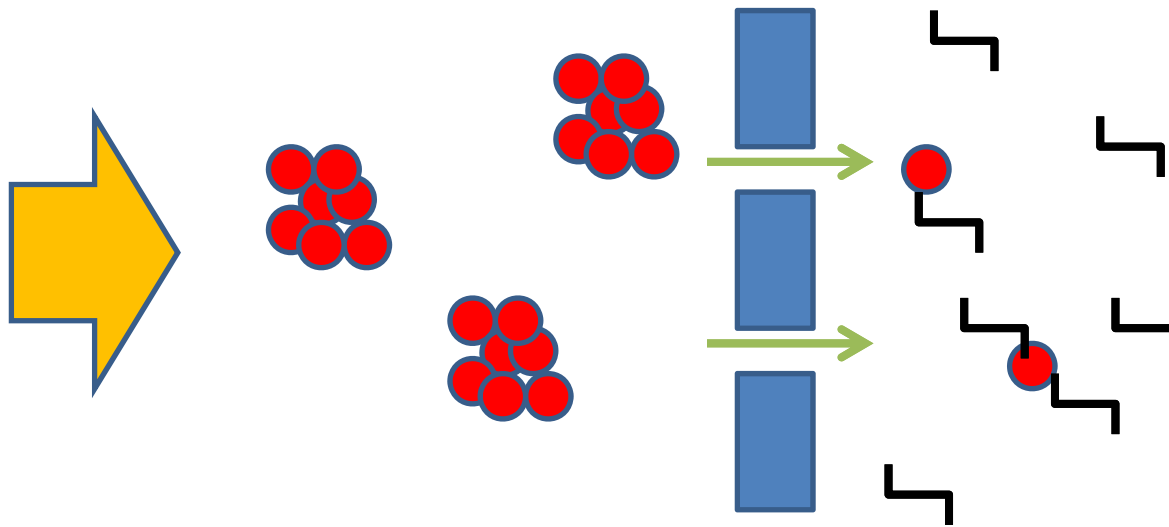
- by SIEVING of existing agglomerated nanoparticles



- *Feed: agglomerates of nanoparticles*
- *Permeate: Stable suspension of e.g. surfactant (anionic soap)*

# PRINCIPLE

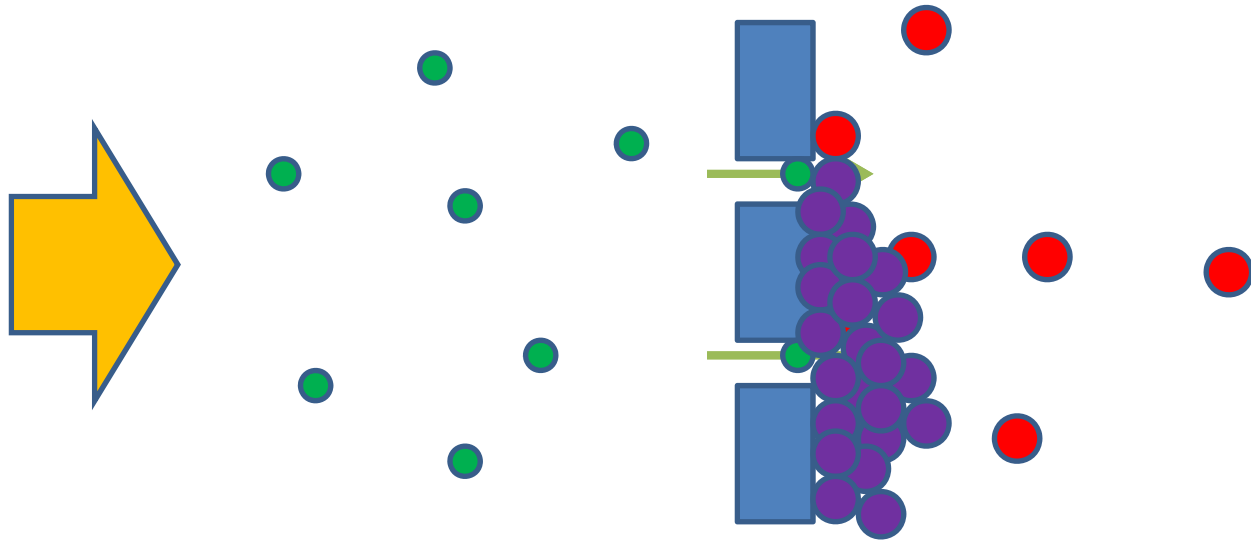
- by SIEVING of existing agglomerated nanoparticles



- *Permeate side should provide anti-agglomeration properties*
- *Pore size should equal desired particle size*

# PRINCIPLE

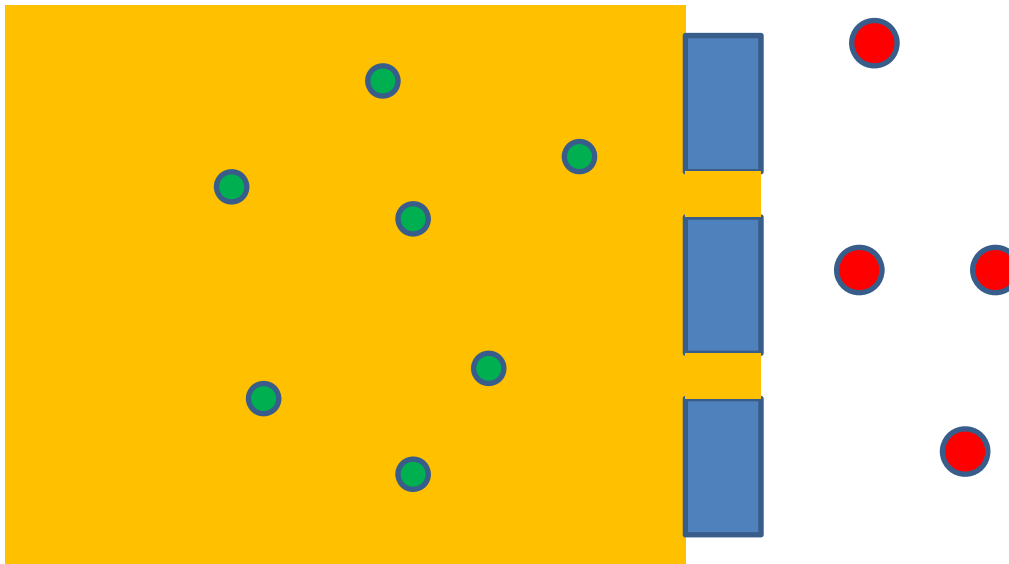
- by MICRO- AND NANOFEEDING



- *Relays of the correct assumption of dozens of micro- and nano injectors in a turbulent stream*
- *Permeate side suffers severe fouling! NOT POSSIBLE.*
- *Reaction: reagent ● + reagent ● → nanoproduct ●*

# PRINCIPLE

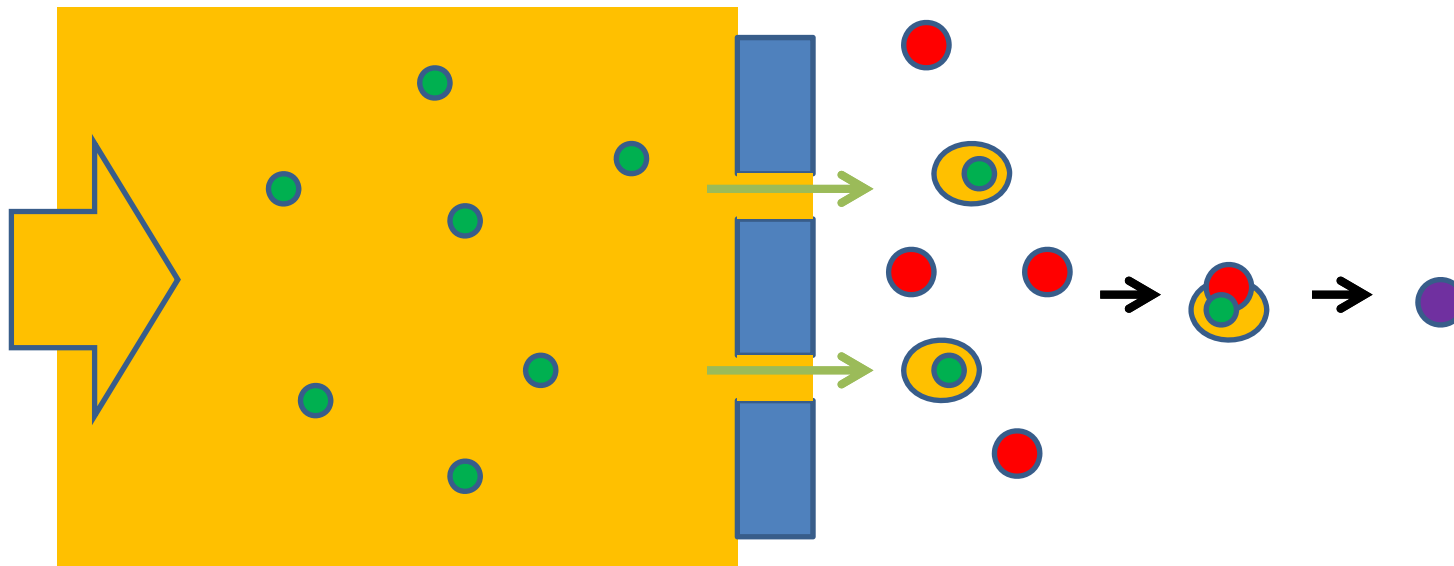
- by MICRO- AND NANOEMULSION



- *Feed: reagent in insoluble bulk*
- *Permate: Other reagent in e.g. water*
- *Reaction: reagent ● + reagent ●  $\rightarrow$  nanoparticle ●*

# PRINCIPLE

- by MICRO- AND NANOEMULSION



- *Permeate side suffers severe fouling*
- *Retardant agents must be used (encapsulation)*
- *Reaction: reagent ● + reagent ● → nanoproduct ●*



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# **MEMBRANE APPLICATIONS IN NANOTECHNOLOGY: FUNCTIONALIZATION**

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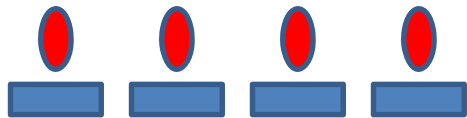
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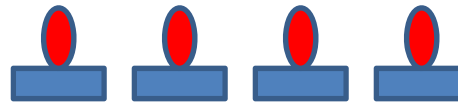
MARCO.STOLLER@UNIROMA1.IT

# HOW IT IS PERFORMED

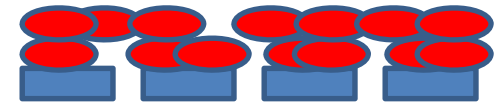
- by MEMBRANE SURFACE MODIFICATION:
  - adsorbtion (a)
  - binding (b)
  - coating (c)



(a)



(b)



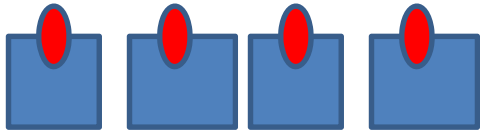
(c)



# HOW IT IS PERFORMED

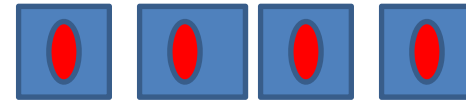
- by INCLUSION of nanoparticles in the membrane

at the surface



and/or

in the matrix



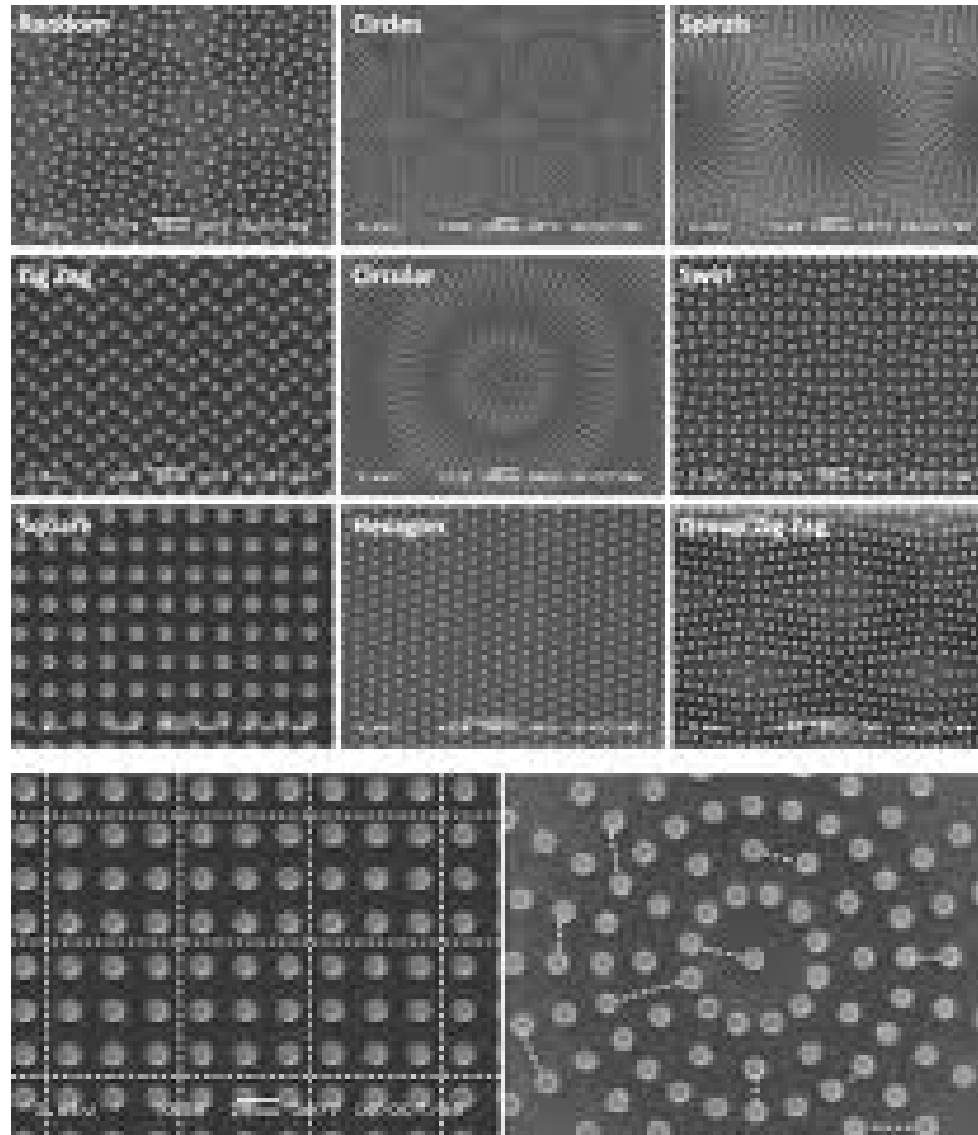
# **FUNCTIONALIZATION: TARGETS**

- **Increase of productivity.**
- **Increase of selectivity.**
- **Reduction of fouling.**
- **Advanced interaction.**
- **Novel membrane characteristics.**

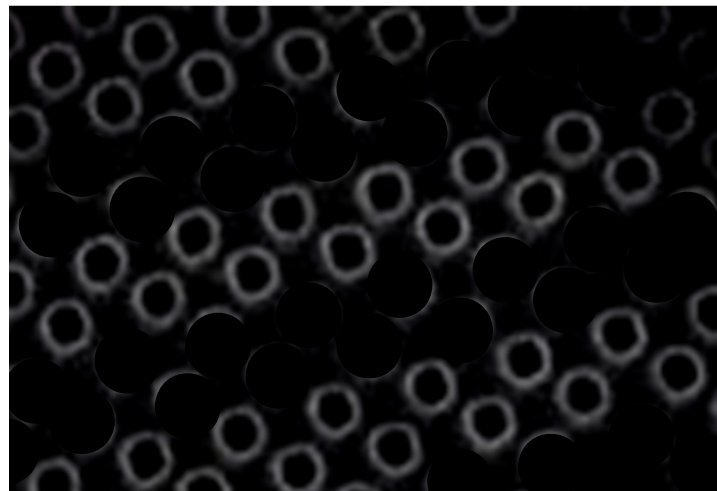
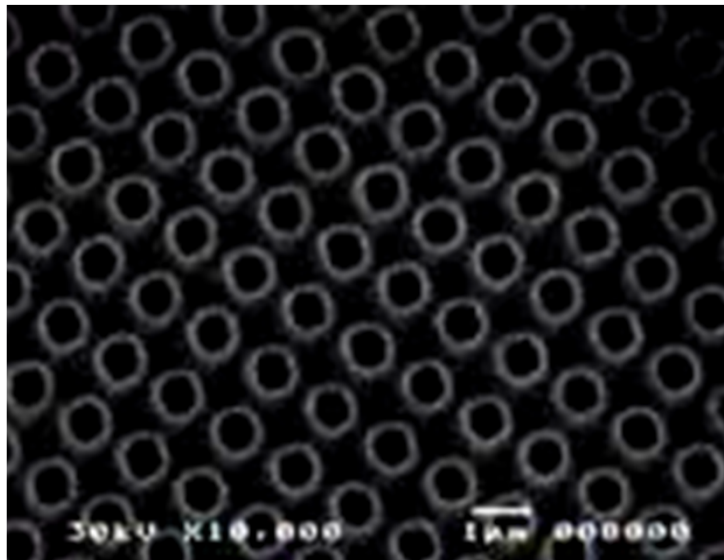
# **FUNCTIONALIZATION: TARGETS**

- **Increase of productivity.**
  - Micro-sieves with high pore density and supported mechanically
  - Nano-sieves with high pore density and supported mechanically
  - Pattern design
  - Hydrophilic or hydrophobic membranes
  - Controlled pore resistance

# PATTERN DESIGN

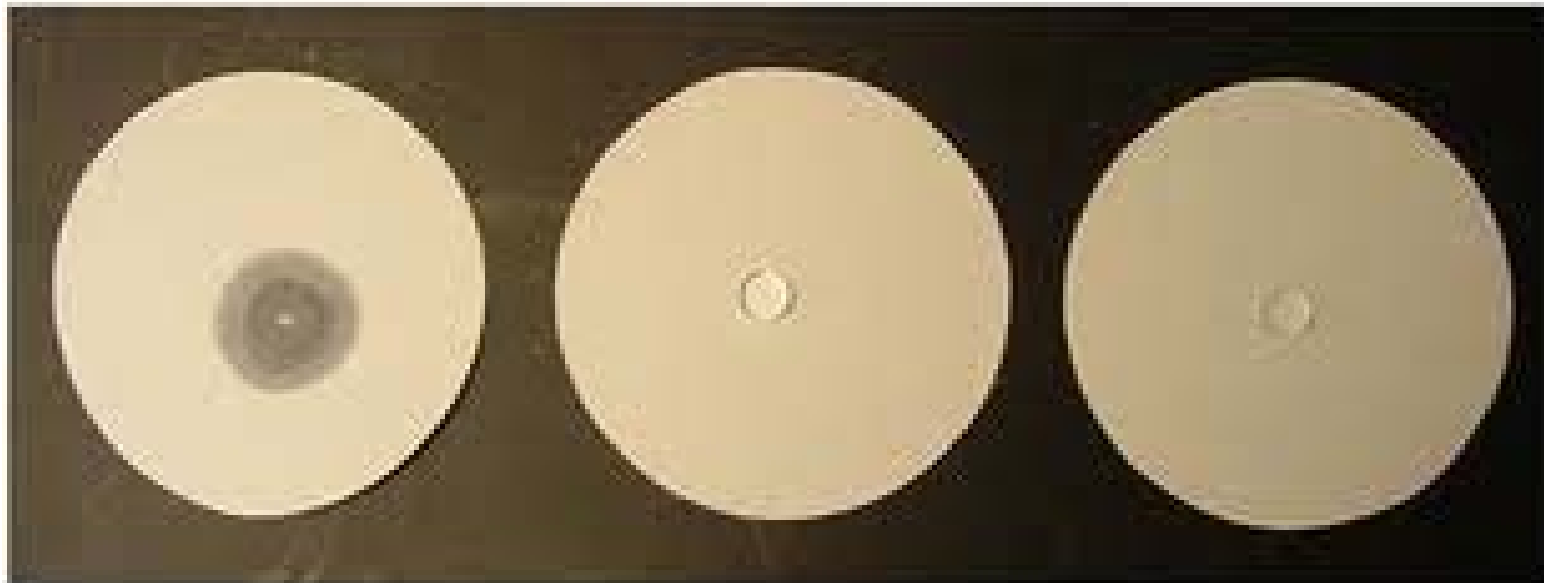


# PATTERN DESIGN



# Hydrophilic or hydrophobic

Water on 0.1  $\mu\text{m}$  PVDF



**HYDROPHILIC**

**HYDROPHOBIC**

**SUPERPHOBIC**



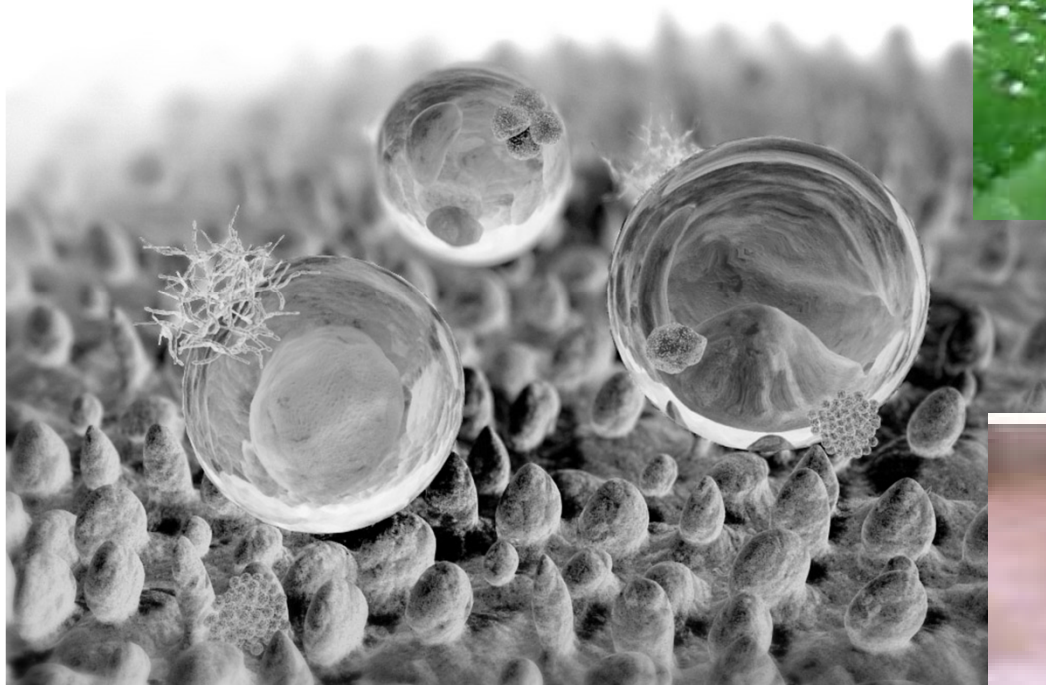
INCREASING FLOW RATES FOR WATER



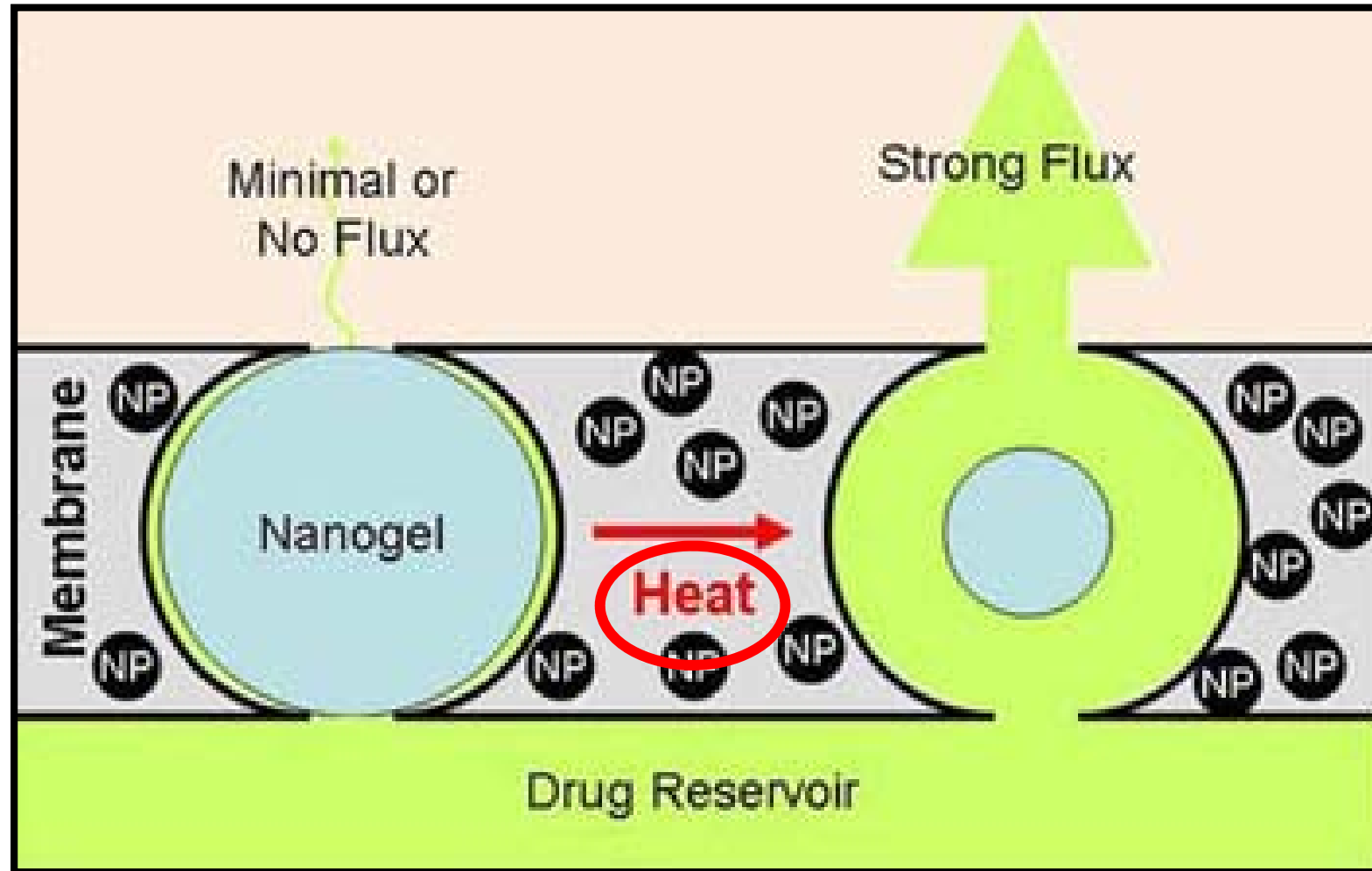
INCREASING FLOW RATES FOR ORGANIC SOLVENTS

# Superphobic membranes

“Loto flower” structures in order to obtain superphobic membranes



# Controlled pore resistance by T





# **FUNCTIONALIZATION: TARGETS**

- **Increase of selectivity.**

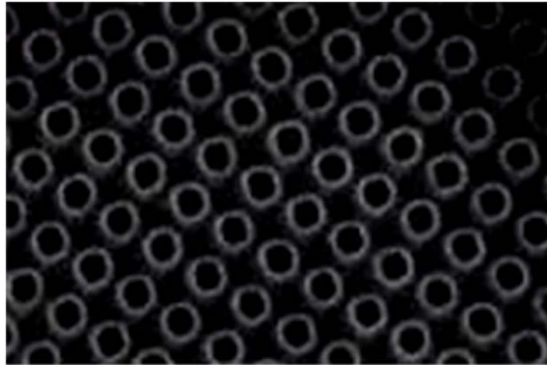
- Micro- and nano-sieves, characterized by a well defined pore size.

- Electrostatic forces by Donnan effect to increase selectivity on cations or anions.

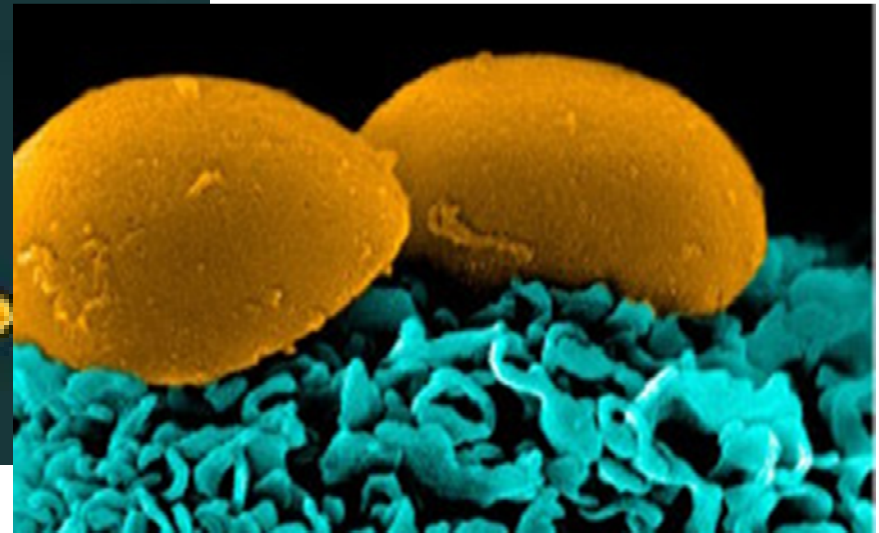
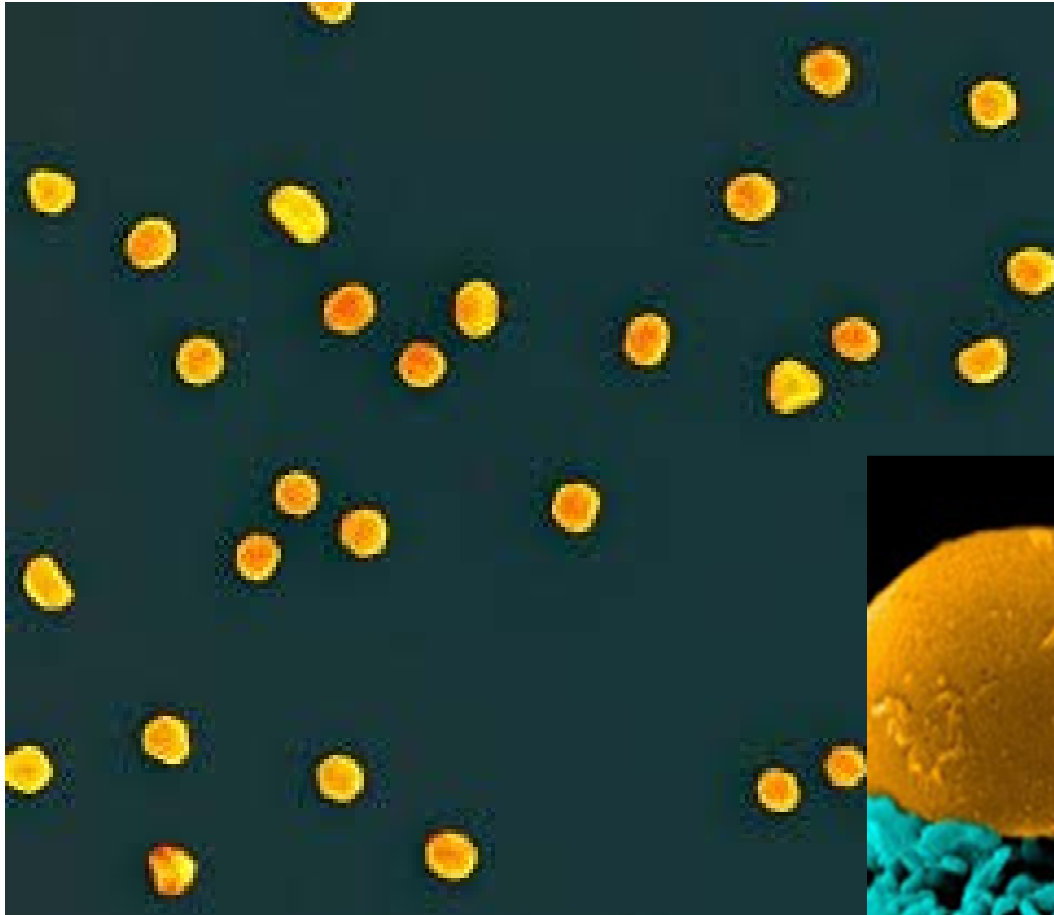
- Au charged nanoparticles inclusion (+)

- Nylon 66 coating and/or inclusion (-)

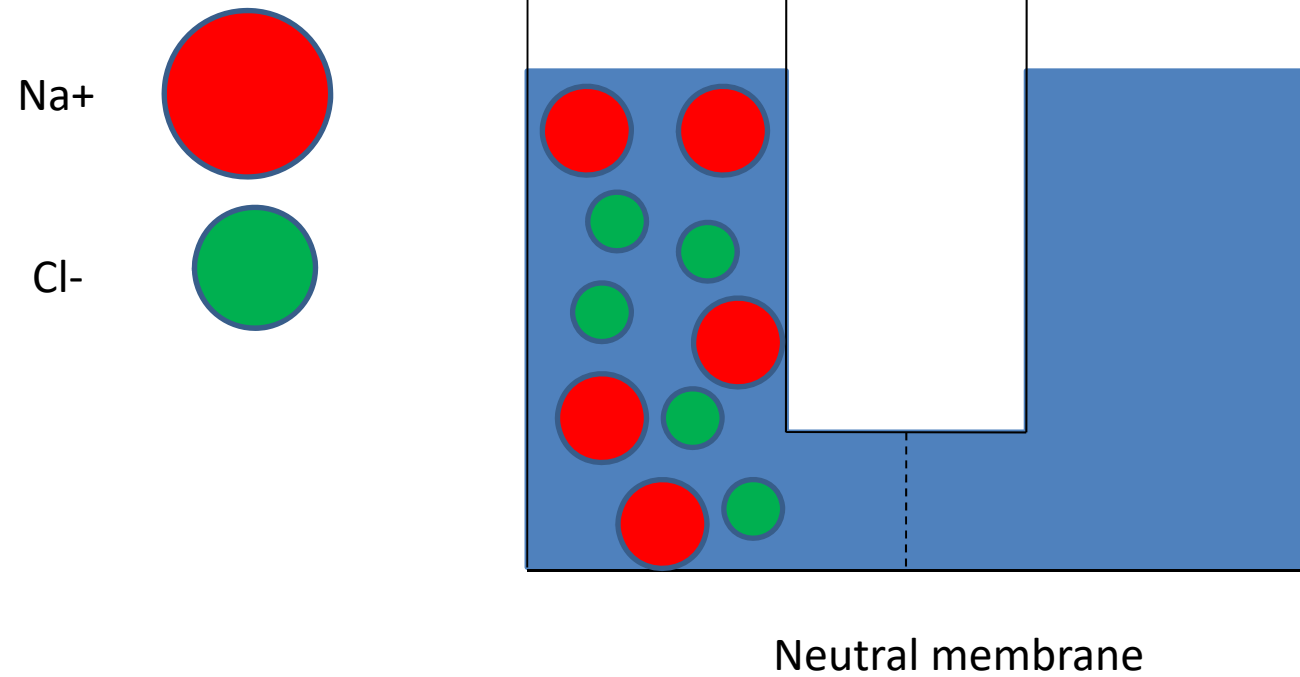
# Different pore size



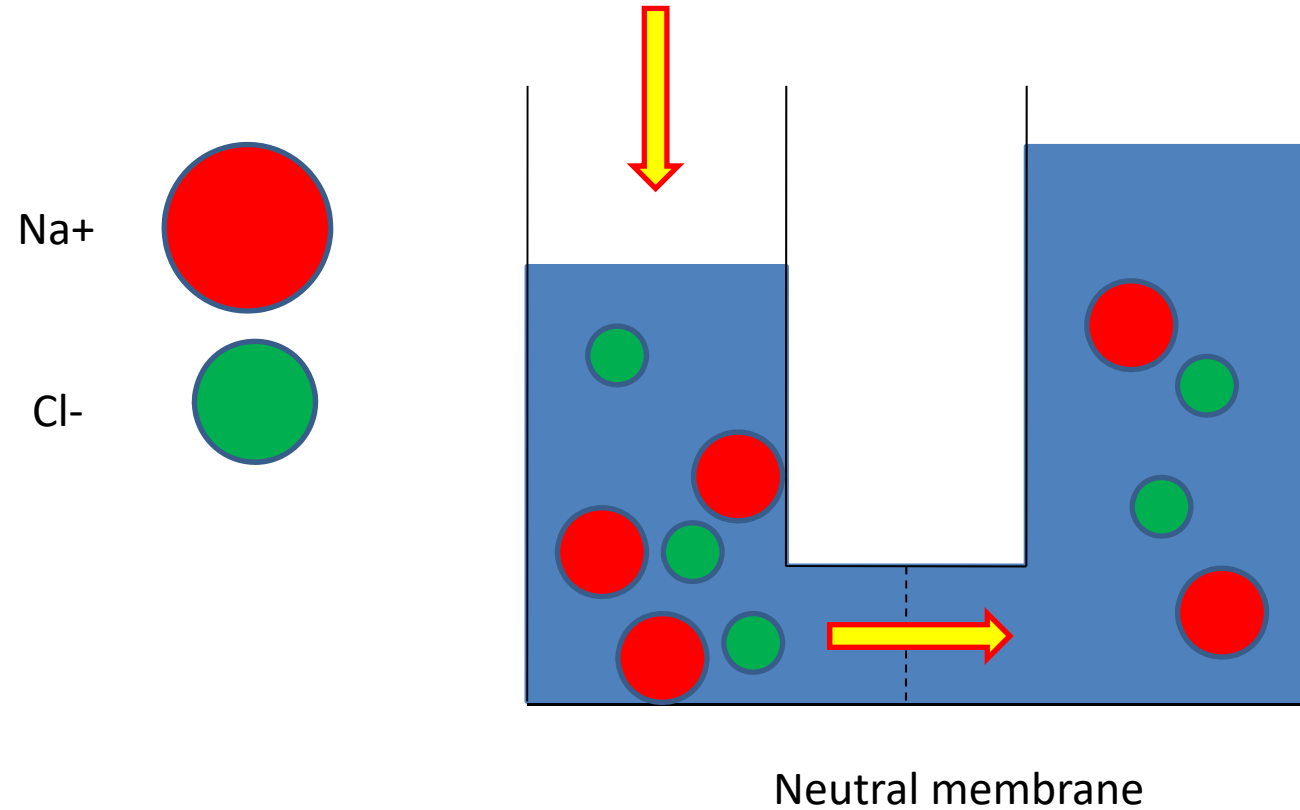
# Au nanoparticles



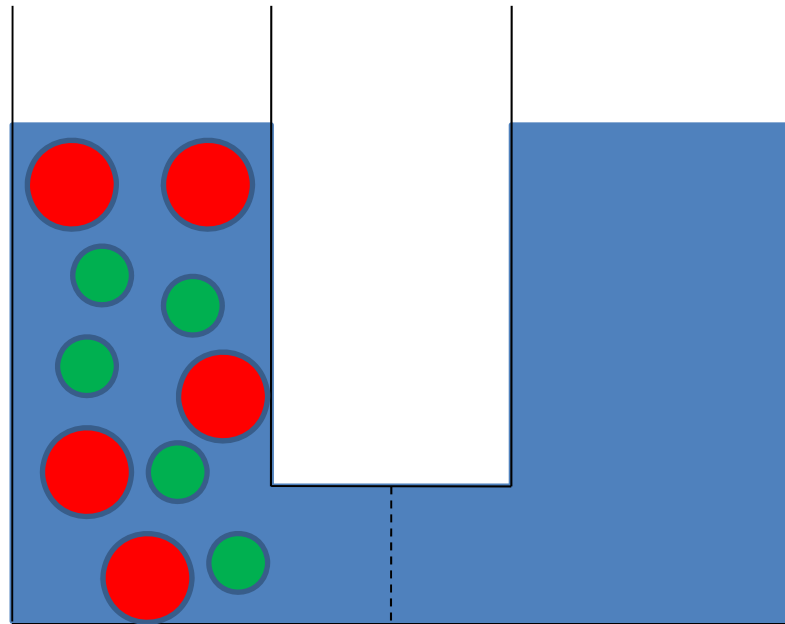
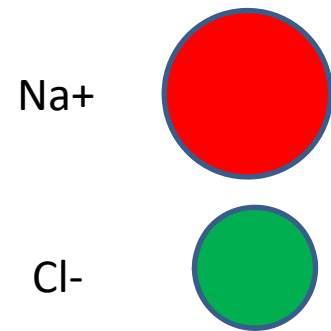
# DONNAN EFFECT



# DONNAN EFFECT

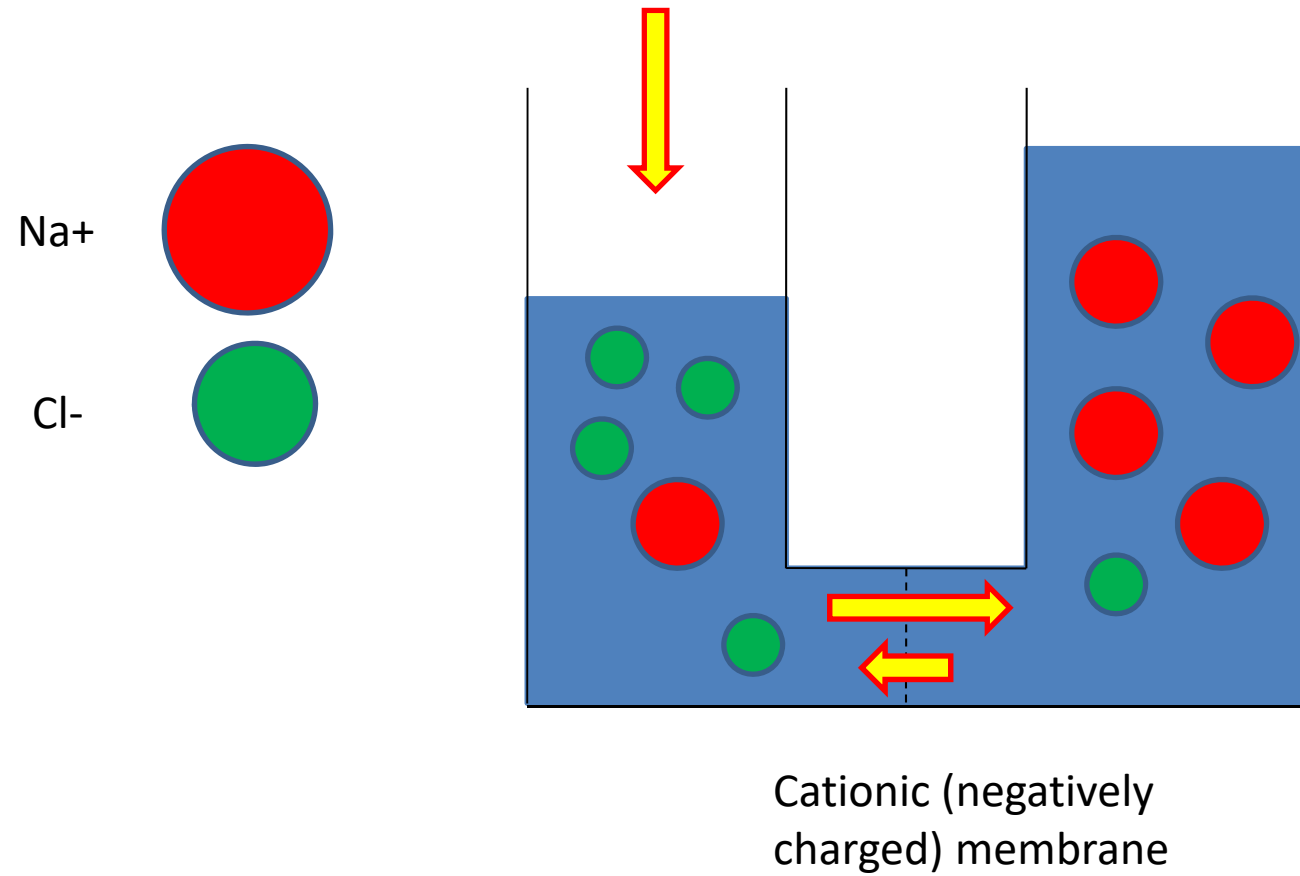


# DONNAN EFFECT

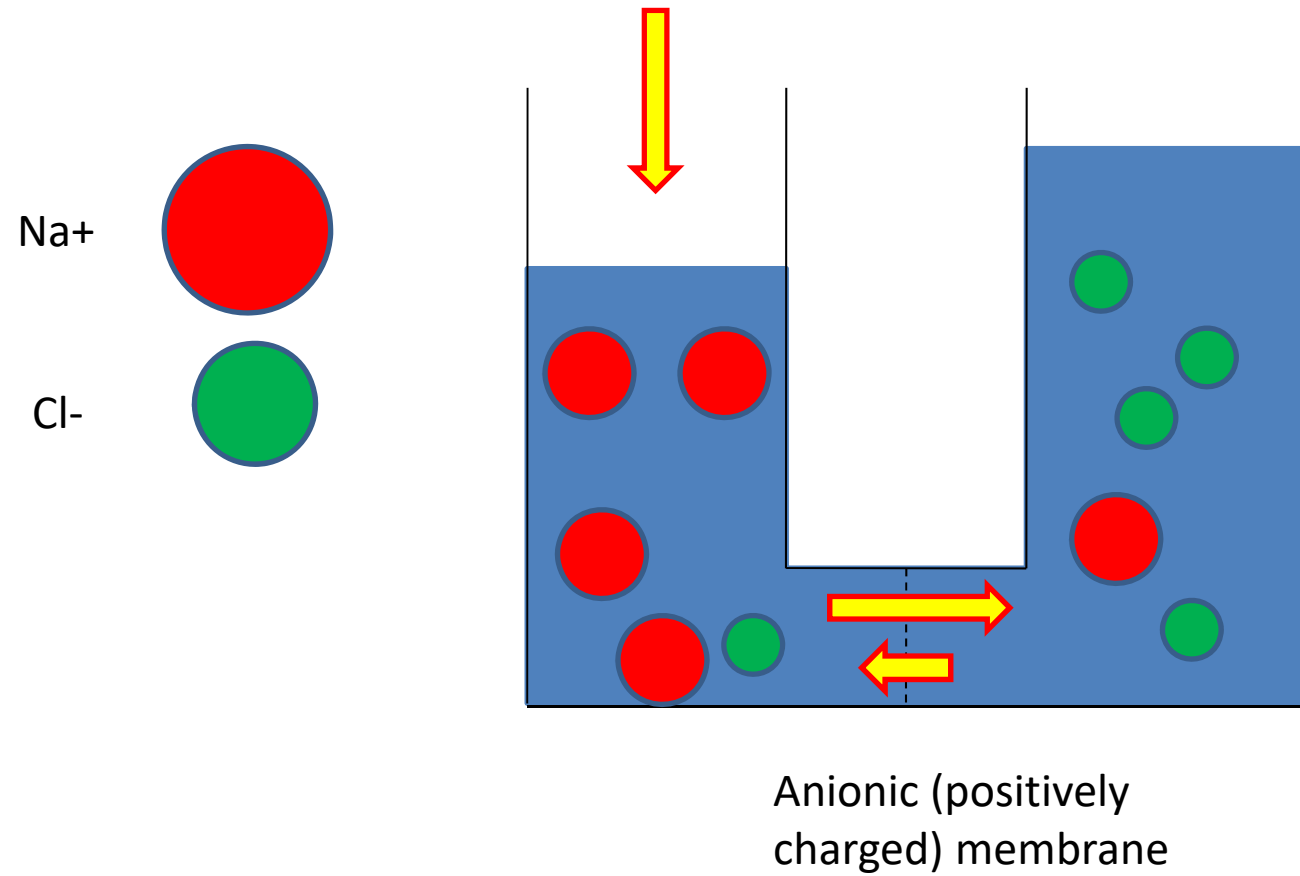


Cationic (negatively  
charged) membrane

# DONNAN EFFECT

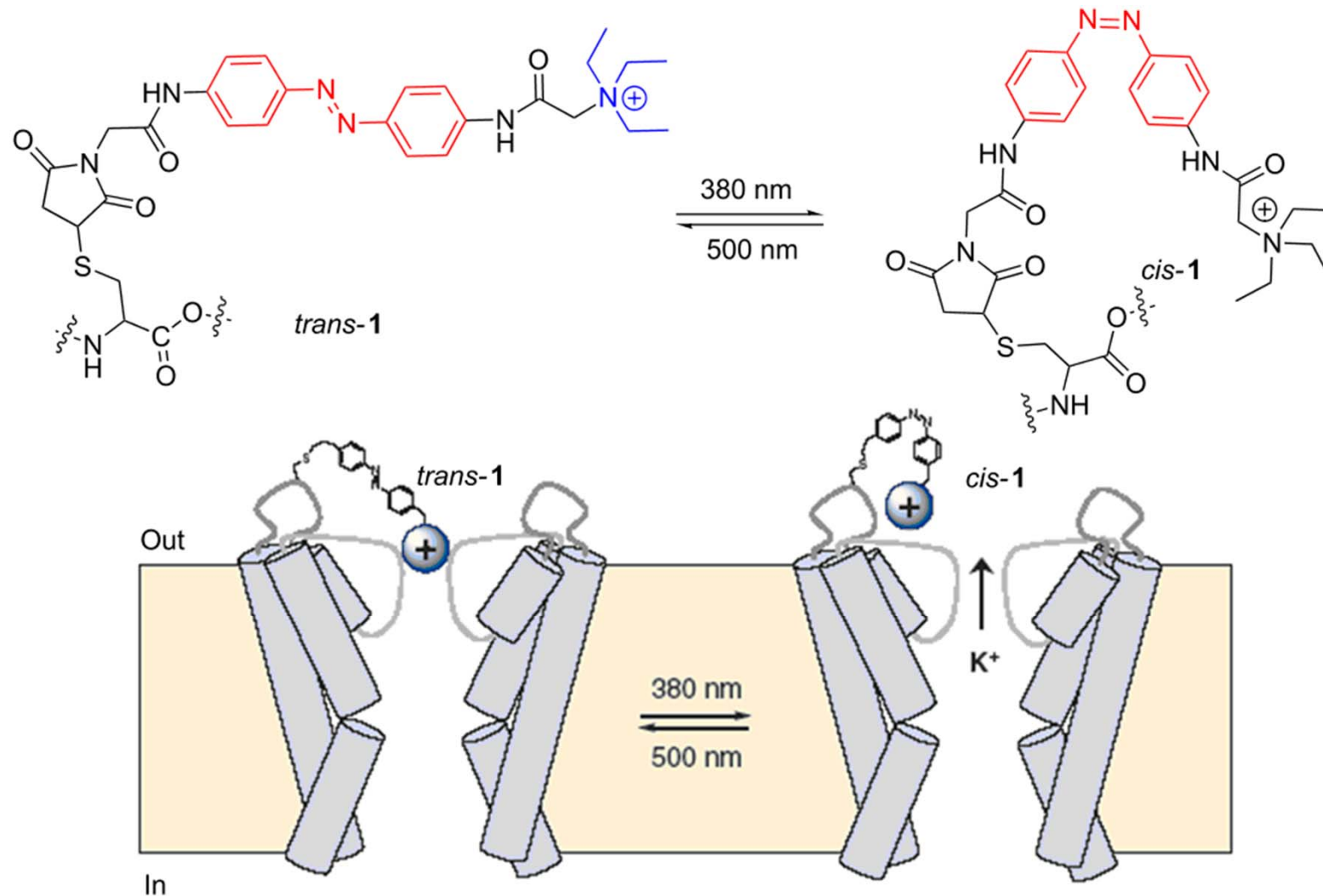


# DONNAN EFFECT

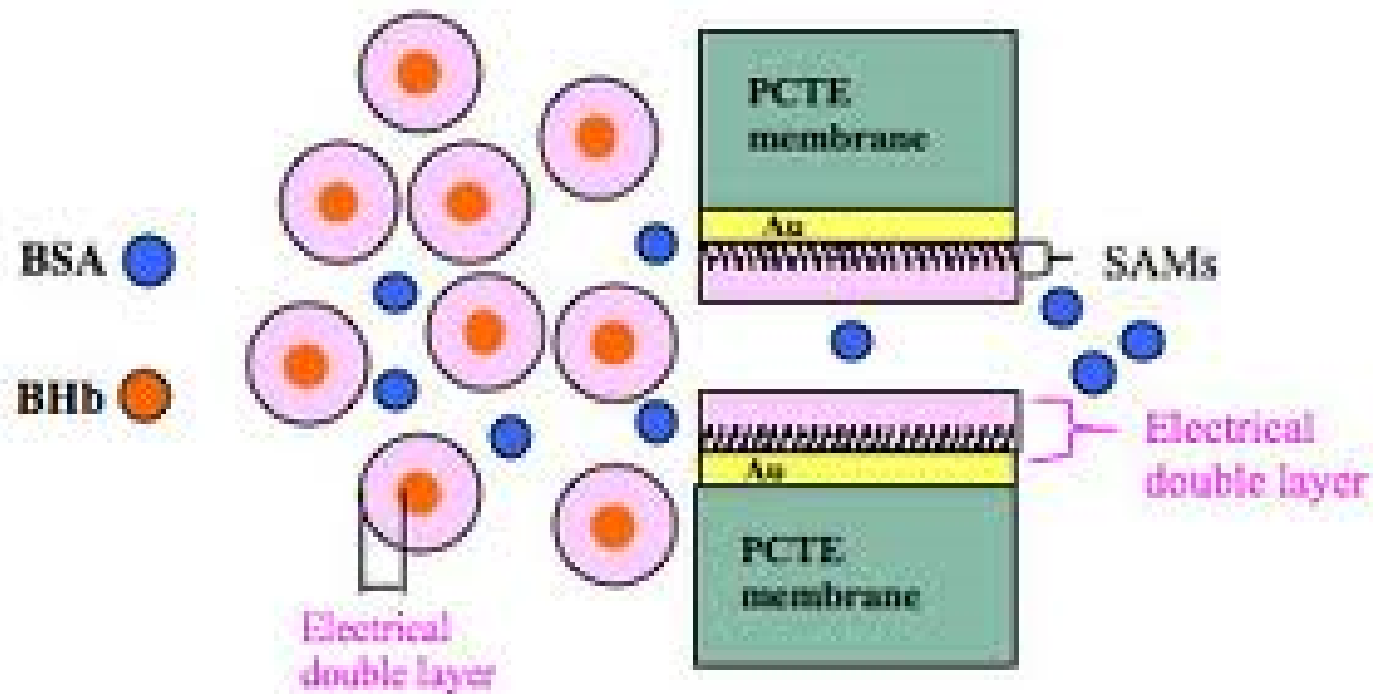




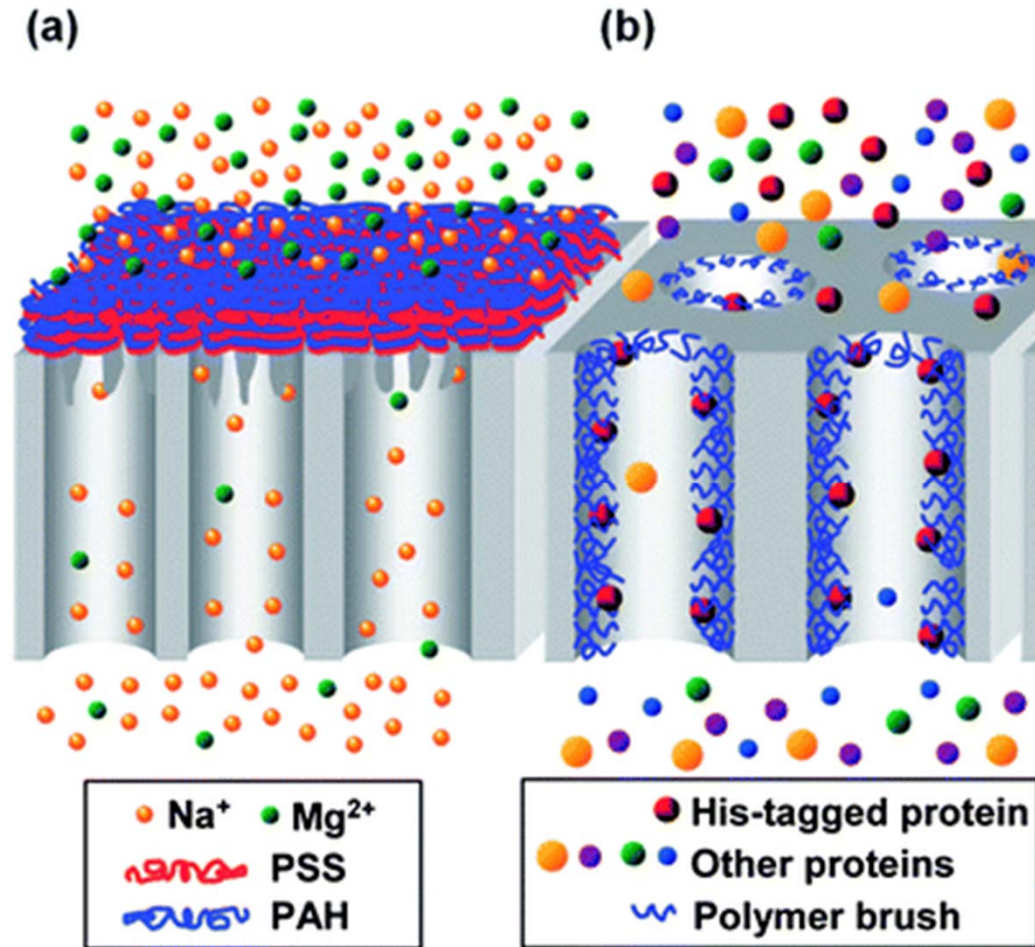
# Selectivity on ions



# Selectivity on species



# Selectivity on species (2)



# **FUNCTIONALIZATION: TARGETS**

- **Reduction of fouling.**

- **Hydrophilic or hydrophobic membrane surface after treatment**

- PEGMA on PVDF for hydrophobic effect

- Surfactants for hydrophilic effect

- **Micro- and nanosieves pattern design**

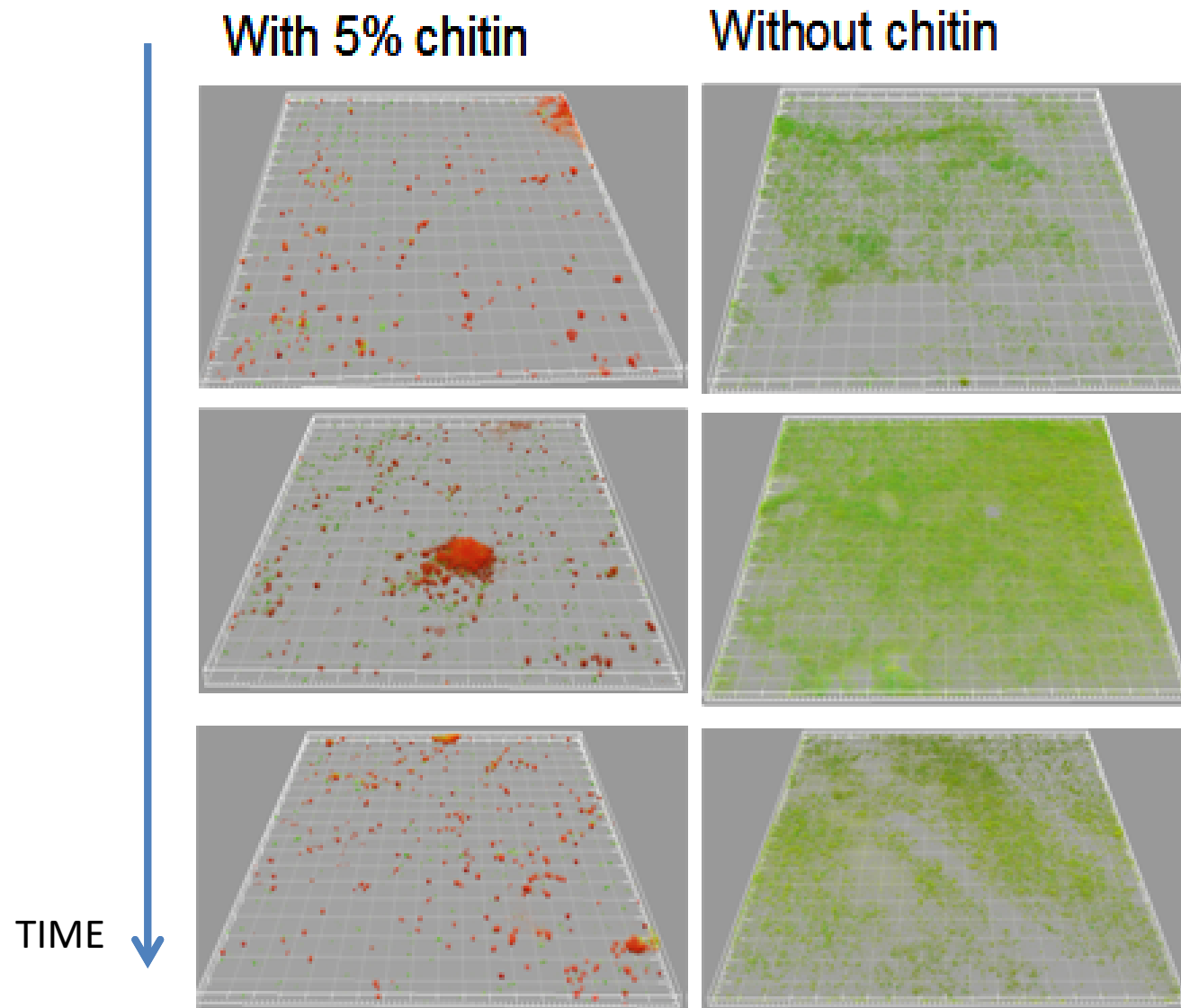
- **Magnetic membranes**

- Magnetic field induces surface movement

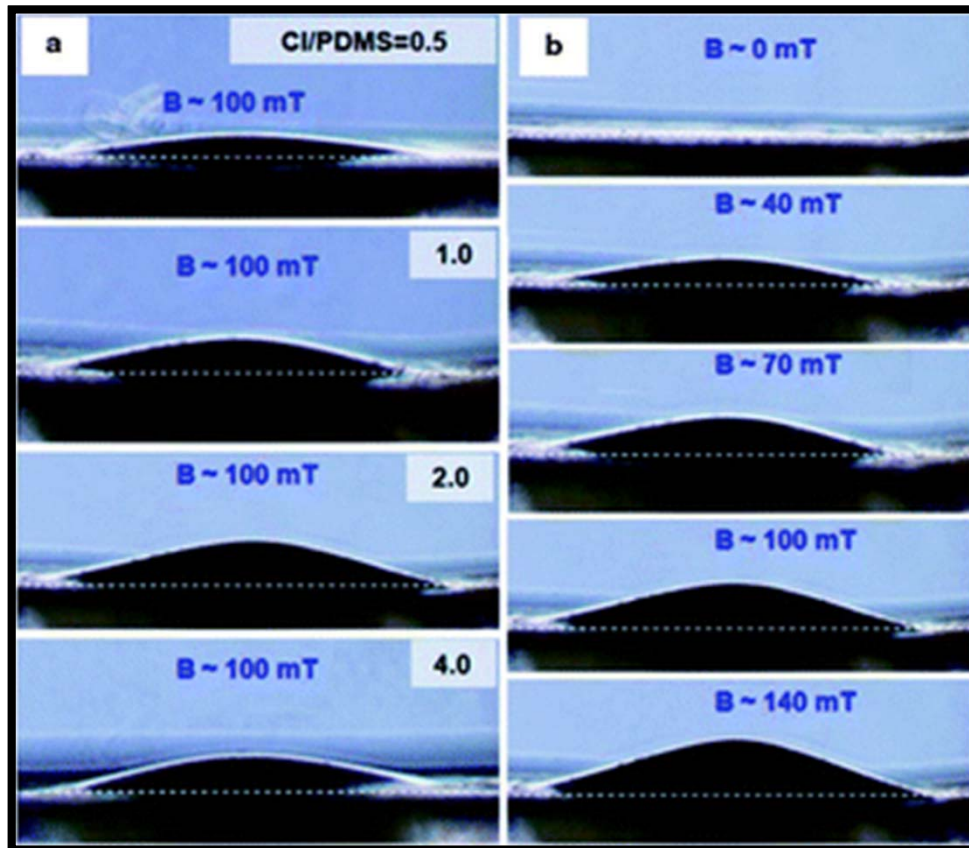
- **Biofouling reduction**

- inclusion of nanochitin, nanochitosan or Ag

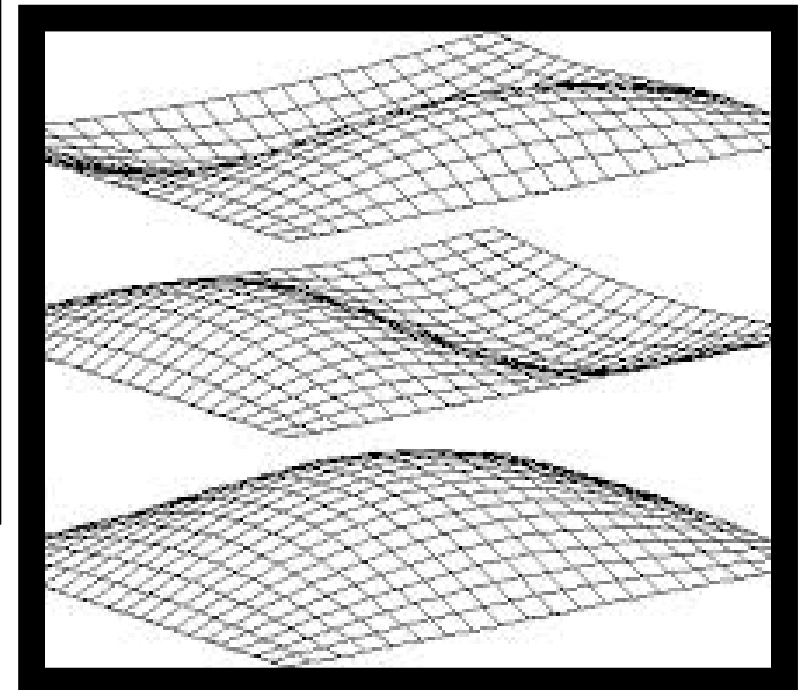
# FUNCTIONALIZATION: TARGETS



# Magnetic membranes



By changing the magnetic field wave movements of the membrane surface were induced.

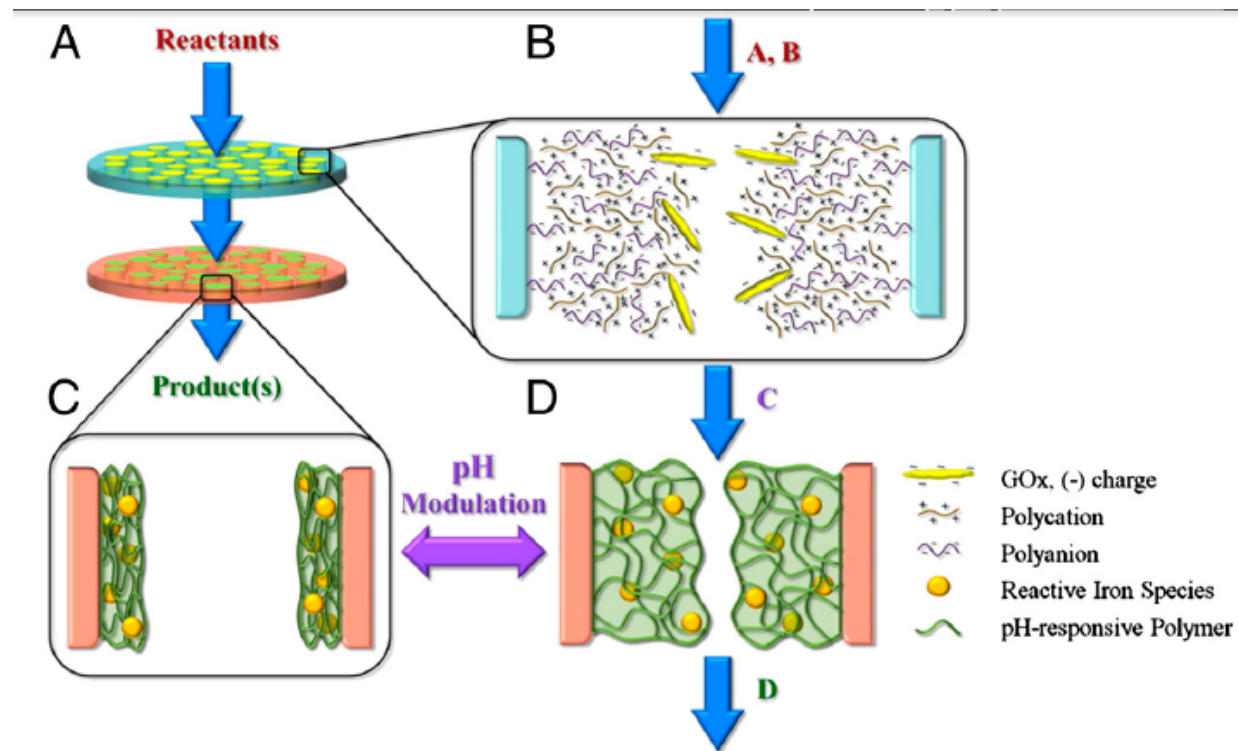


# **FUNCTIONALIZATION: TARGETS**

- **Advanced interaction.**
  - Reactive membranes (chemical, enzymes, etc.) embedded in the matrix or on permeate surface side
  - Membrane reactors (static, dynamic)

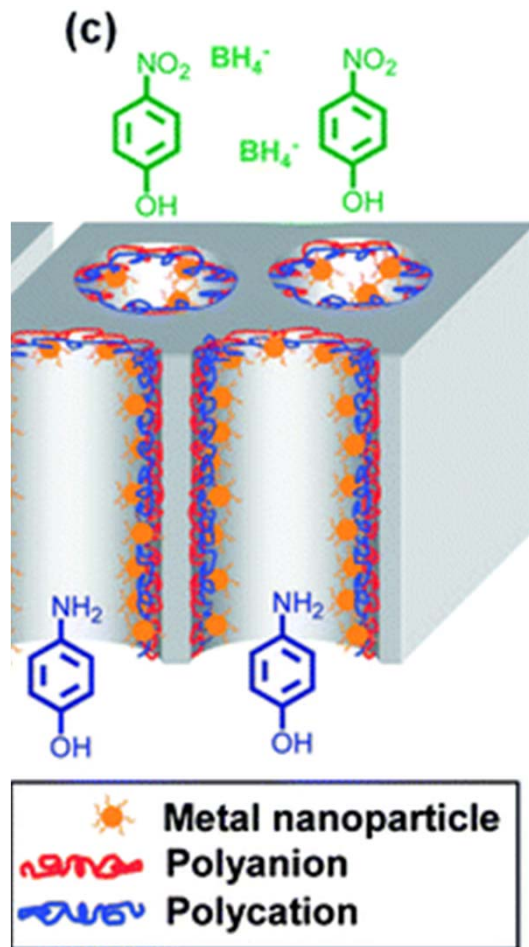
# REACTIVE MEMBRANE

Two reactants A and B are on the first membrane, where enzymes were immobilized and give a product C. Final conversion to product D is given by iron ions immobilized in the second membrane, within a polymeric matrix. The conversion from C to D give rise to a pH change, which affect the pore opening and guarantees reaction completeness.





# REACTIVE MEMBRANE (2)



Embedded gold nanoparticles within the pores permit the reaction

# **FUNCTIONALIZATION: TARGETS**

- **Novel membrane characteristics.**

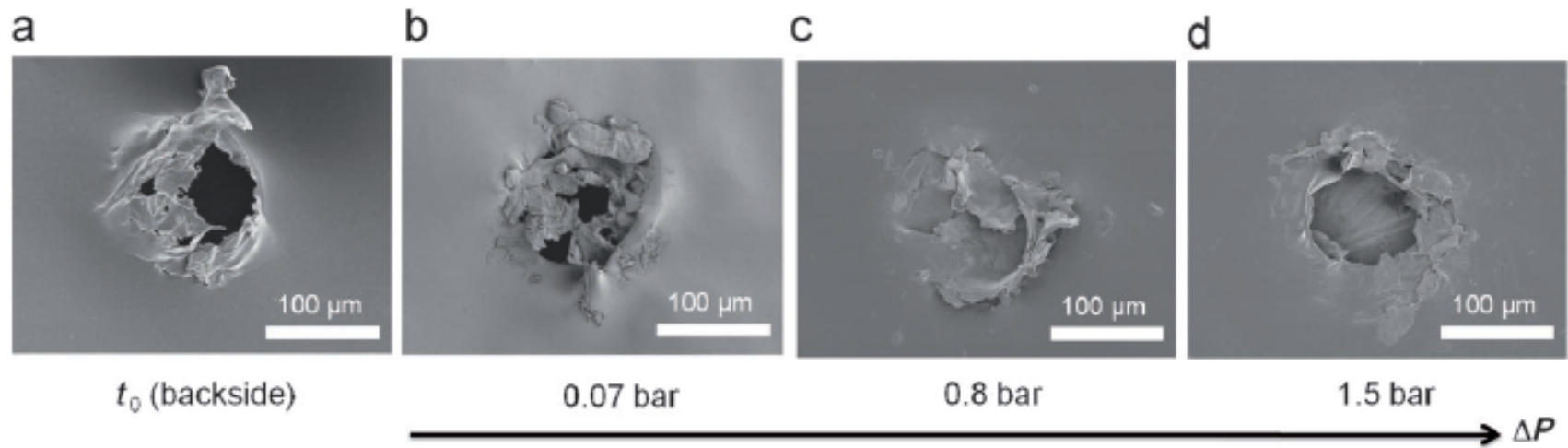
- **Self healing membranes**

- nanoparticles migrate to failure point sealing the hole.

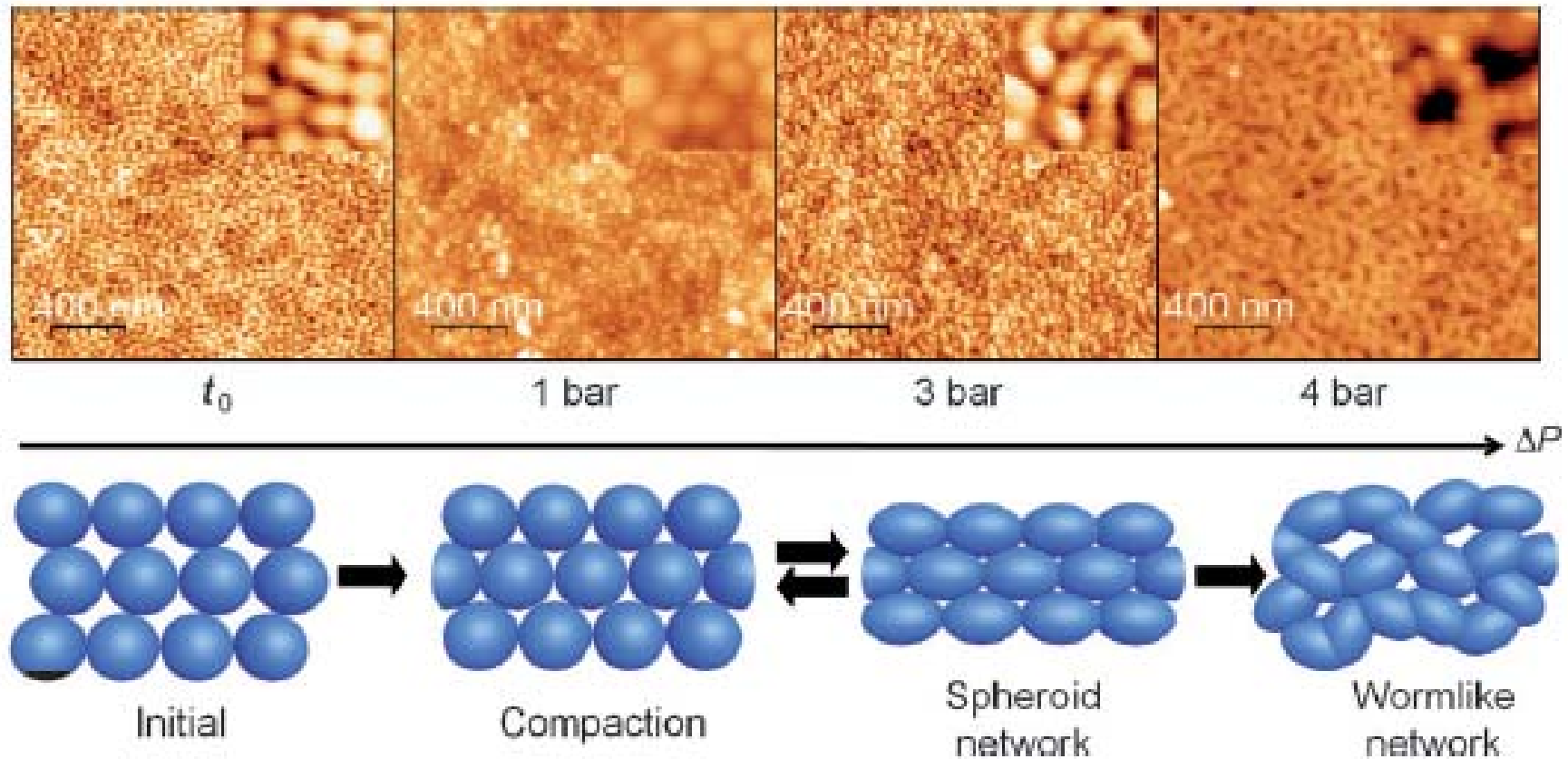
- **Dynamic membranes**

- varying the TMP and operating conditions, nanoparticles concentrates or distributes I the membrane matrix, tighten or loosen the membrane pores accordingly.

# SELF HEALING MEMBRANE



# DYNAMIC MEMBRANE



# **FUNCTIONALIZATION: TARGETS**

- **Novel membrane characteristics.**

- **“Hairy” membranes**

- carbon nanotubes vertically build up on membrane surface.

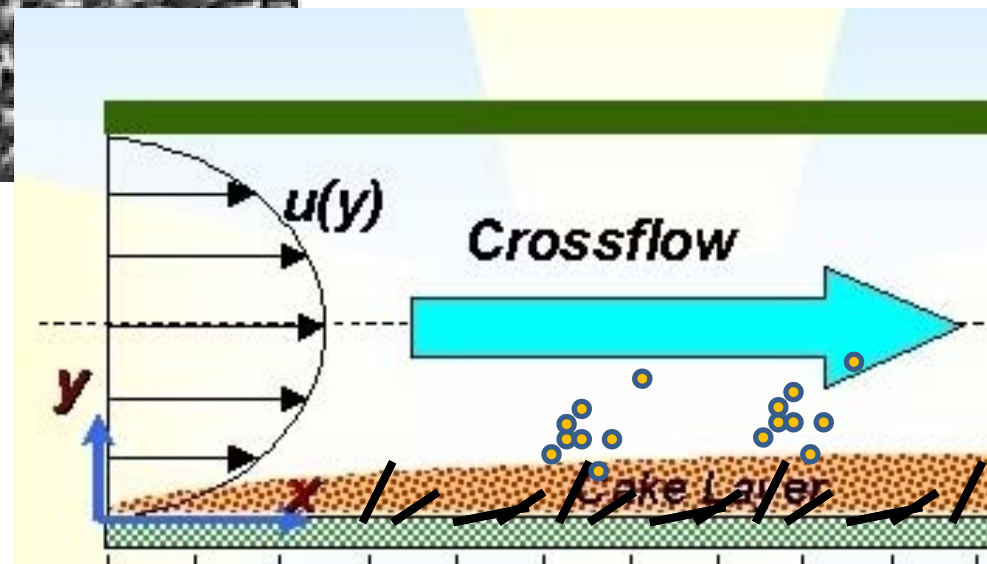
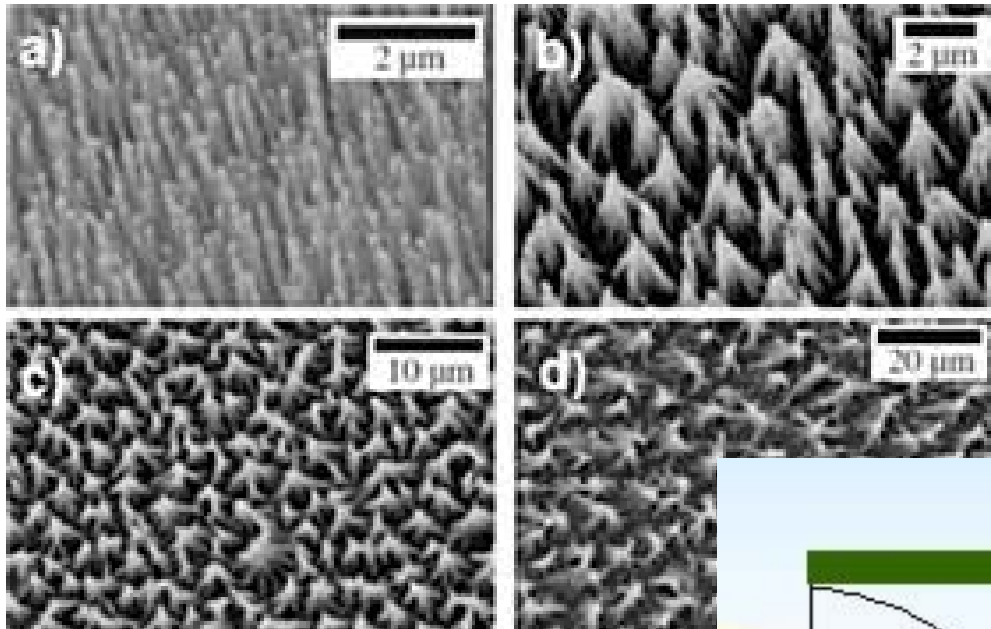
- **Embedded nanofibers for efficient blockage**

- improved enzyme adsorption.

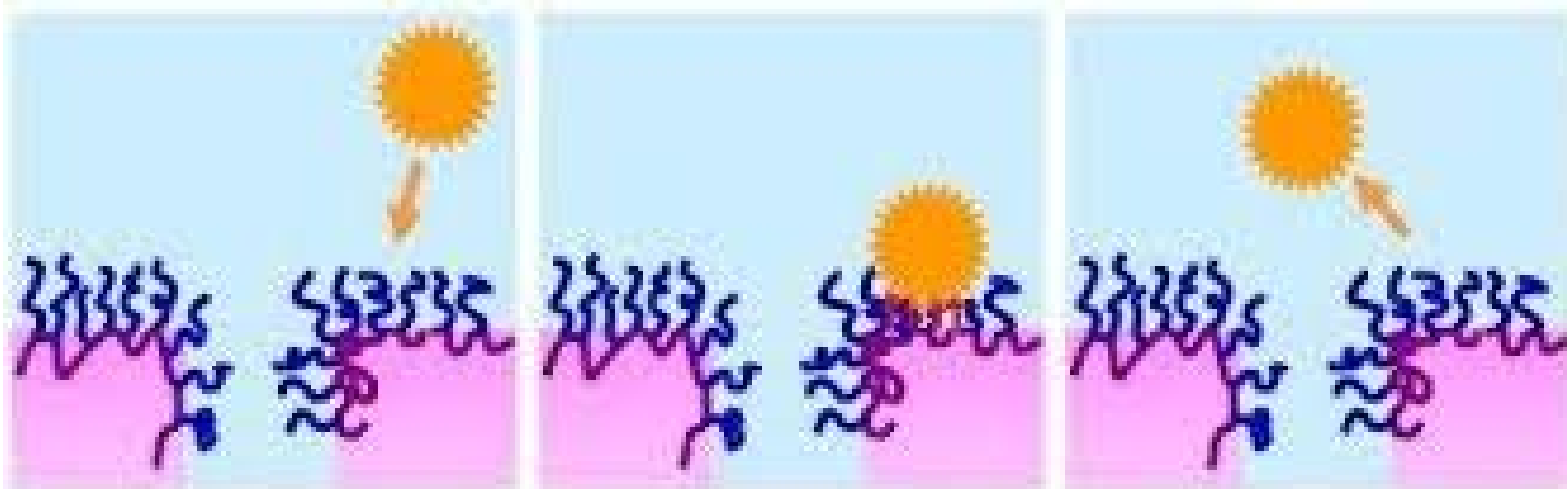
- **3D pores**

- Leave space for big particle deposition in pore side

# “Hairy” membranes

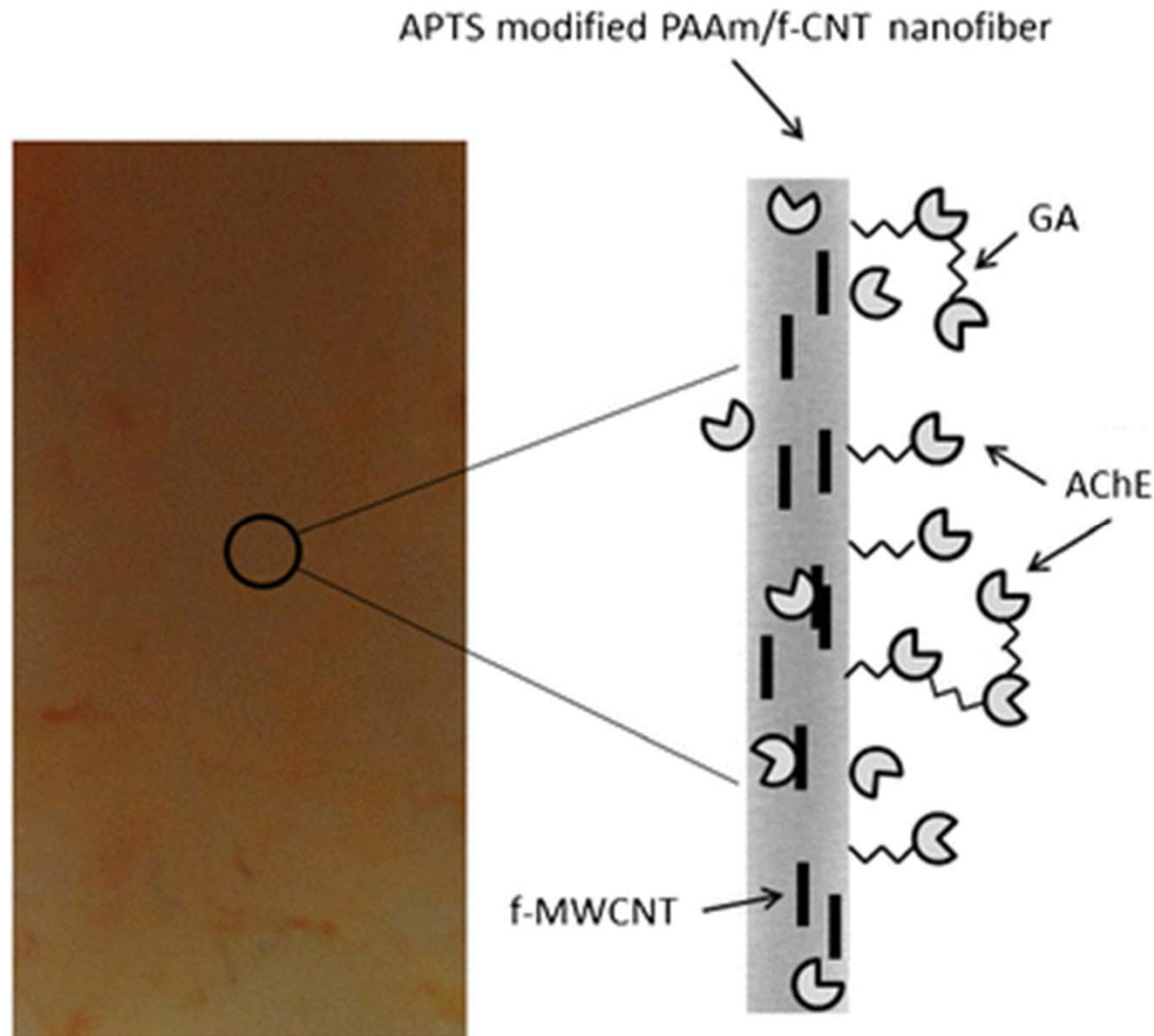


# “Hairy” membranes



When the foulant (orange) approaches the brush-covered membrane surface, it compresses the PEO chains. As the chains spring back, the foulant is pushed away.

# Enzyme adsorption



Hollow fiber membrane let pass aqueous solution containing enzymes which are blocked by the nanocarbon fibres embedded in the membrane matrix. Without the fibres the enzymes would pass in the permeate stream.



# 3D pores

