

Nanostructured functional membranes: perspectives and challenges

Cristiana Boi

DICAM, Alma Mater Studiorum-Università di Bologna

Via Terracini 28, 40131 Bologna, Italy



ALMA MATER STUDIORUM - UNIVERSITÀ DI BOLOGNA

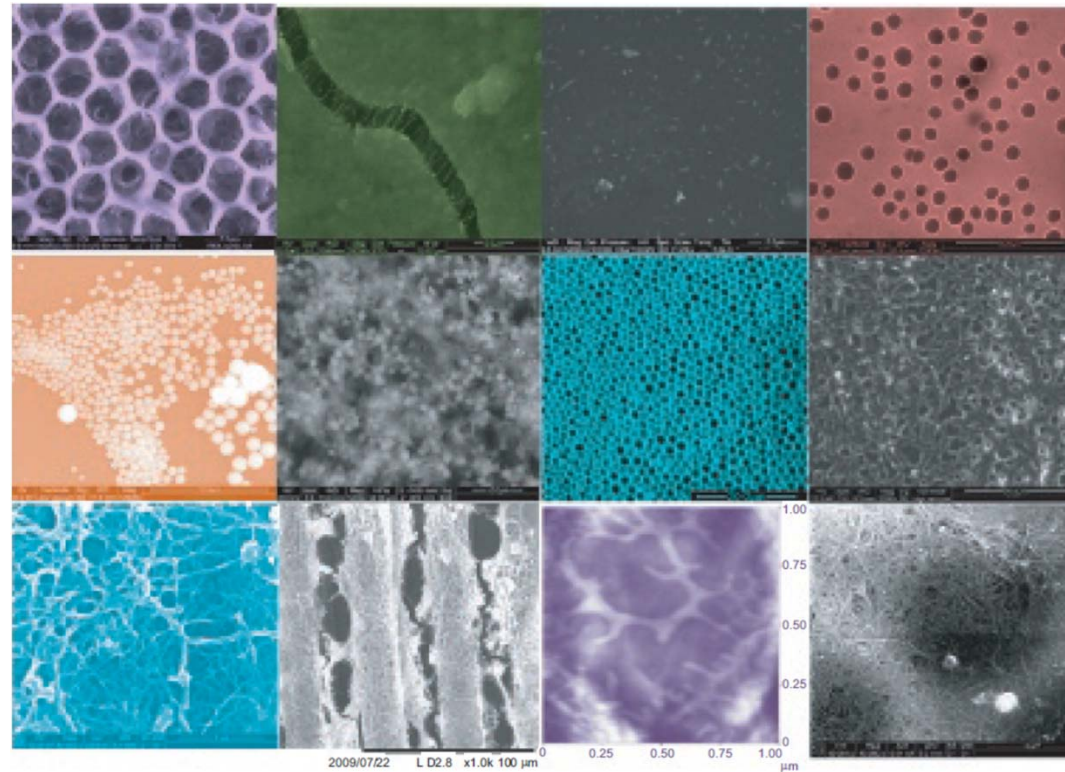
IL PRESENTE MATERIALE È RISERVATO AL PERSONALE DELL'UNIVERSITÀ DI BOLOGNA E NON PUÒ ESSERE UTILIZZATO AI TERMINI DI LEGGE DA ALTRE PERSONE O PER FINI NON ISTITUZIONALI

Nanostructured membranes

Nano-scaled features can be into the **bulk** or throughout the **surface**.

- Pores with size from 1 to 100 nm are structural elements that allow membranes to be classified as nanostructures;
 - The inclusion of nanofillers in polymer matrices also makes the membranes categorized as nanostructures;
-
- The creation of hierarchically textured membrane surfaces is another requisite for falling into the class of nanostructures.

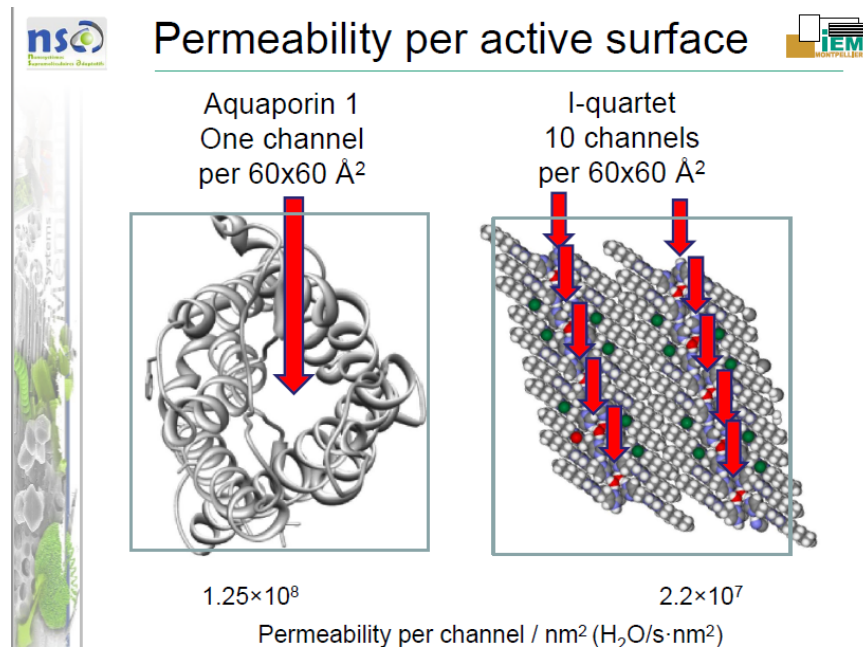
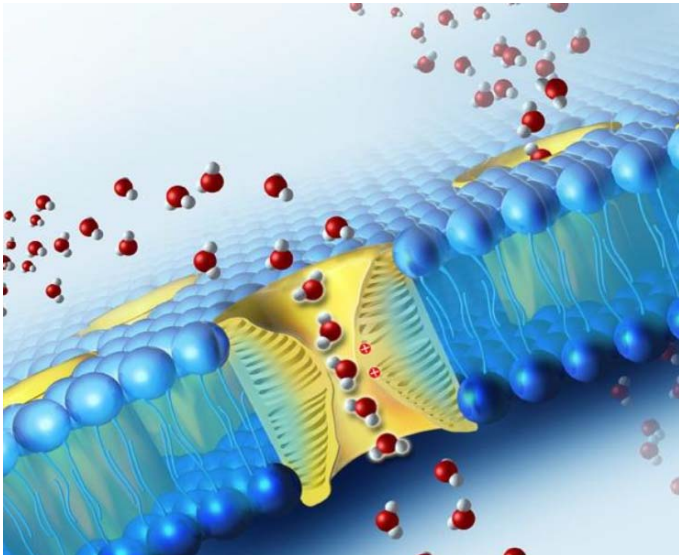
Nanostructured membranes



from «Functional Nanostructured Membranes», E. Drioli, L. Giorno, A. Gugliuzza Eds., Pan Stanford Publishing 2019.

Bio-inspired Nanostructured membranes

Water transport through membranes

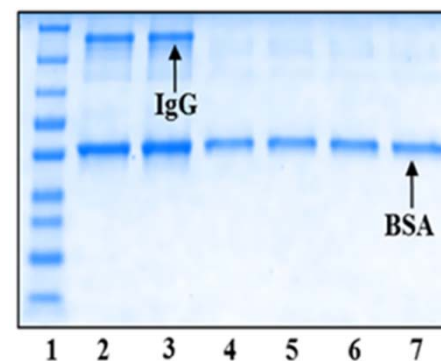
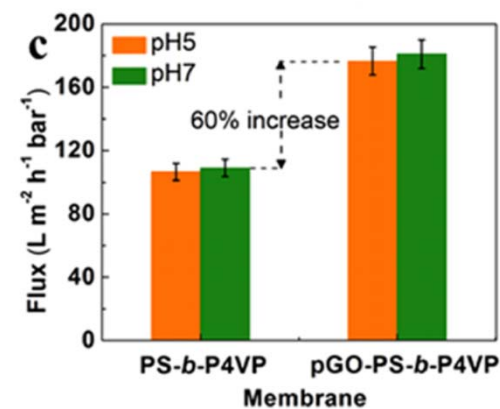
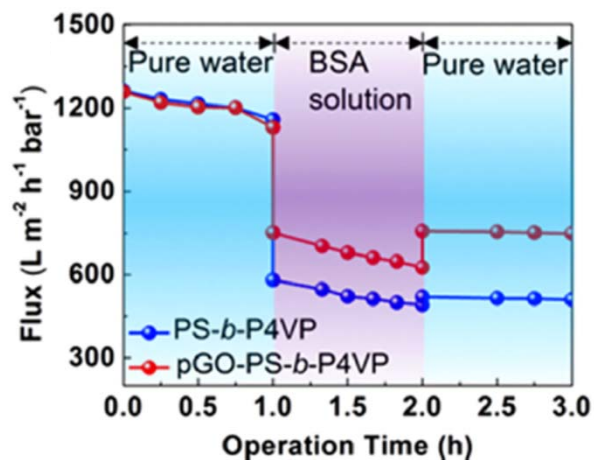
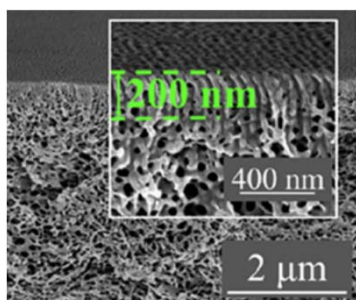
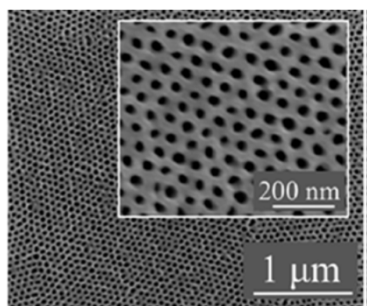


Mihail Barboiu, « From natural to bioassisted and biomimetic artificial water channel systems », Lecture at the XXXIII EMS Summer School, Bertinoro Italy, 2016.

Hybrid Isoporous membranes

PDMAEMA-grafted GO (pGO) nanosheets
Polystyrene-*b*-poly(4-vinylpyridine) block copolymer

pGO-PS-*b*-P4VP
membranes



R. Shevate *et al.*, ACS Appl. Mater. Interfaces 2019, 11, 8507–8516

Cristiana Boi, EuroNanoForum2019, Bucharest, Romania, April 13th 2019



ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA

Mixed Matrix Membranes Adsorbers (MMMAs) for the removal of water contaminants

DICAM, Alma Mater Studiorum-Università di Bologna

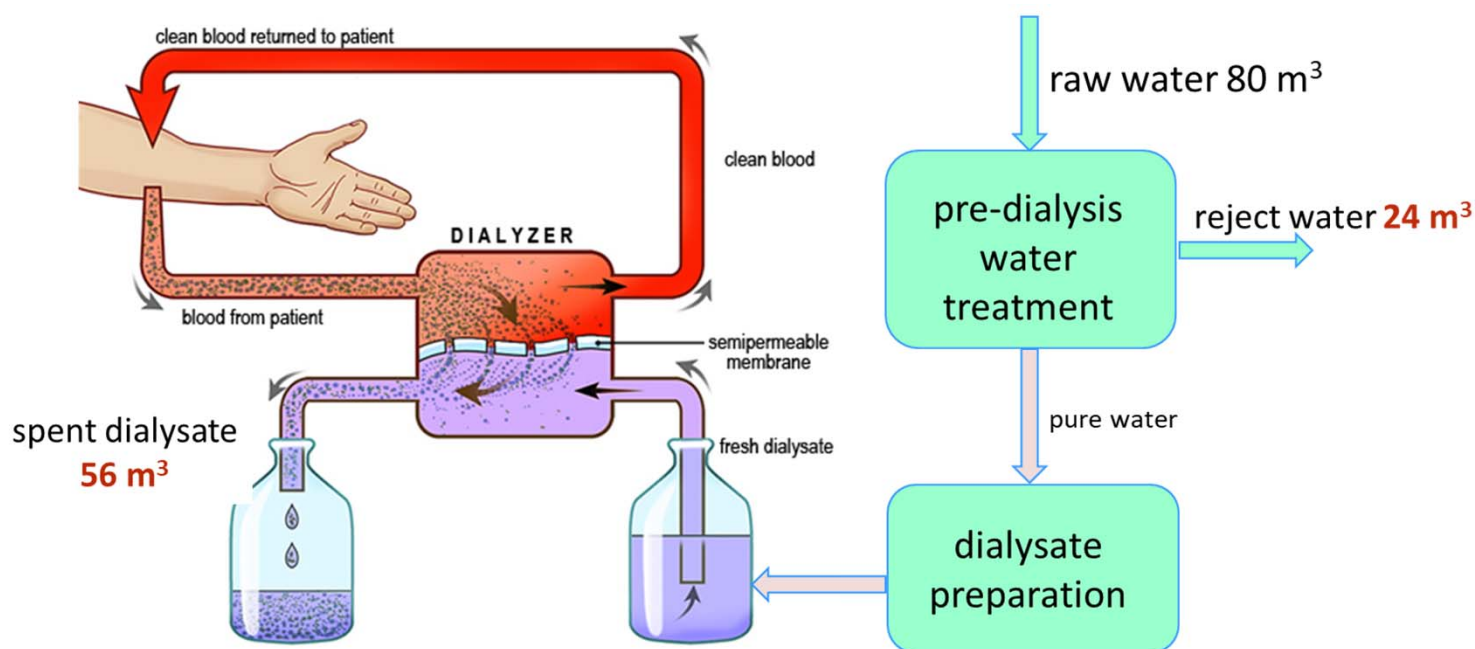


Matilde De Pascale

Project goal

The aim of the project is to prepare porous Mixed Matrix Membranes Adsorbers (MMMA) to purify the spent dialysate from uremic toxins. This will allow the recirculation of the stream to the process and the consequent saving of a great amount of water.

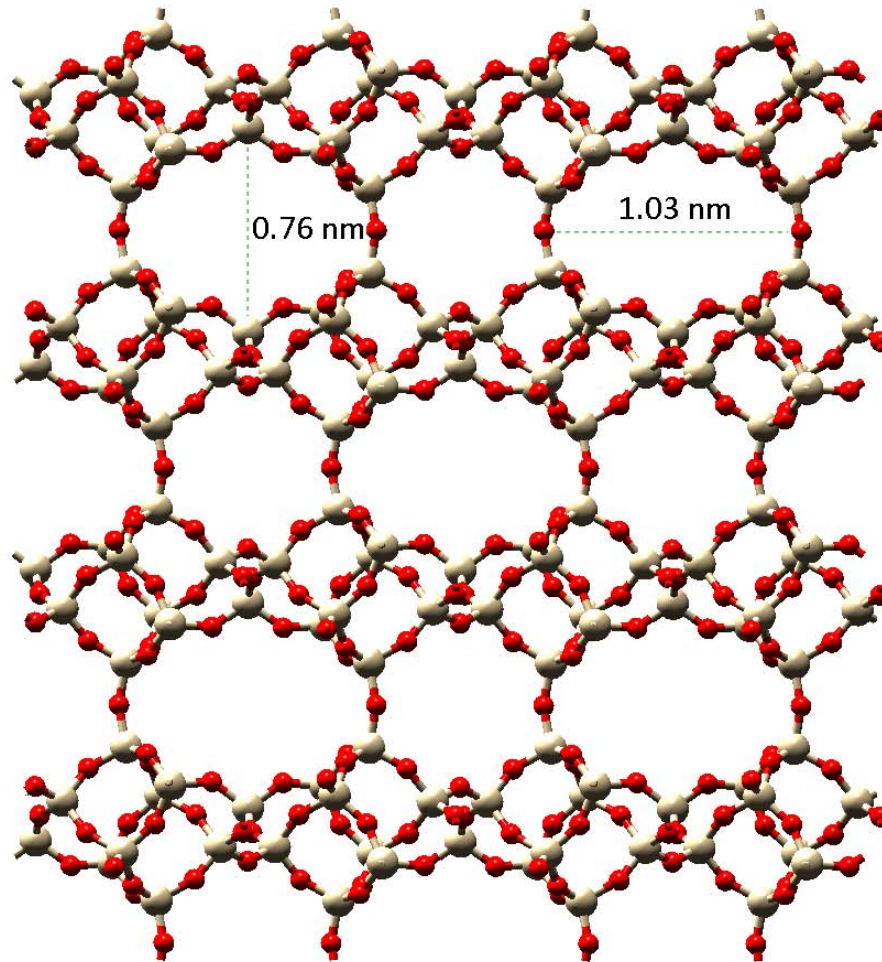
120L water/(patient*treatment) are needed to produce dialysate



Toxins

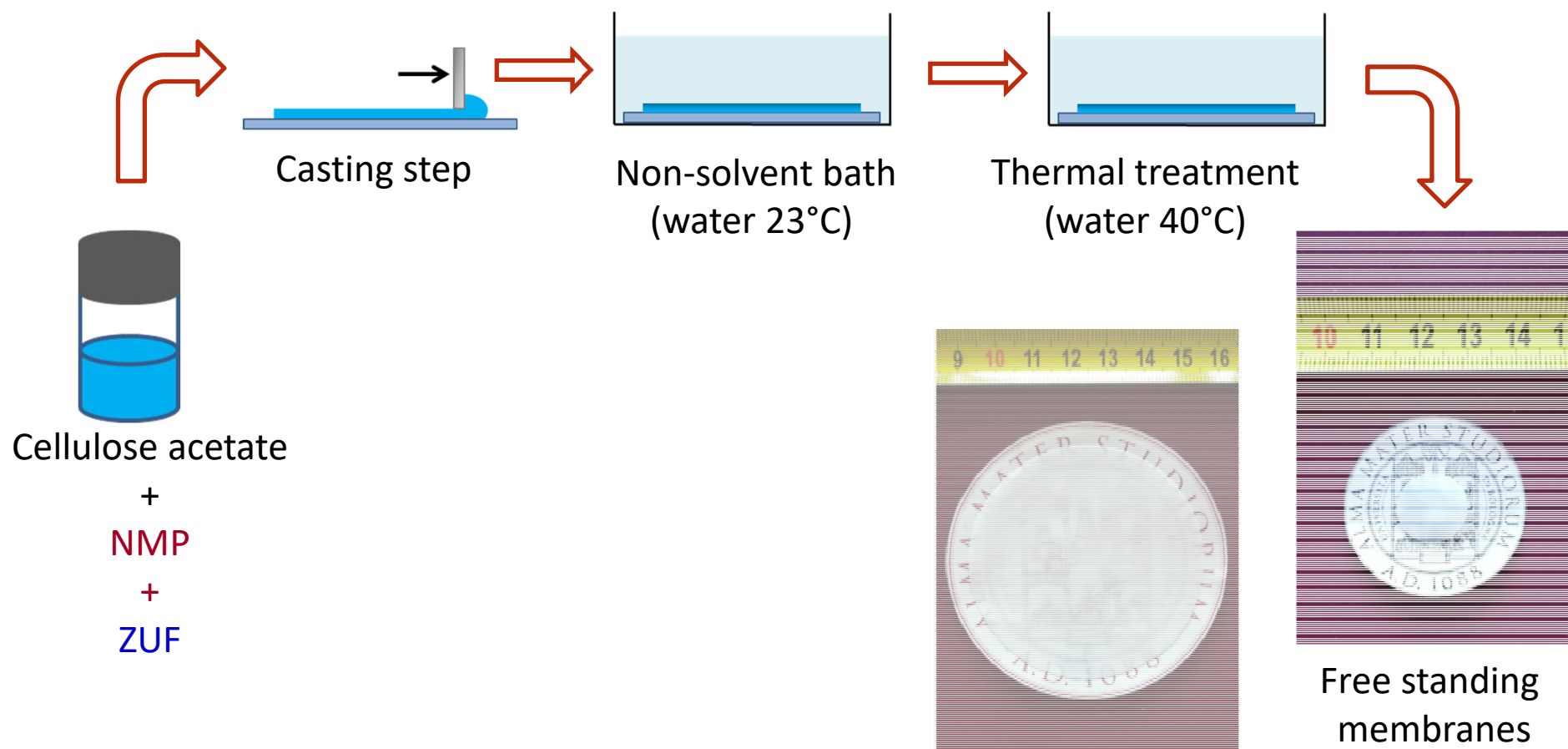
	M_w (g/mol)	C_n (mg/mL)	C_{max} (mg/mL)
Urea	60.00	0.400	4.60
Creatinine	113.12	0.012	0.24
Uric Acid	168.11	0.067	0.15

Materials



Zeolite structures obtained with the MD software MAPS from Scienomics

Membrane Preparation



MMMA-0

MMMA-10

MMMA-30

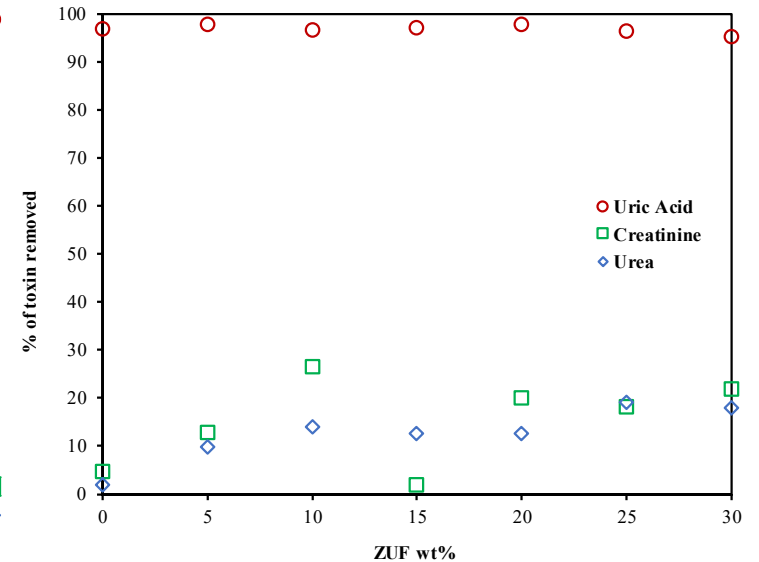
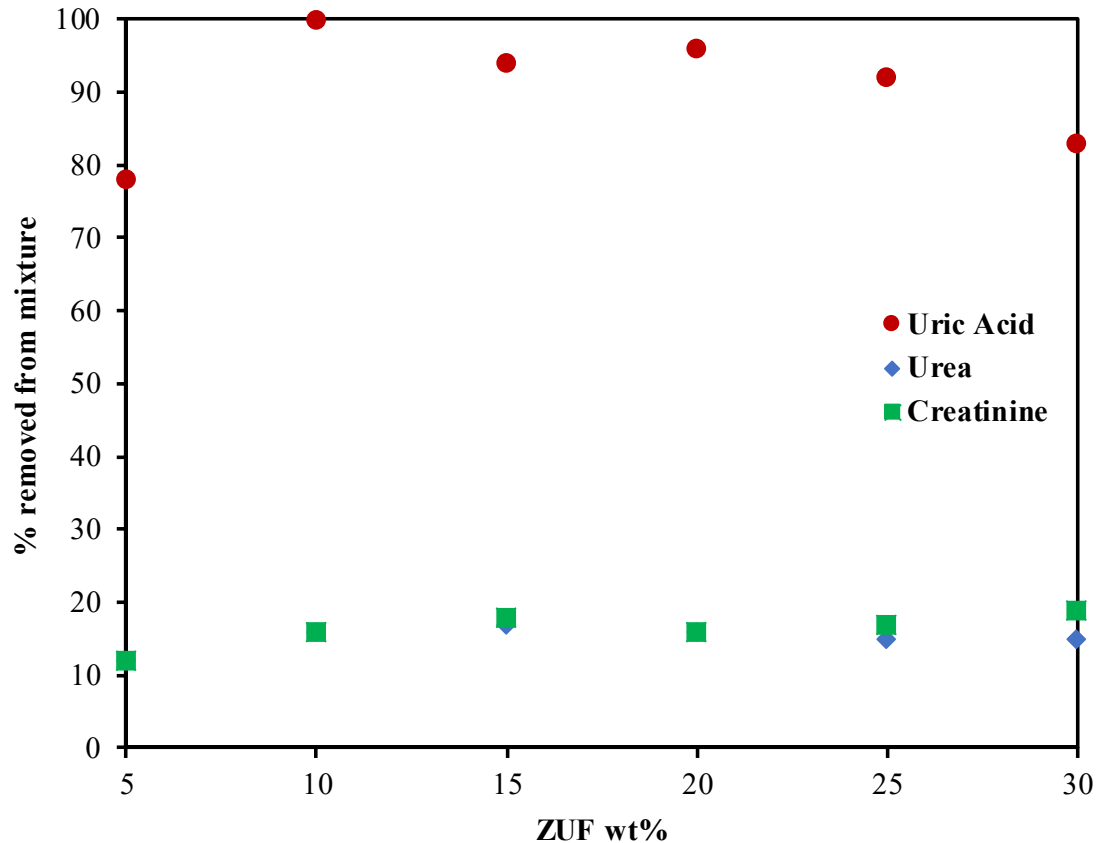
Acc.V Spot
20.0 kV 3.5

Acc.V Spot Magn Det WD Exp |-----| 50 μ m
20.0 kV 3.5 500x SE 11.6 1

Acc.V Spot Magn Det WD Exp |-----| 100 μ m
25.0 kV 3.1 350x SE 2.7 0

Acc.V Spot Magn Det WD Exp |-----| 100 μ m
20.0 kV 3.0 250x SE 8.0 0

MMMAs batch characterization



Experimental conditions:

- 2 mL of a mixture of toxins at c_{MAX}
- 2 membrane discs of 15 mm diameter
- Leave under mild agitation for 24 h

Electrospun nanofiber membranes

Collaboration with prof Maria Letizia Focarete

Chemistry Department “G. Ciamician”

Alma Mater Studiorum-Università di Bologna



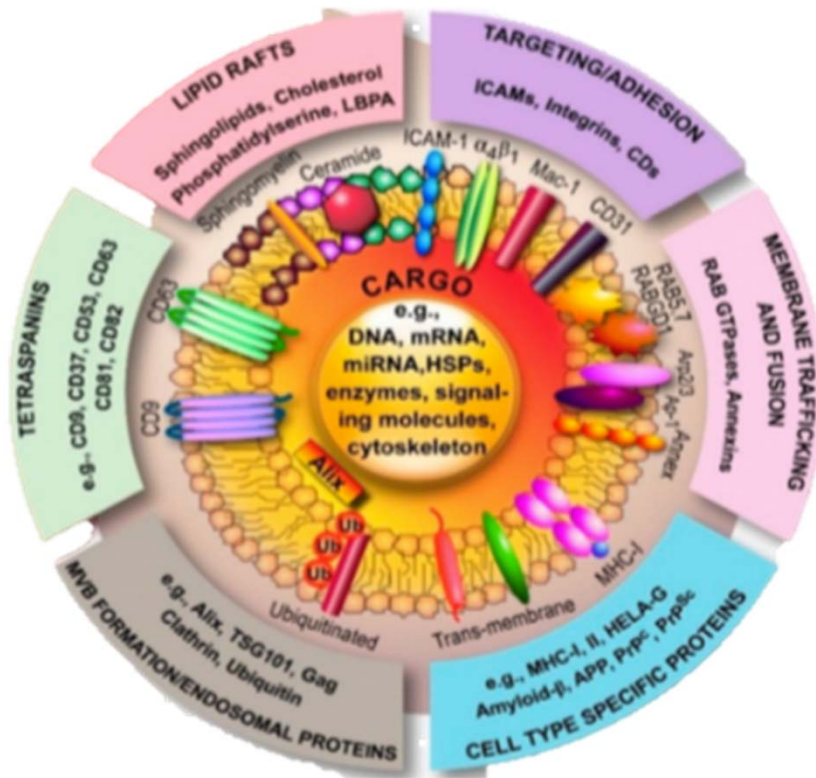
Margherita Animini



ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA

Aim of the research

Production of an affinity membrane for the isolation of
Extracellular Vesicles (EVs)



EXTRACELLULAR VESICLES
INVOLVED IN INTERCELLULAR
COMMUNICATION

Dimension: 30-150 nm diameter

Biogenesis: inward budding of
endosomal membranes



Affinity Membrane

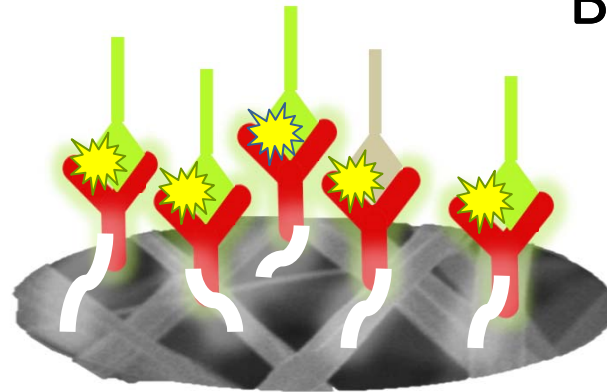
SELECTIVE INTERACTION LIGAND and TARGET MOLECULE

ELECTROSPINNING

Nano-scaled Fibers

↑ Porosity

↑ Interconnectivity



BIOCONJUGATION

Grafting of a
BIOMOLECULE:
Antibodies,
Enzymes, Peptides

FUNCTIONALIZATION

Introduction of FUNCTIONAL GROUPS and
ACTIVATION of the membrane

Unpublished work



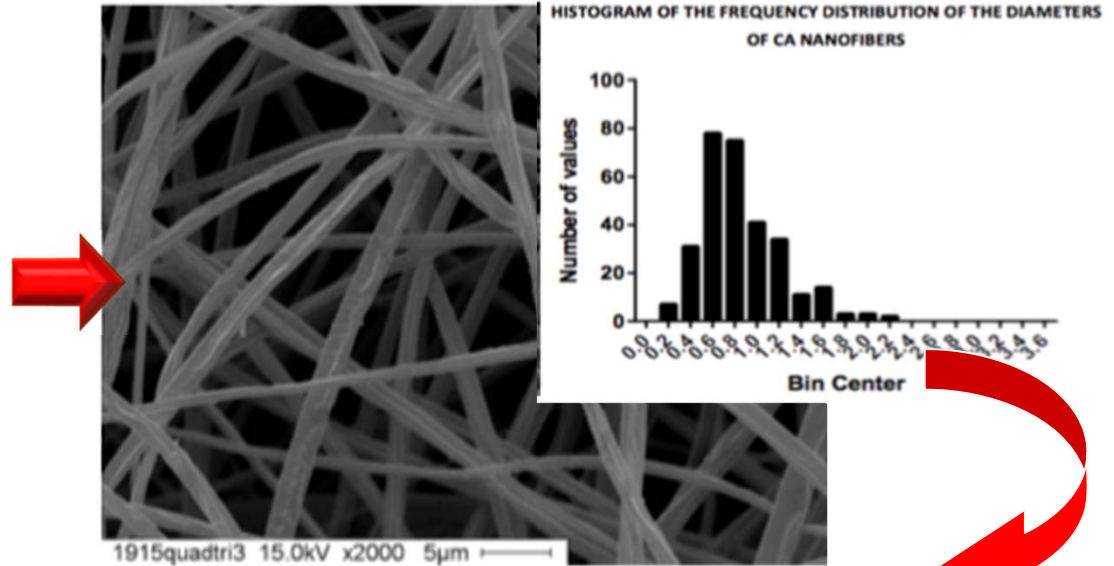
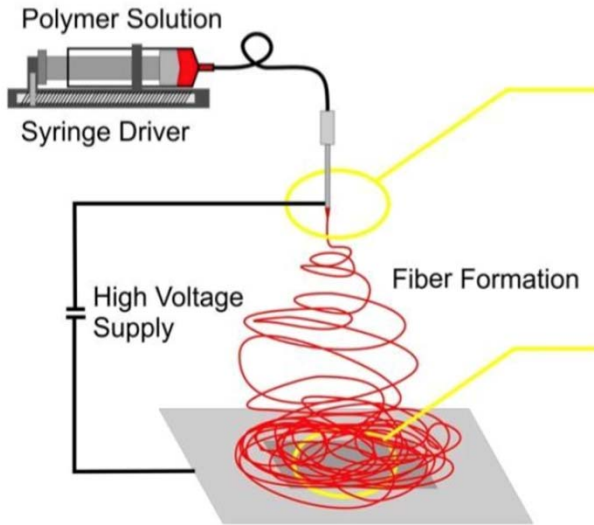
ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA

Cellulose Acetate Nanofibers

CELLULOSE
INSOLUBILITY



ELECTROSPINNING of
CELLULOSE ACETATE



**SUB-MICROMETRIC DIAMETER:
600-800 nm**

Unpublished work



ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA

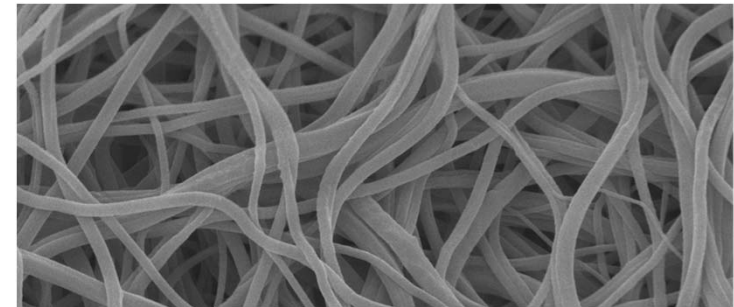
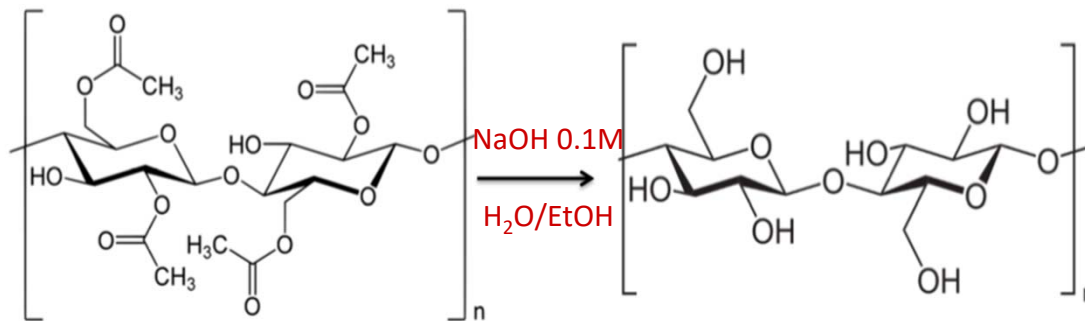
Cellulose Regeneration

HEAT TREATMENT

180°C for 1 h.

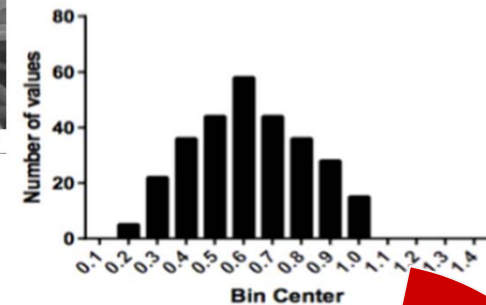


DEACETYLATION



1925 tritri 15.0kV

HISTOGRAM OF THE FREQUENCY DISTRIBUTION OF THE DIAMETERS OF REGENERATED CELLULOSE NANOFIBERS



SUB-MICROMETRIC DIAMETER:
400-800nm

Unpublished work



ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA

XPS Analysis

Cellulose Acetate

O/C RATIO:

0,69%

COMPOSITION:

O = 40,9%

C = 59,1%

5 CHEMICAL STATES:

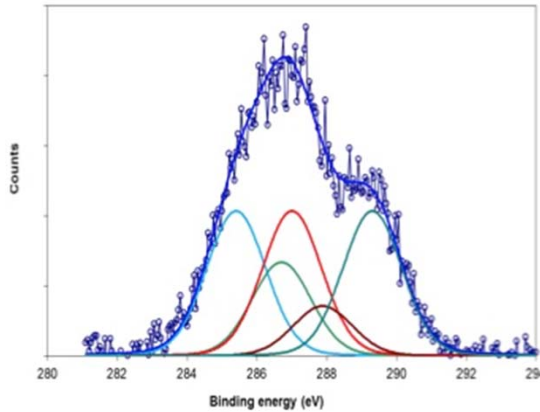
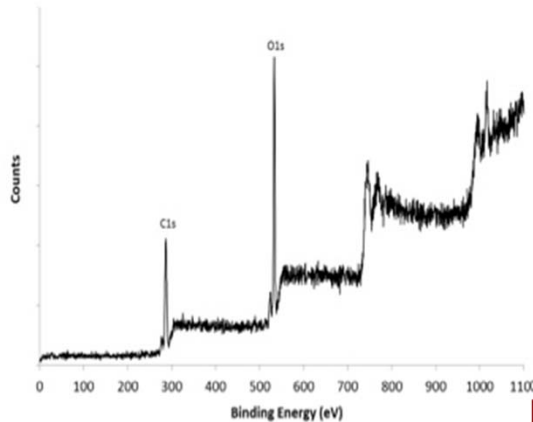
CH₃COOH

C-O

C-O-C=O

O-C-O

C=OOH



Theoretical values and area ratio RESPECTED

Regenerated Cellulose

O/C RATIO:

0,85%

COMPOSITION:

O = 45,9%

C = 54,1%

Values

RESPECTED

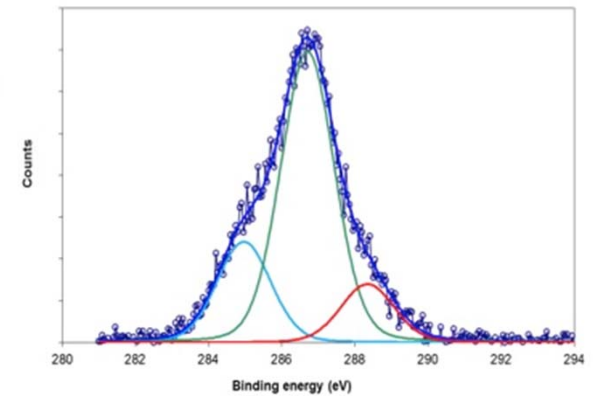
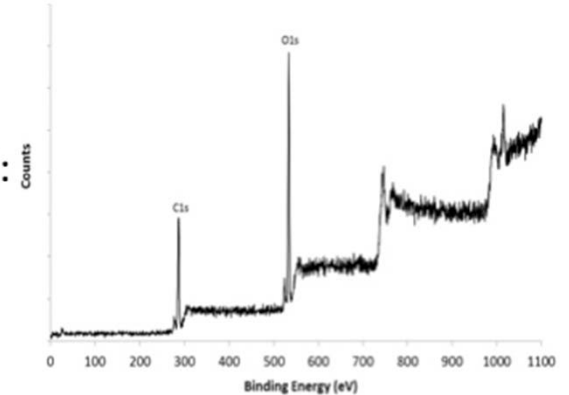
2 CHEMICAL STATES:

C-O

O-C-O

Areas ratio

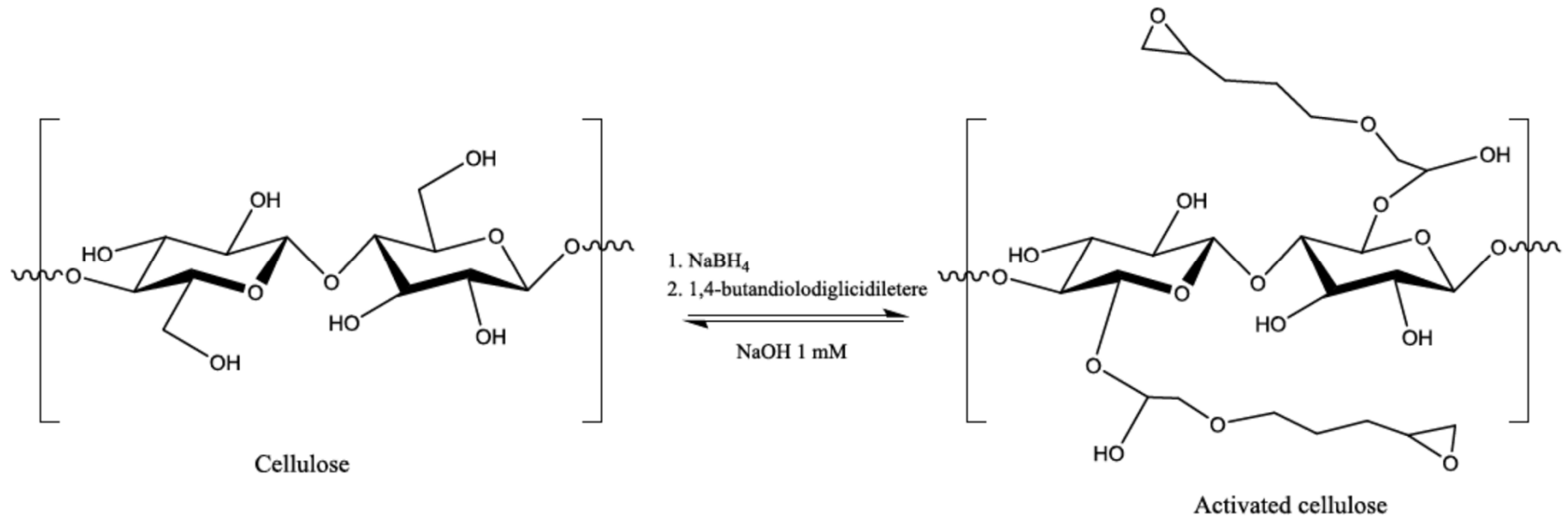
RESPECTED



Theoretical values and area ratio RESPECTED

Membrane activation

EPOXIDIZATION OF REGENERATED CELLULOSE



Unpublished work



ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA

XPS Analysis

Regenerated Cellulose

O/C RATIO:

0,85%

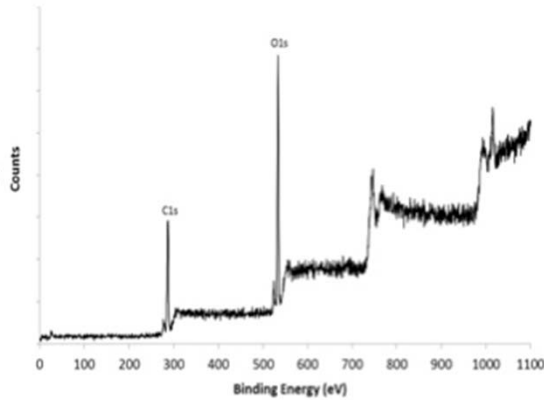
COMPOSITION:

O = 45,9%

C = 54,1%

Values

RESPECTED



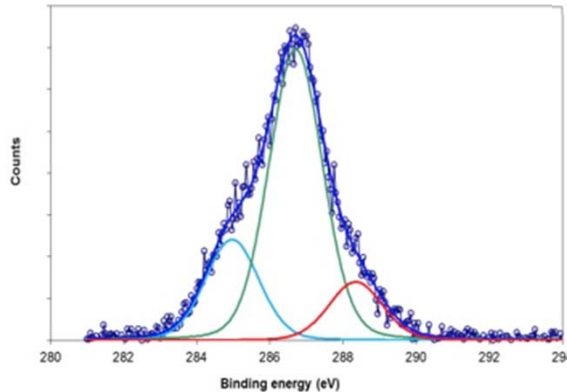
2 CHEMICAL STATES:

C-O

O-C-O

Areas ratio

RESPECTED



Theoretical values and areas ratio RESPECTED

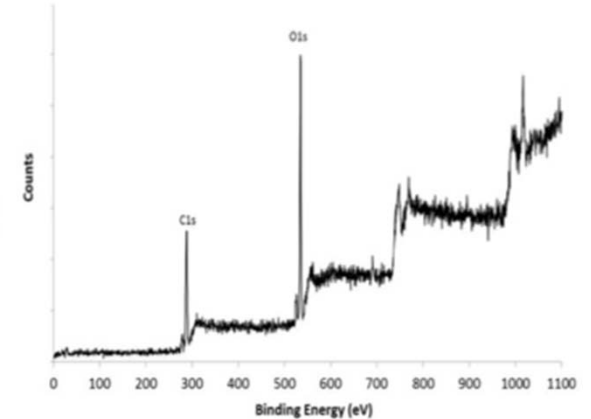
Epoxidized Cellulose

O/C RATIO:

0,59%

Values

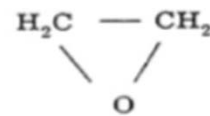
RESPECTED



3 CHEMICAL STATES:

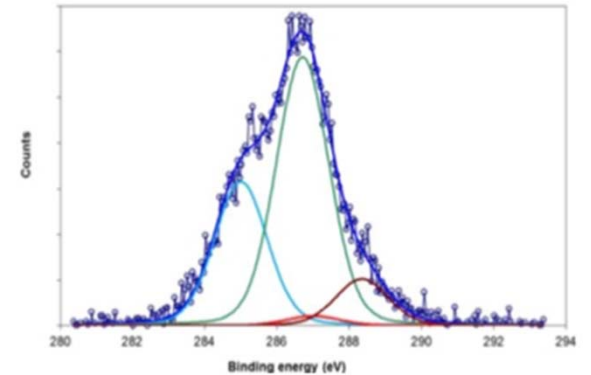
C-O

O-C-O



Areas ratio

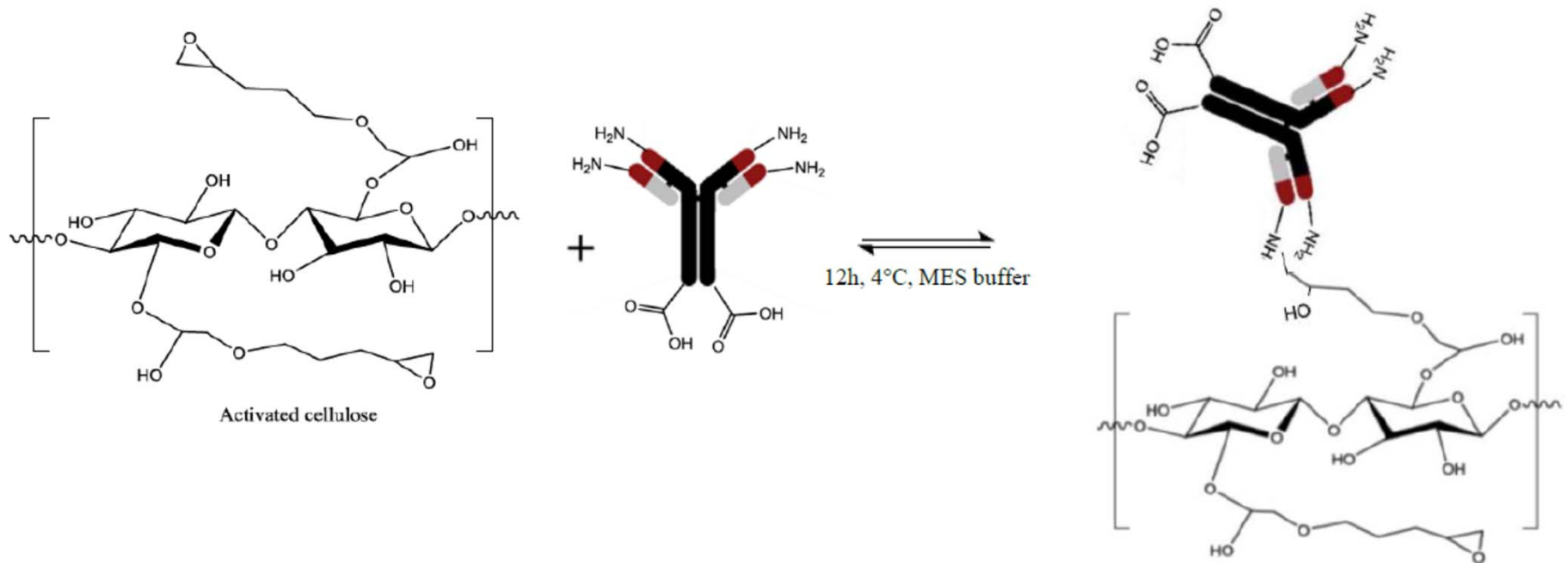
RESPECTED



Theoretical values and areas ratio RESPECTED

Functionalization

BIOCONJUGATION of Anti-CD63 (FITC) on REGENERATED CELLULOSE

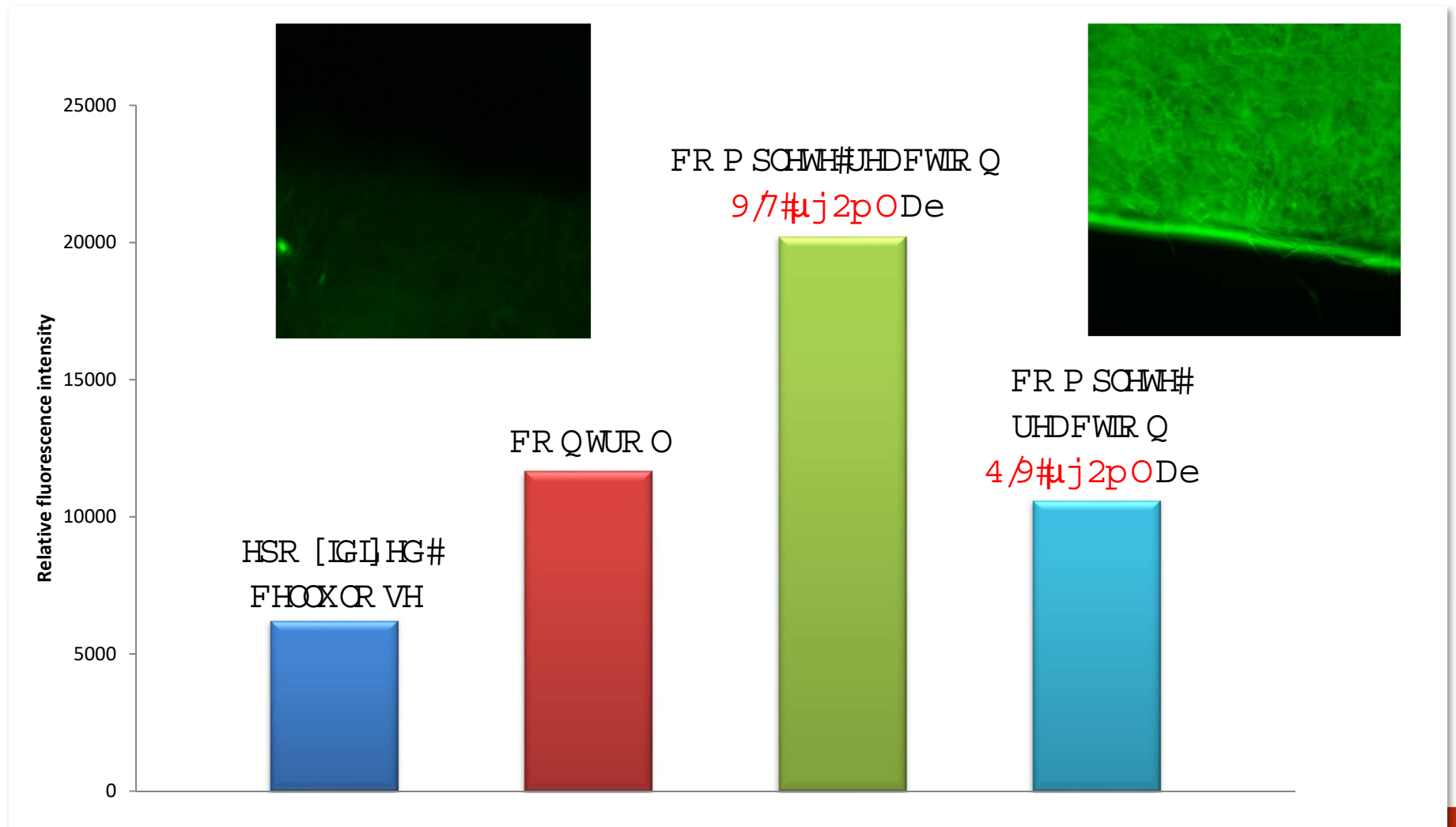


Unpublished work



ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA

Fluorescence Microscopy

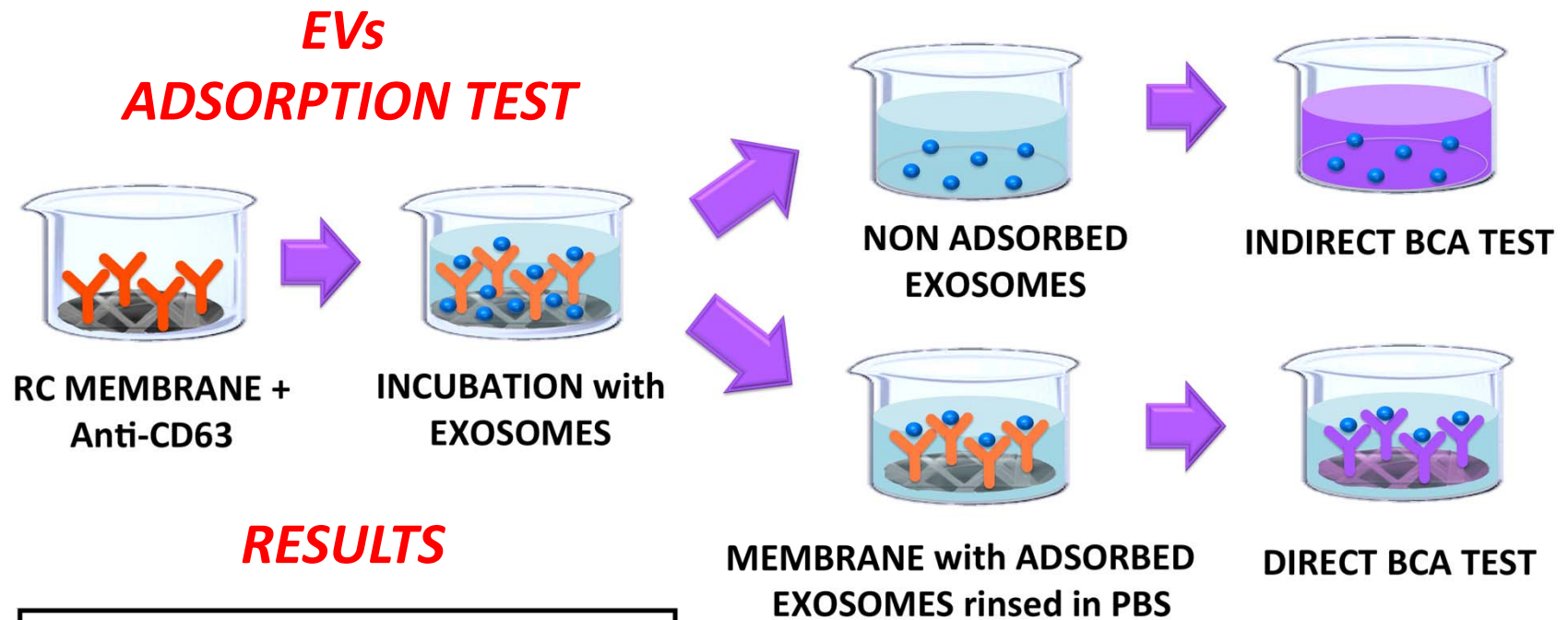


Unpublished work



ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA

Adsorption



RESULTS

QUANTIFICATION of ADSORBED EXOSOMES	
<u>DIRECTLY</u>	<u>INDIRECTLY</u>
0,0478 mg	0,0508 mg

EVs
CAPTURED

Unpublished work



ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA

CONCLUSIONS

This study led to the preparation of a regenerated cellulose affinity membrane which represents a promising candidate for the capture isolation of extracellular vesicles.

PERSPECTIVES AND CHALLENGES

- ✓ Optimization of the degree of functionalization and bioconjugation
- ✓ Study of the Antigen-Antibody binding kinetic
- ✓ Development of a suitable module to use these membranes in a flow configuration

Nanostructured Membranes for Gas Separation

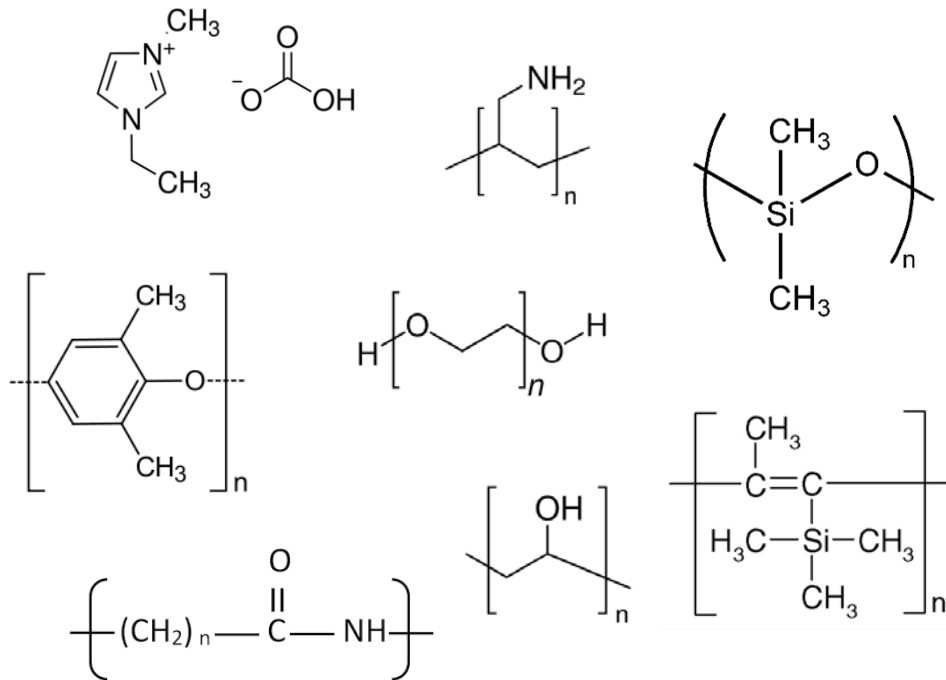
Maria Grazia De Angelis, Matteo Minelli, **Marco Giacinti Baschetti**

DICAM, Alma Mater Studiorum-Università di Bologna



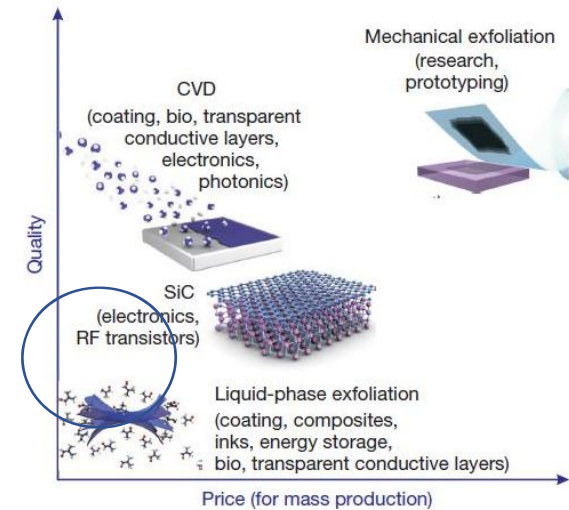
NANOMEMC² is a H2020 funded project focusing on use of nanofiller to boost membrane performances in Carbon capture (CCS) applications.

Polymers

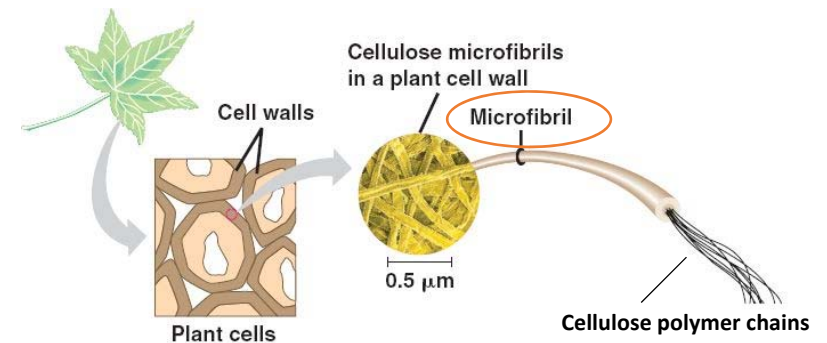


Fillers

Graphene

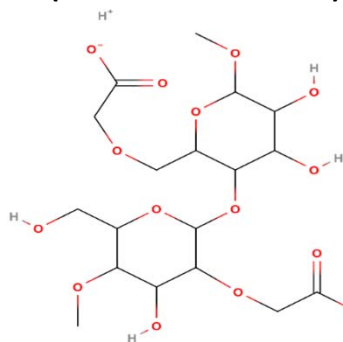


Nanocellulose

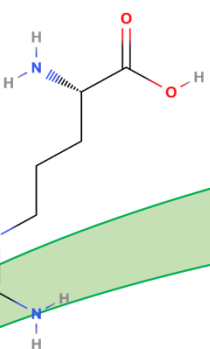


Nanocellulose based facilitated transport membranes

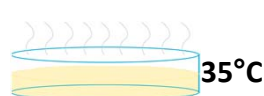
**CARBOXYMETHYLATED
NANOCELLULOSE (CMC-NFC)
(WATER SUSPENSION)**



L-ARGININE



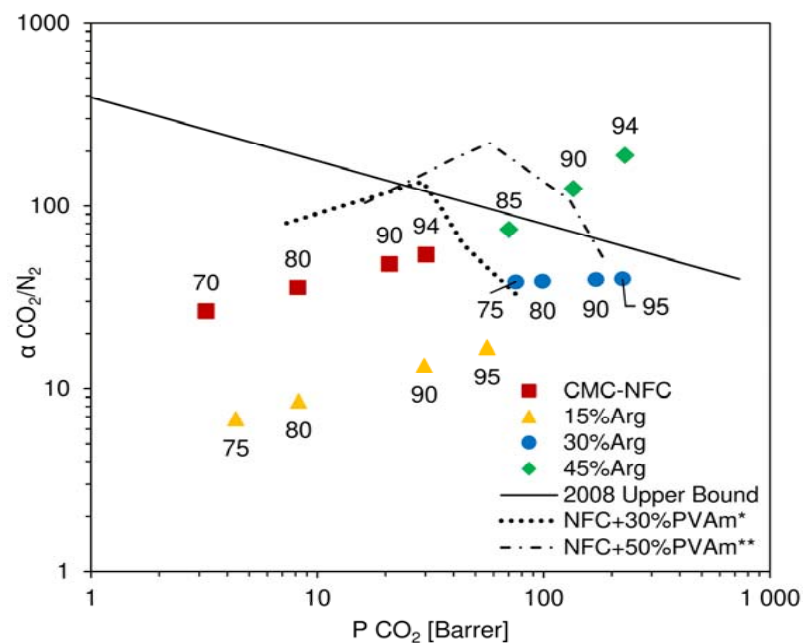
SOLVENT CASTING



~ 50 μm



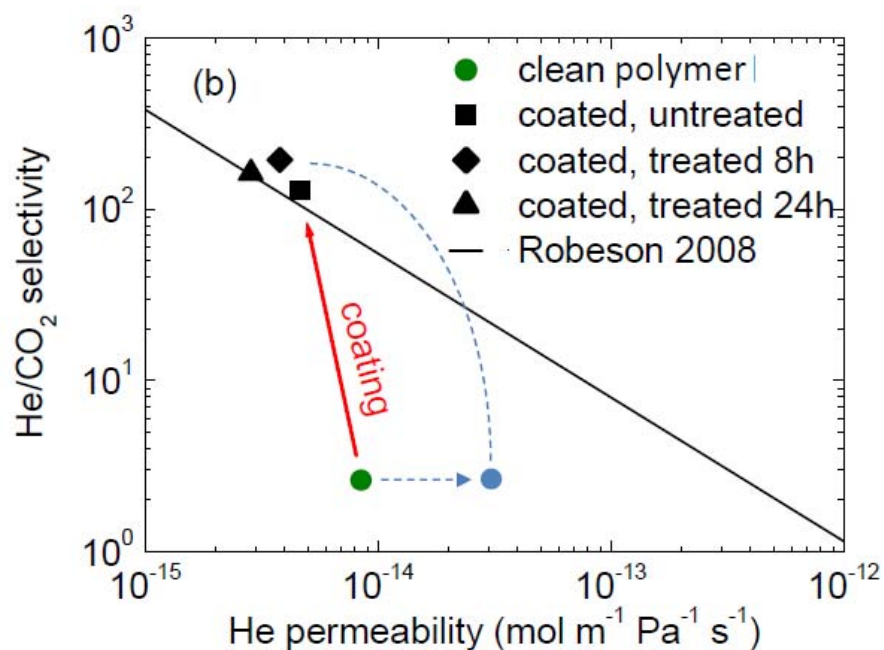
Simple mixing allows to obtain stable membranes with extremely high potential for application in CCS and other CO₂ separation processes



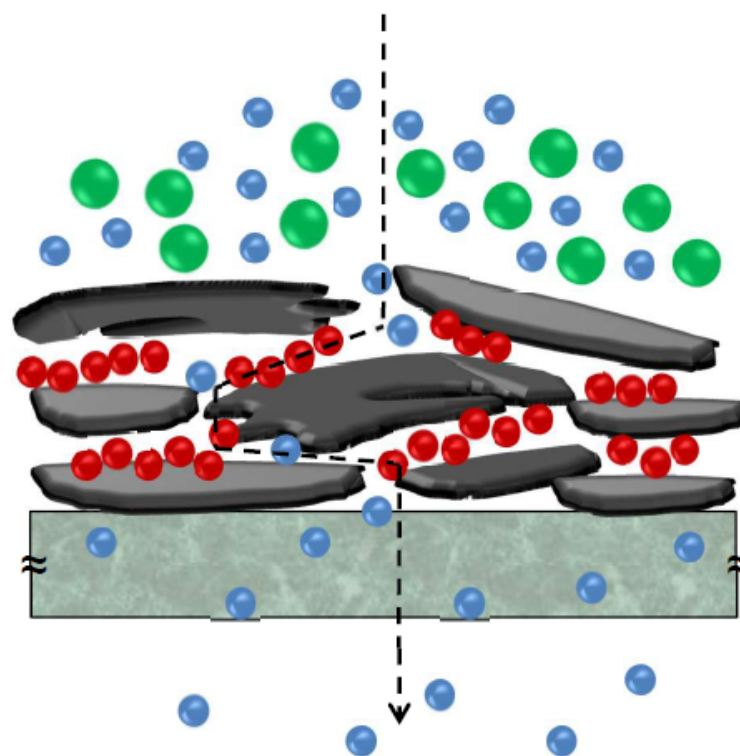
Graphene membranes by LbL deposition

Graphene is deposited via layer by layer (LbL) deposition on the top of a support

The membrane appeared to offer **extremely high He/CO₂ selectivity**



Selective Tortuous path



Pierleoni et al - ACS Appl. Mater. Interfaces **2018**, 10, 11242

Almost there-what's next?

Membrane technology is well-established in water desalination, wastewater treatment, gas separation, energy power and storage, biomanufacturing, chemical and petrochemical, and agro-food industry.

However, we are still far from the complete exploitation of this technology.

Fouling, aging, membrane lifetime, improved selectivity and transport are among the remaining challenges.

The design of new nanostructured membranes with improved properties is a key issue to these challenges.



membranes

an Open Access Journal by MDPI



Special Issue

Membrane Chromatography for Biomolecules Purification

Special Issue Editors:



Prof. Dr. Cristiana Boi

Alma Mater Studiorum-Università di Bologna,
Italy

E-mail: cristiana.boi@unibo.it

Submission Deadline: 31 July 2019

This themed issue aims to collect key contributions to the field and give an overview of novel adsorptive membranes with improved properties and functionalities, new applications, and more efficient module design and mathematical modelling, addressing both fundamental aspects and applied research.

Keywords

- Membrane chromatography
- Membrane adsorbers
- Affinity
- Ion exchange
- Hydrophobic interactions
- Biomolecules
- Proteins
- Antibodies
- Surface modification
- Mathematical modelling



Membranes Editorial Office
St. Alban-Anlage 66
4052, Basel, Switzerland

✉ membranes@mdpi.com
▶ www.mdpi.com/journal/membranes
🐦 @Membranes_MDPI



ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA



ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA

THANK YOU

cristiana.boi@unibo.it



ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA