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Micro-Structured Alumina Hollow Fibre Membranes – Potential Applications in Wastewater Treatment

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Membrane research at Imperial College

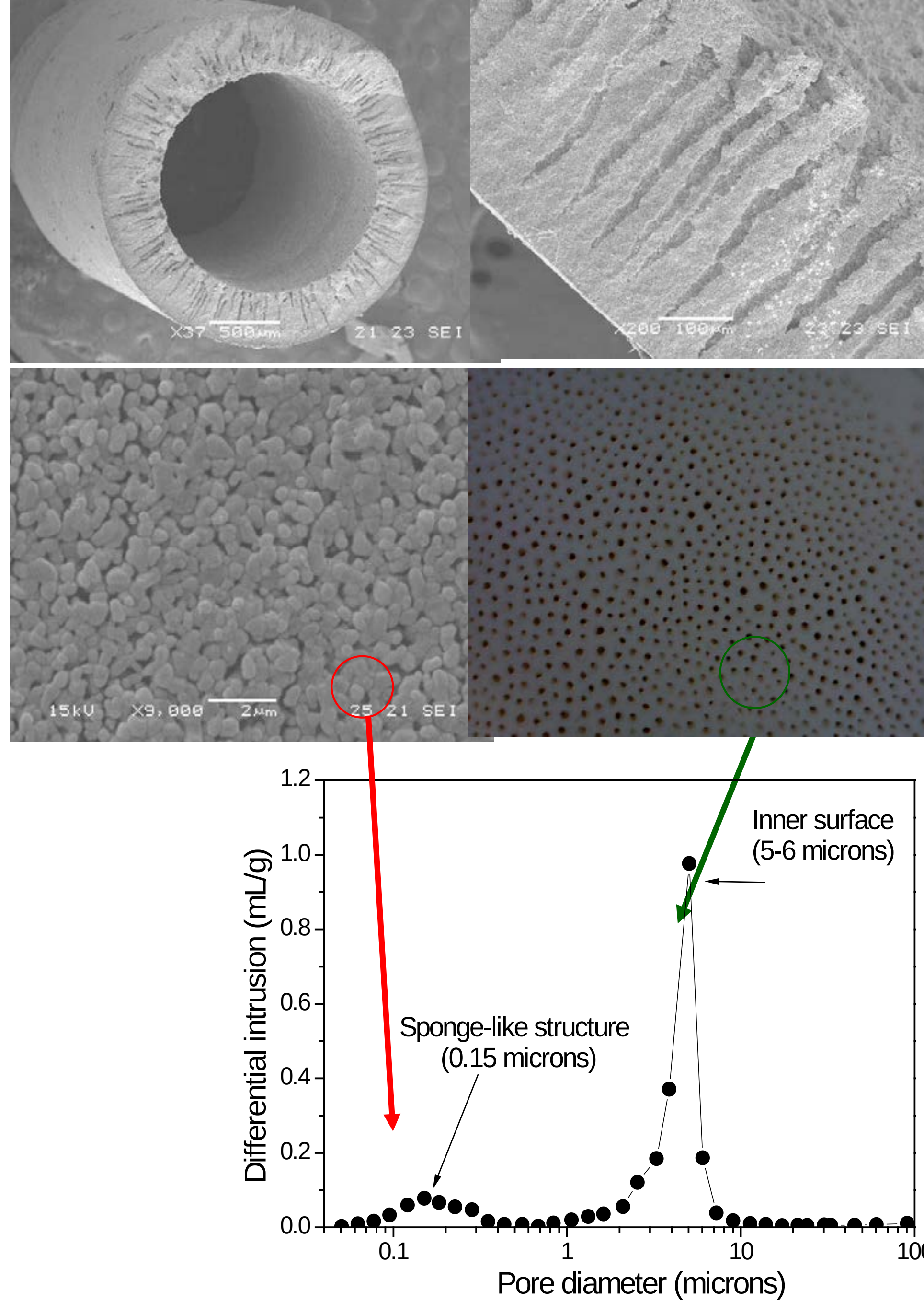
- **Membrane Formation**
  - Flat sheet, hollow fibres and dual-layer hollow fibres
- **Membrane Separations**
  - Applications to solvent systems
  - NH3 removal from water
  - Removal of VOC from water
  - Decolorization of dye-containing wastewater
  - Forward osmosis for seawater desalination
- **Membrane Reactors**
  - Membrane reactors for energy applications
  - Membrane reactors for dehydrogenation reactions
  - Membrane Bioreactors/Artificial Organs
  - Chlorophenol elimination
  - Membrane reactors for water purification

Outline:

(1) Micro-Structured Alumina Hollow Fibre Membranes

(2) Possible applications

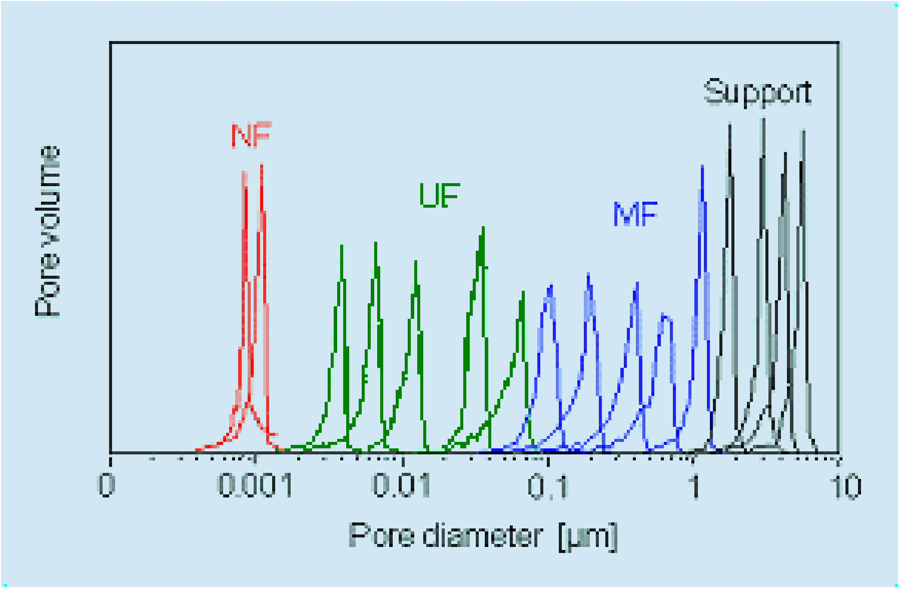
(3) Graphene based ceramic composite membranes

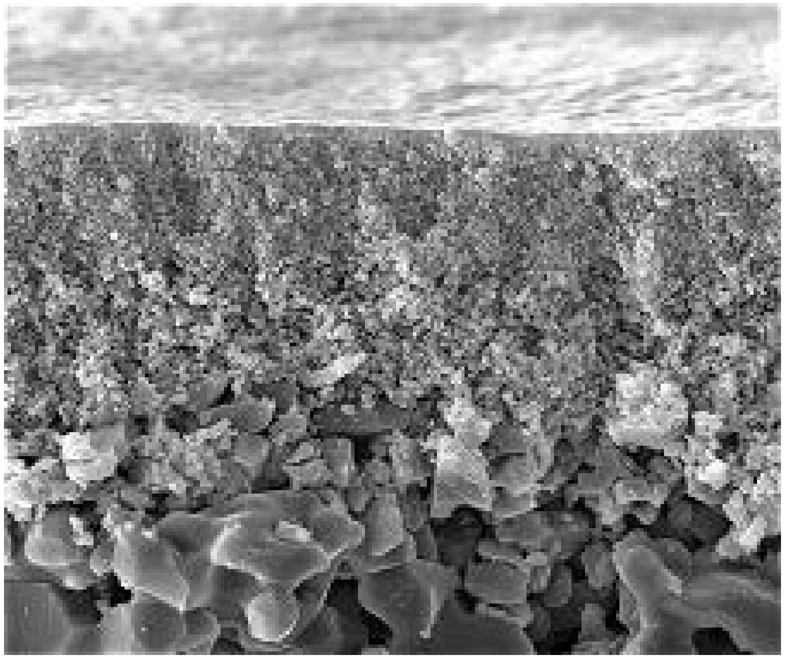


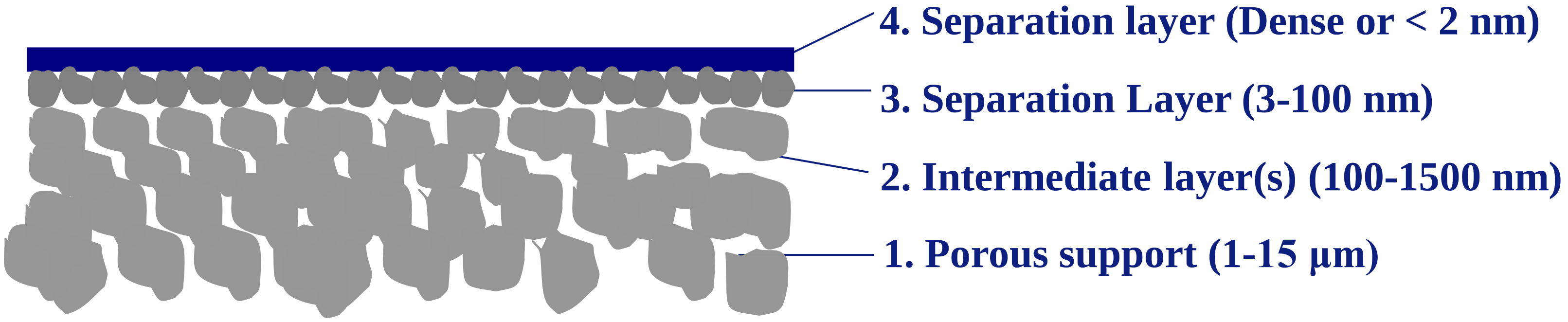
Bi-modal pore size distribution

1. Asymmetric ceramic hollow fibre membranes

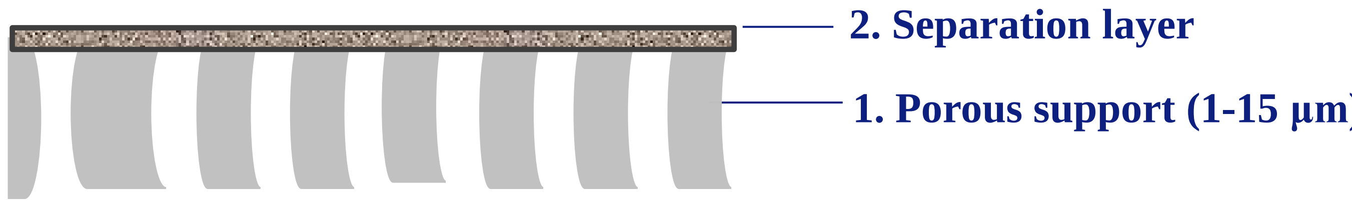
Current commercial ceramic membranes







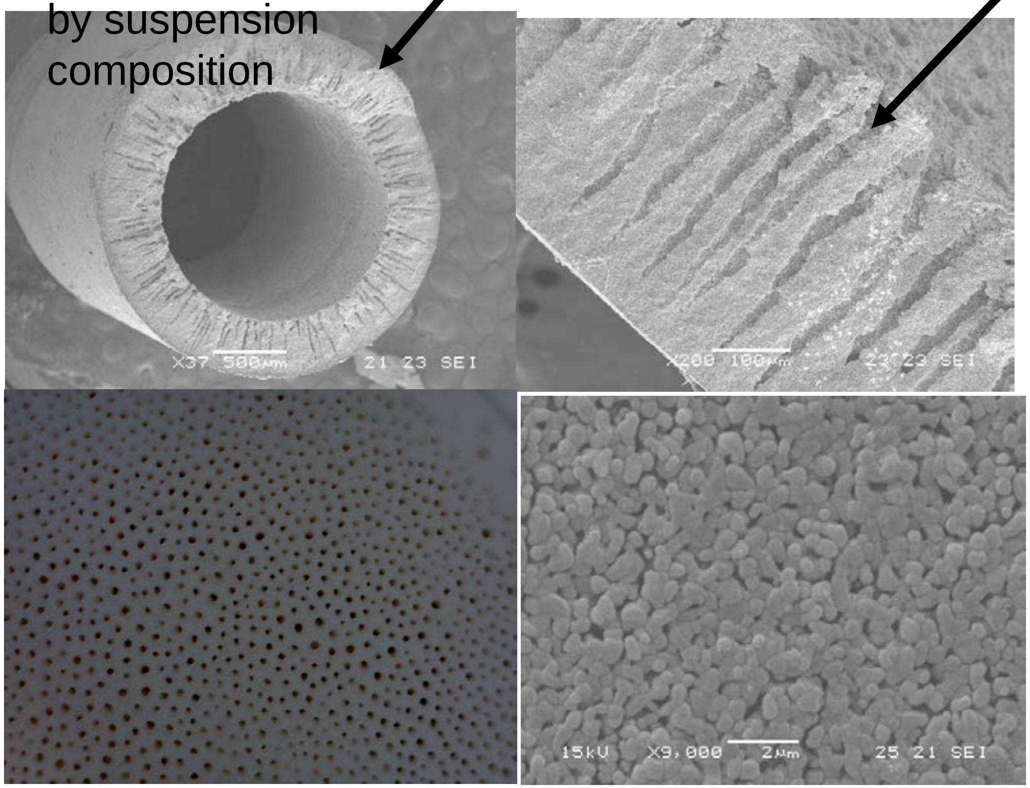
Asymmetric Structure



- Randomly packed particles
- Properties determined by suspension composition

Sponge-like structure

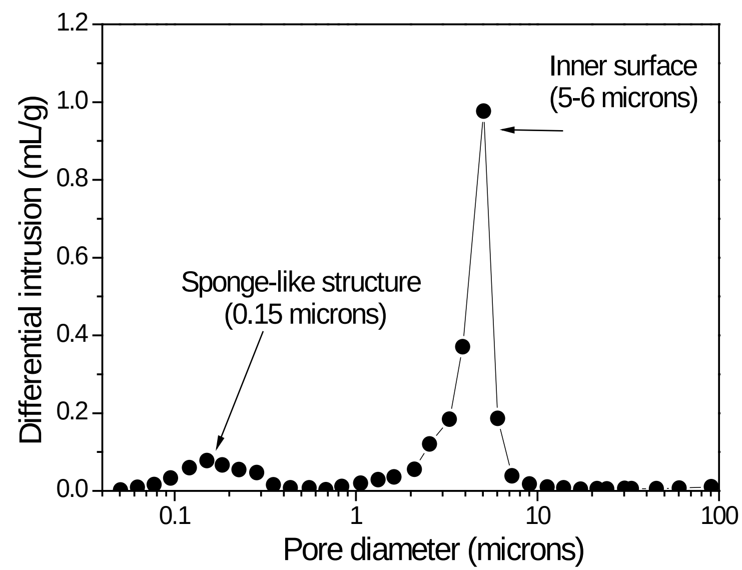
Micro-channels



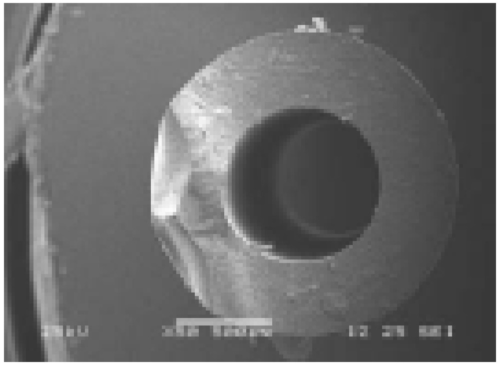
Inner surface **Outer surface**

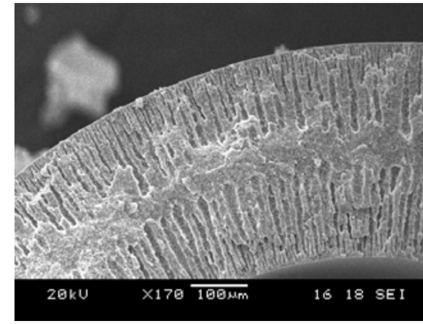
- Micro-channels result from hydrodynamically unstable viscous fingering
- Micro-channel structure is retained during heat treatment

Bi-modal pore size distribution



Preparation method





Starting suspension

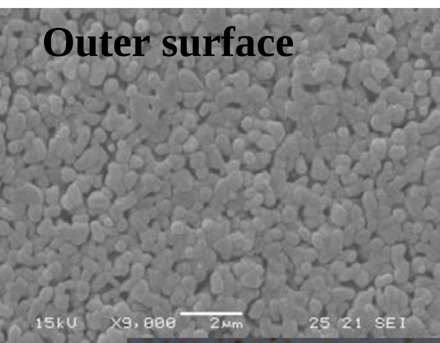
Dispersion of particles

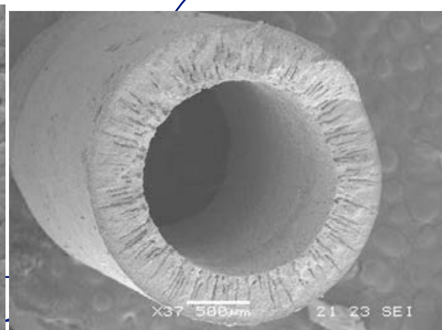
Rheology of the suspension

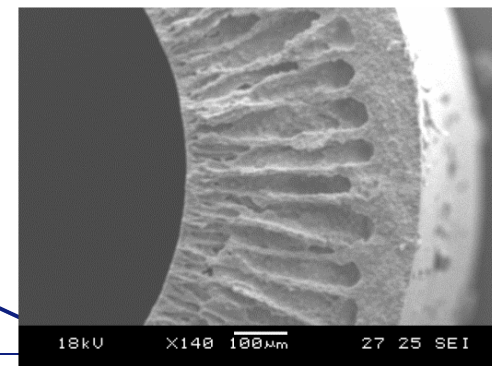
Successful

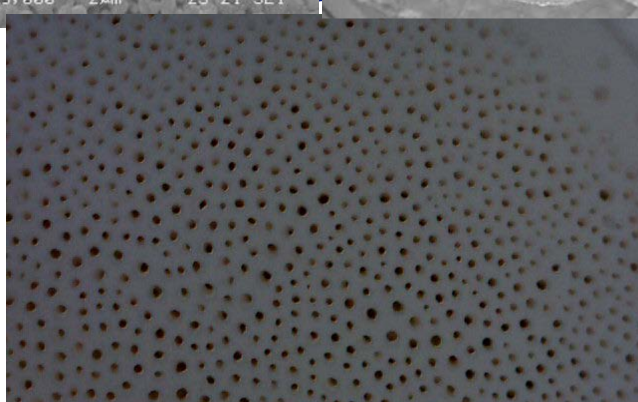
☺

branes









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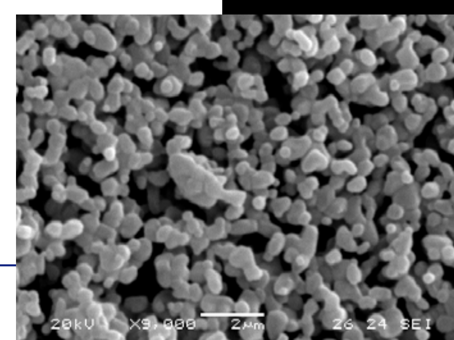
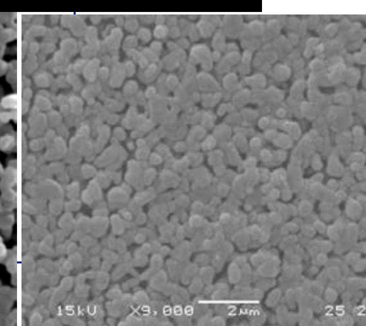
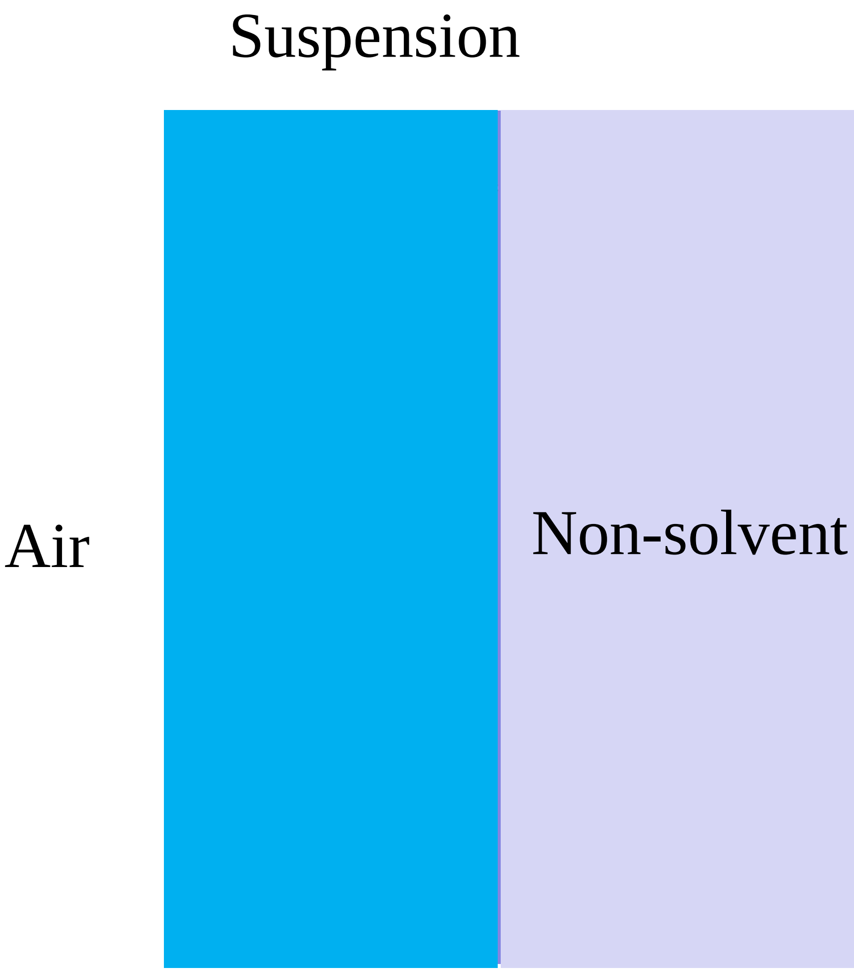


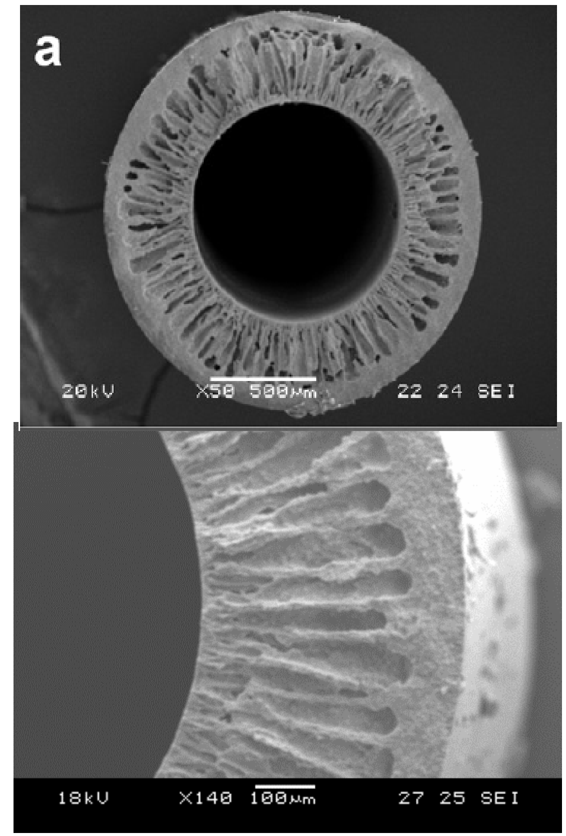
Inner surface



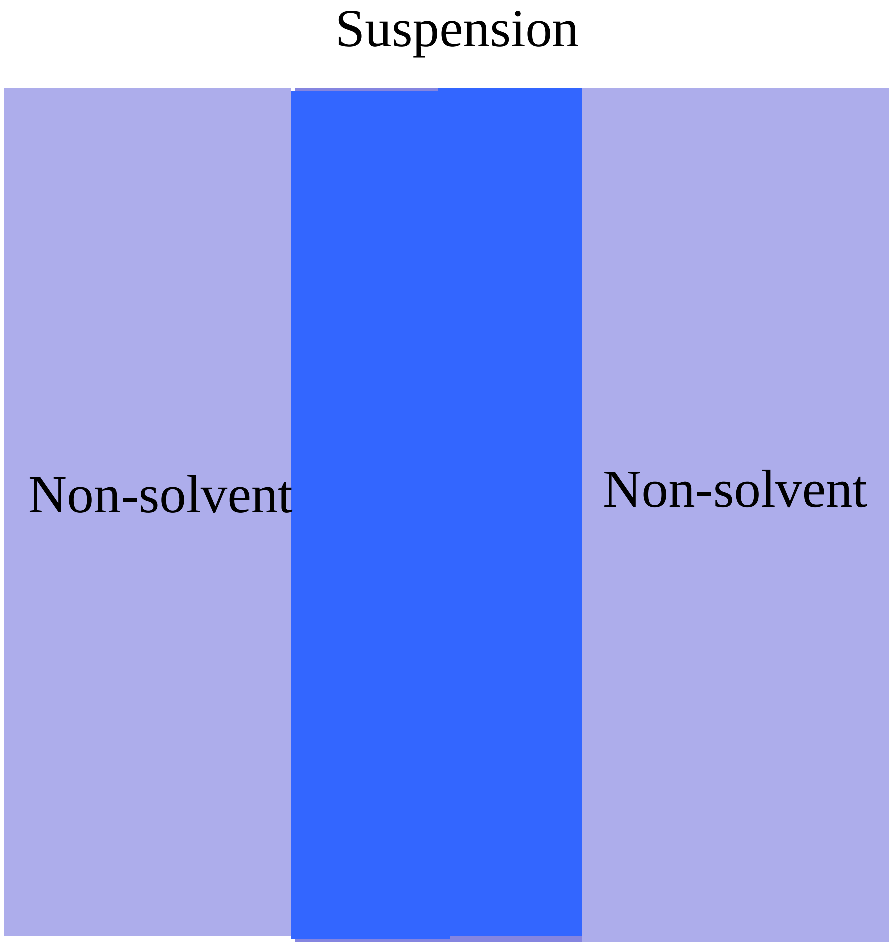
Outer surfa

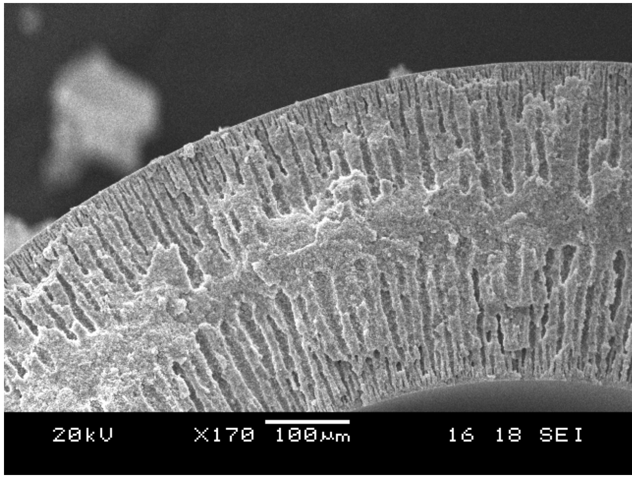
Micro channel formation mechanism (viscous fingering)



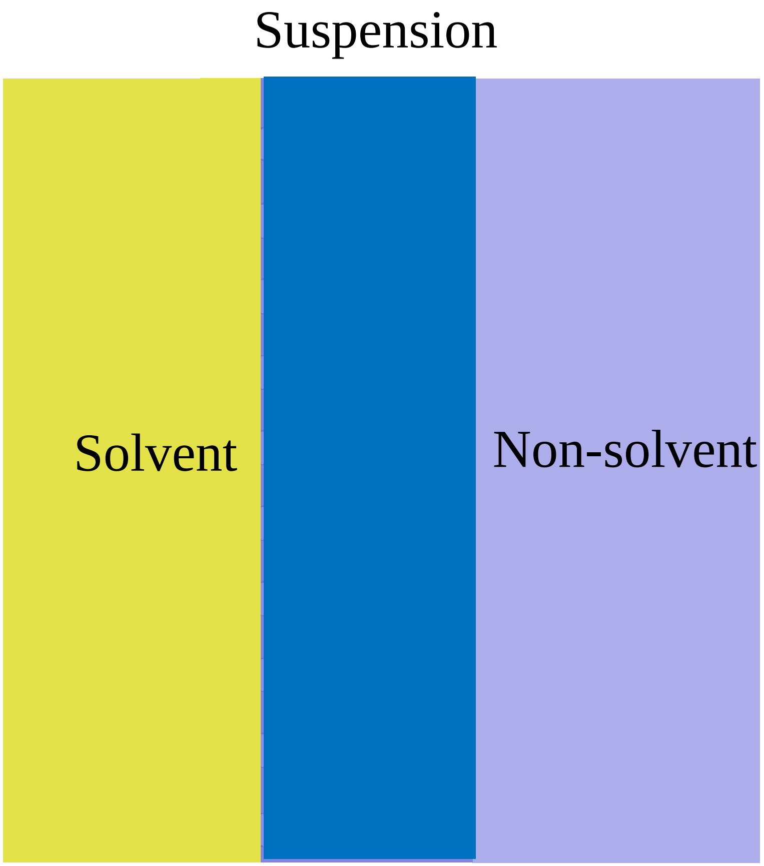


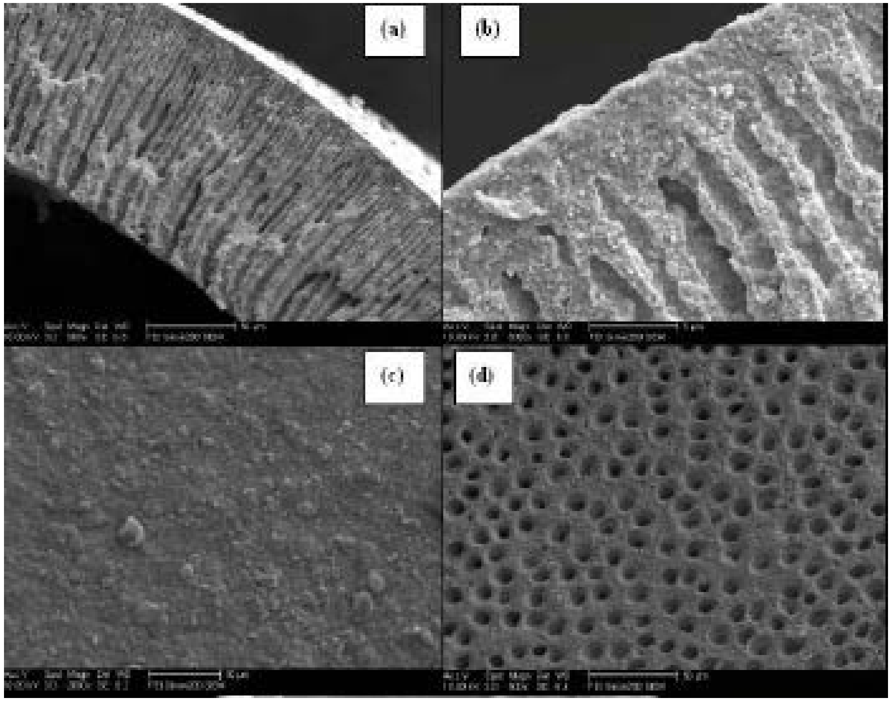
Micro channel formation mechanism

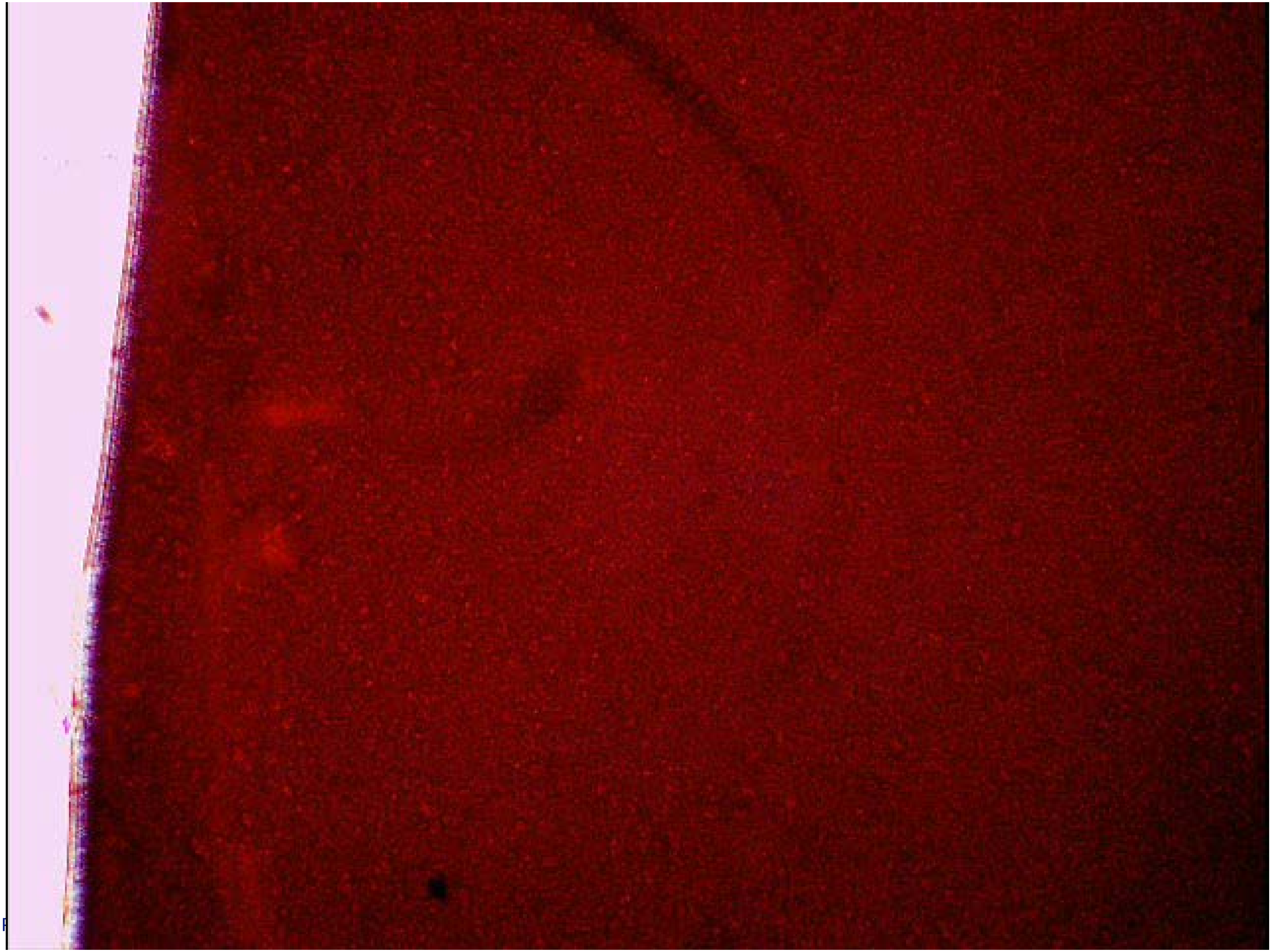




Micro channel formation mechanism

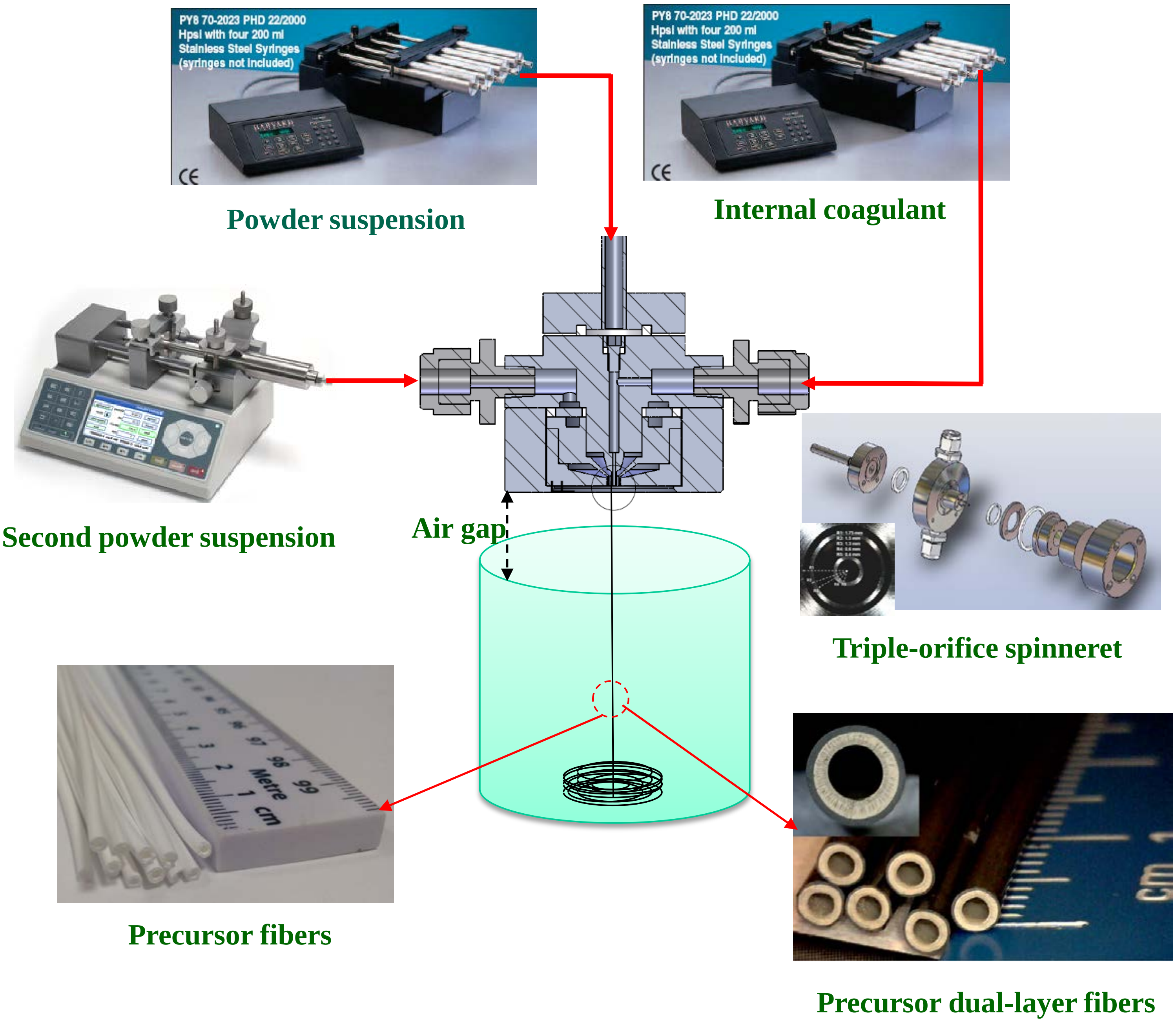






Membrane precursors

Phase inversion technique/Viscous fingering



Sintering

Normal sintering
(in static air)

Precursor HF
(ceramic particle & polymer)

1
RT-600 ºC
Fully removing polymer

2
600-1450 ºC
Sintering of ceramic particle

3
1450-RT ºC
Cooling down

Ceramic HF

Controllable sintering
(in controlled atmosphere)

Precursor HF
(ceramic particle & polymer)

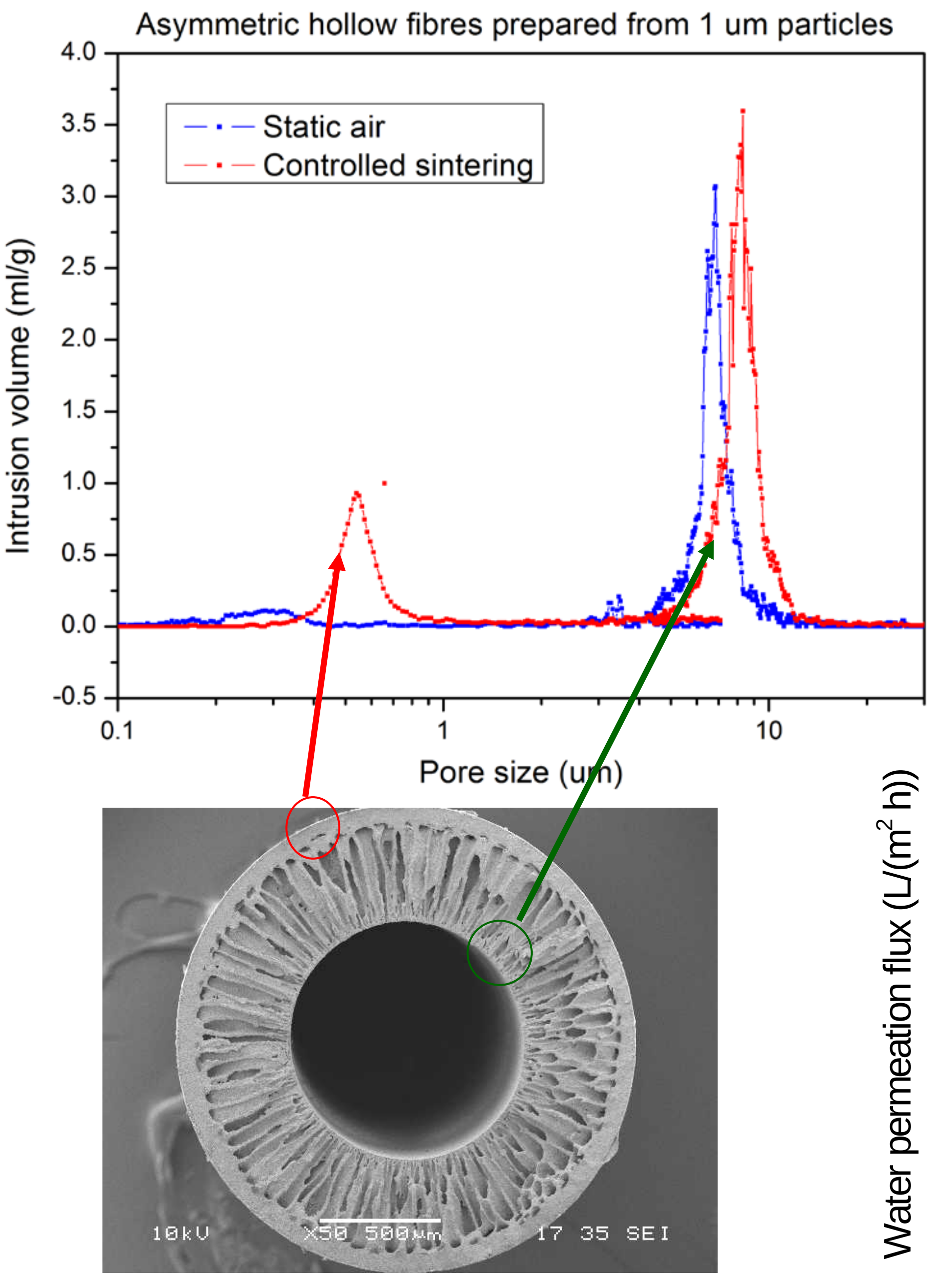
1
RT-T1 ºC
Partially removing polymer
In static air

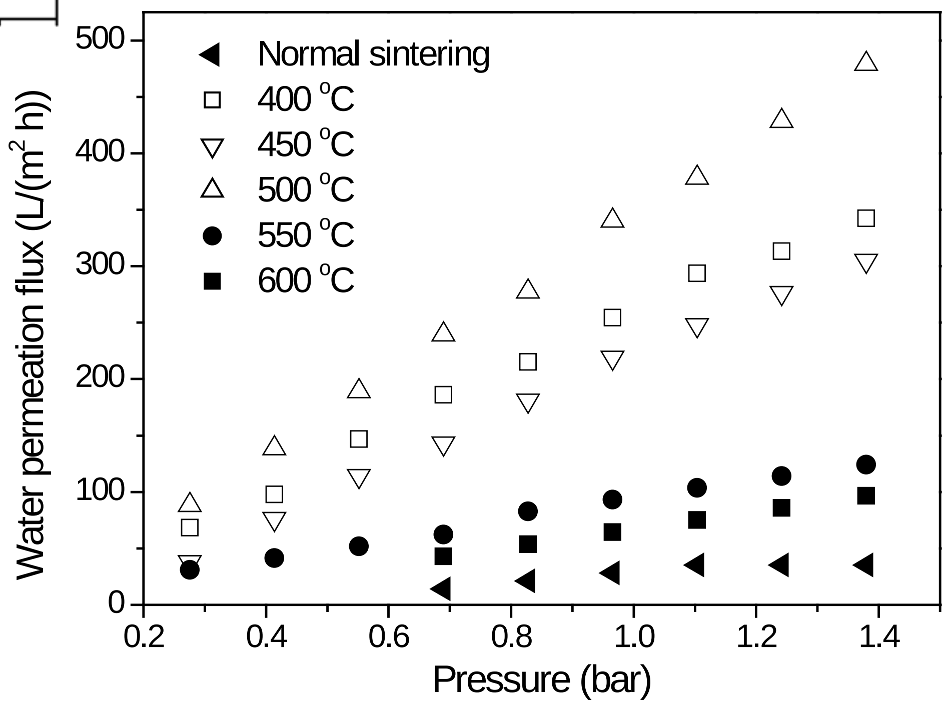
2
T1-1450 ºC
Sintering of membrane
In pure N_2

1450-RT ºC
Cooling down
In pure N_2

3
RT-T2 ºC
Fully removing carbon
In static air

Ceramic HF

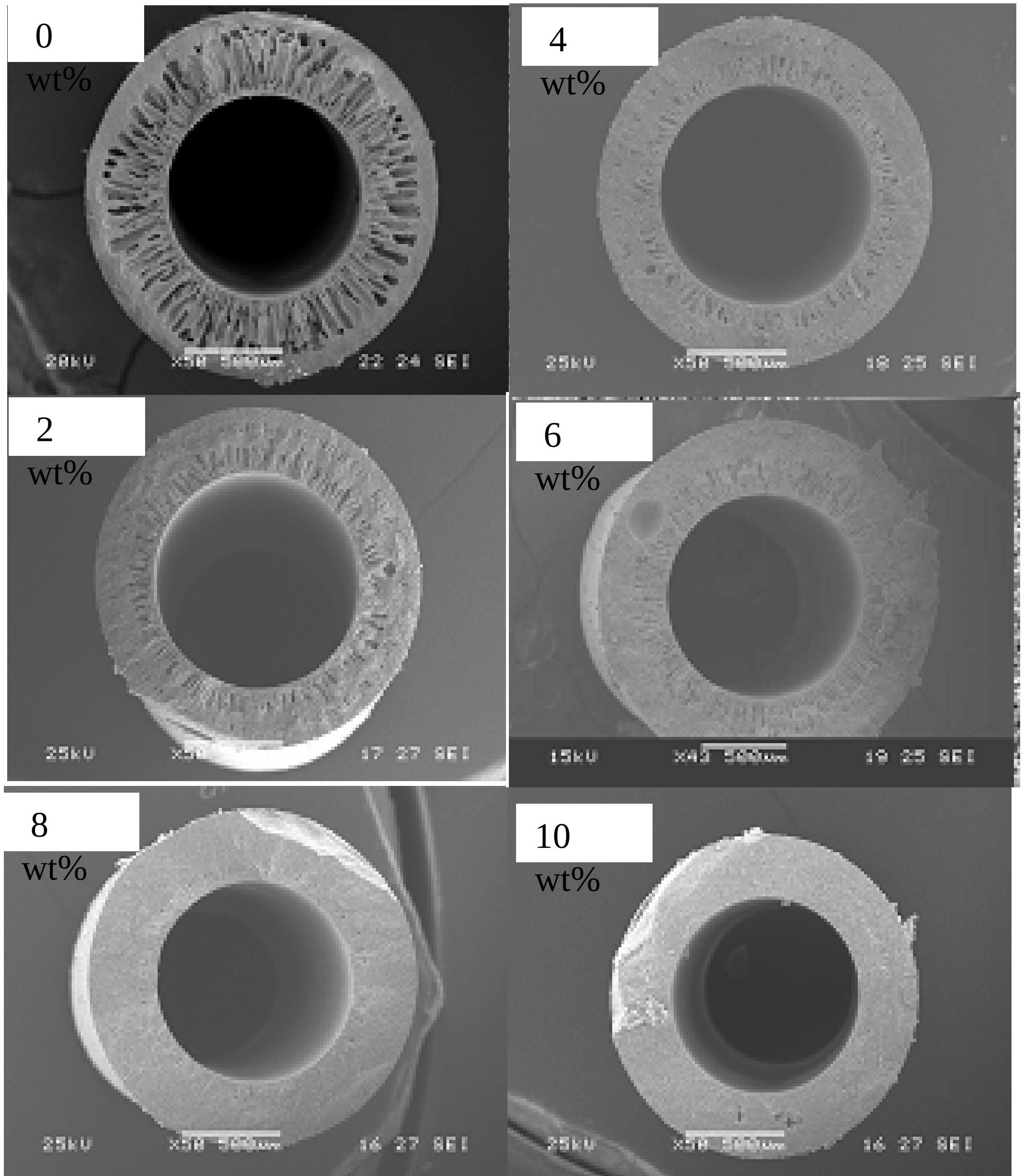


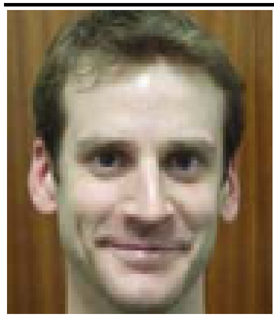


Wu et al, JMS, in press

Fibre morphology:

Effect of Non-solvent additive (water)

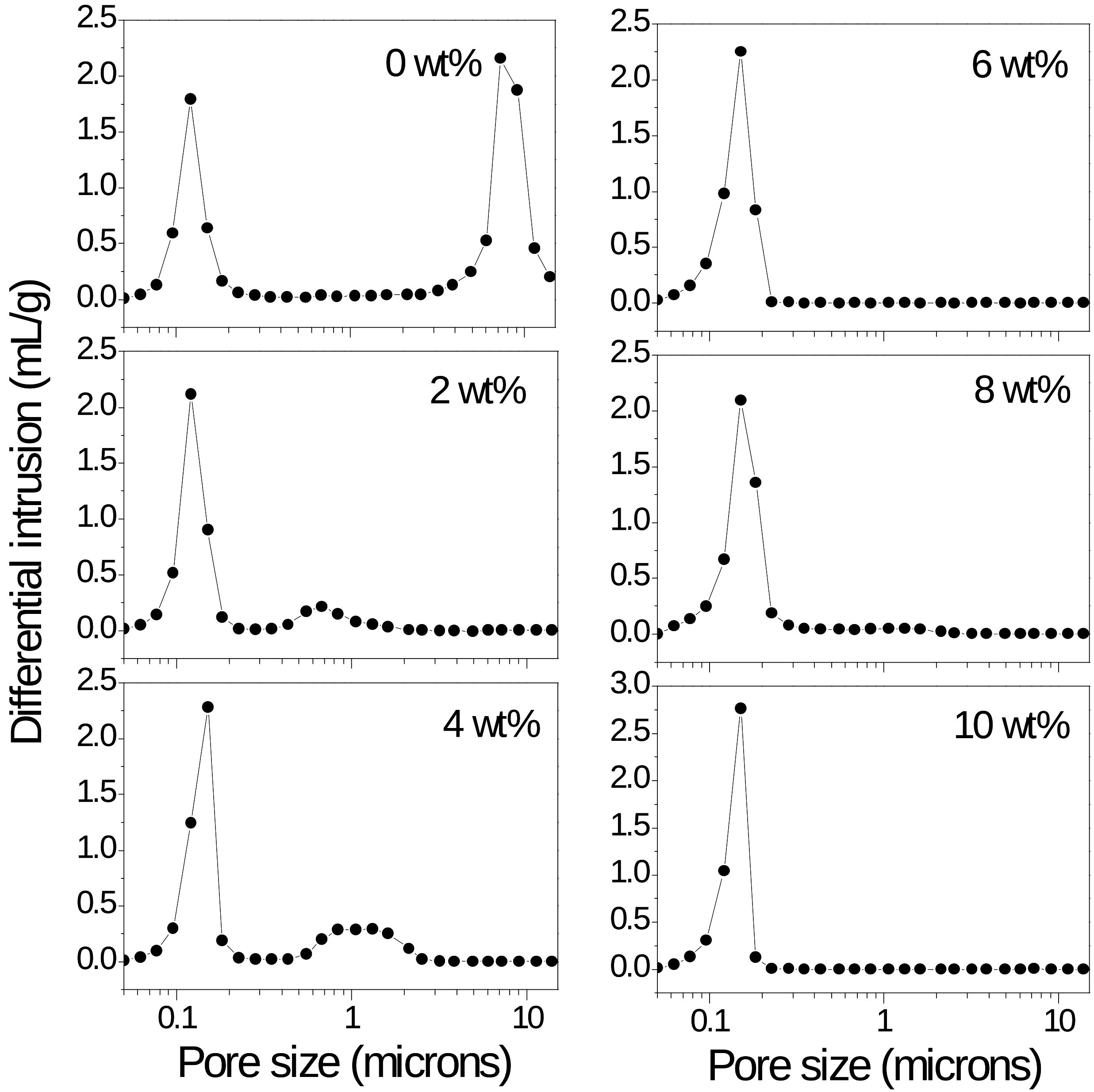




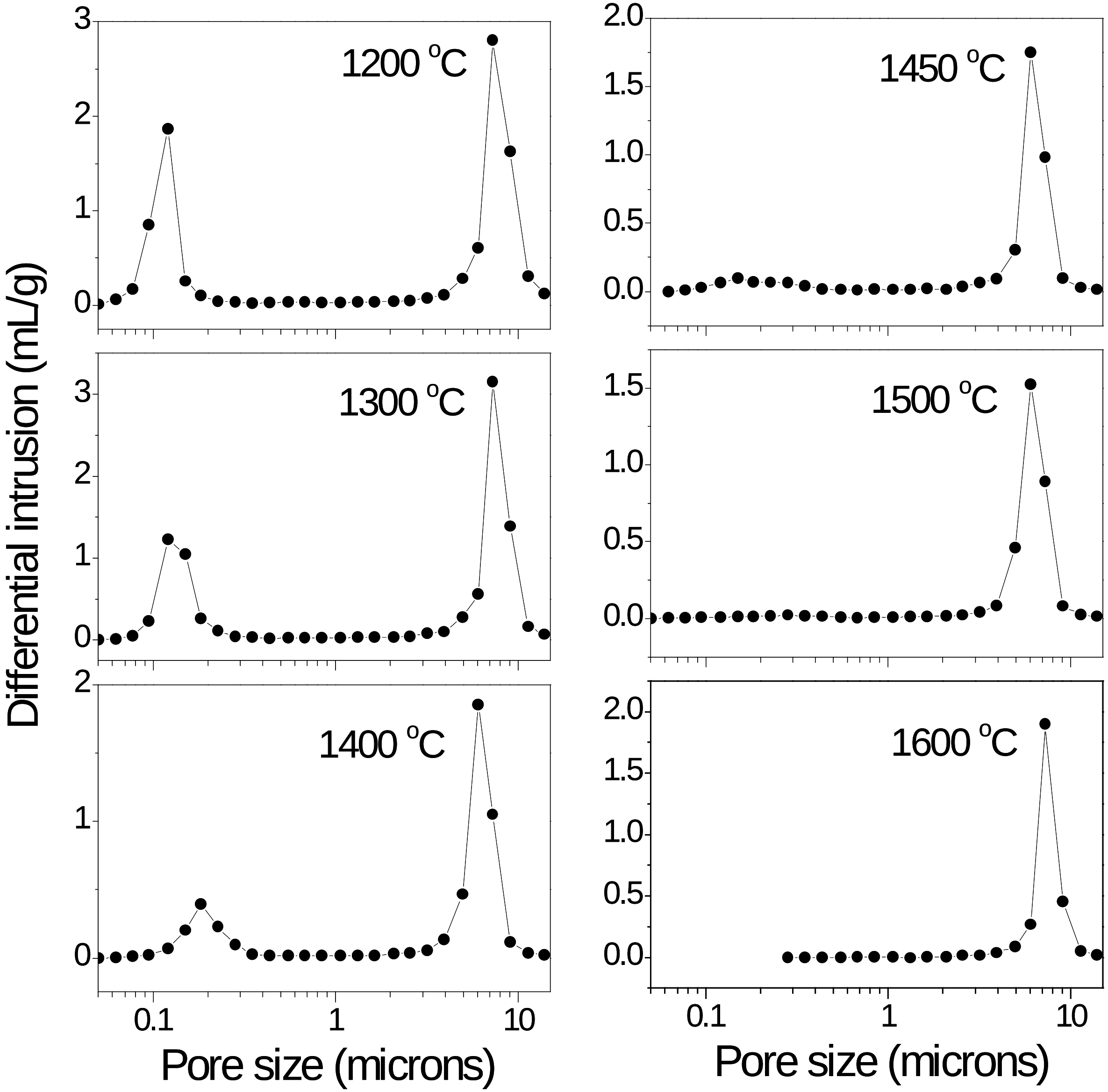
Benjamin KINGSBURY

B.F.K. Kingsbury, K. Li / Journal of Membrane Science 328 (2009) 134–140

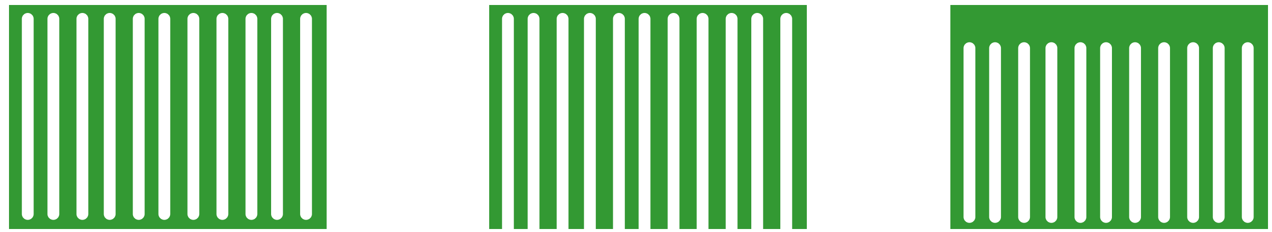
Mercury intrusion data for fibres prepared with 0 wt%-10 wt% water calcined at 1200 ^{o}C at static air



Mercury intrusion data of pore size vs. sintering temperature for an asymmetric hollow fibre prepared with 0% water



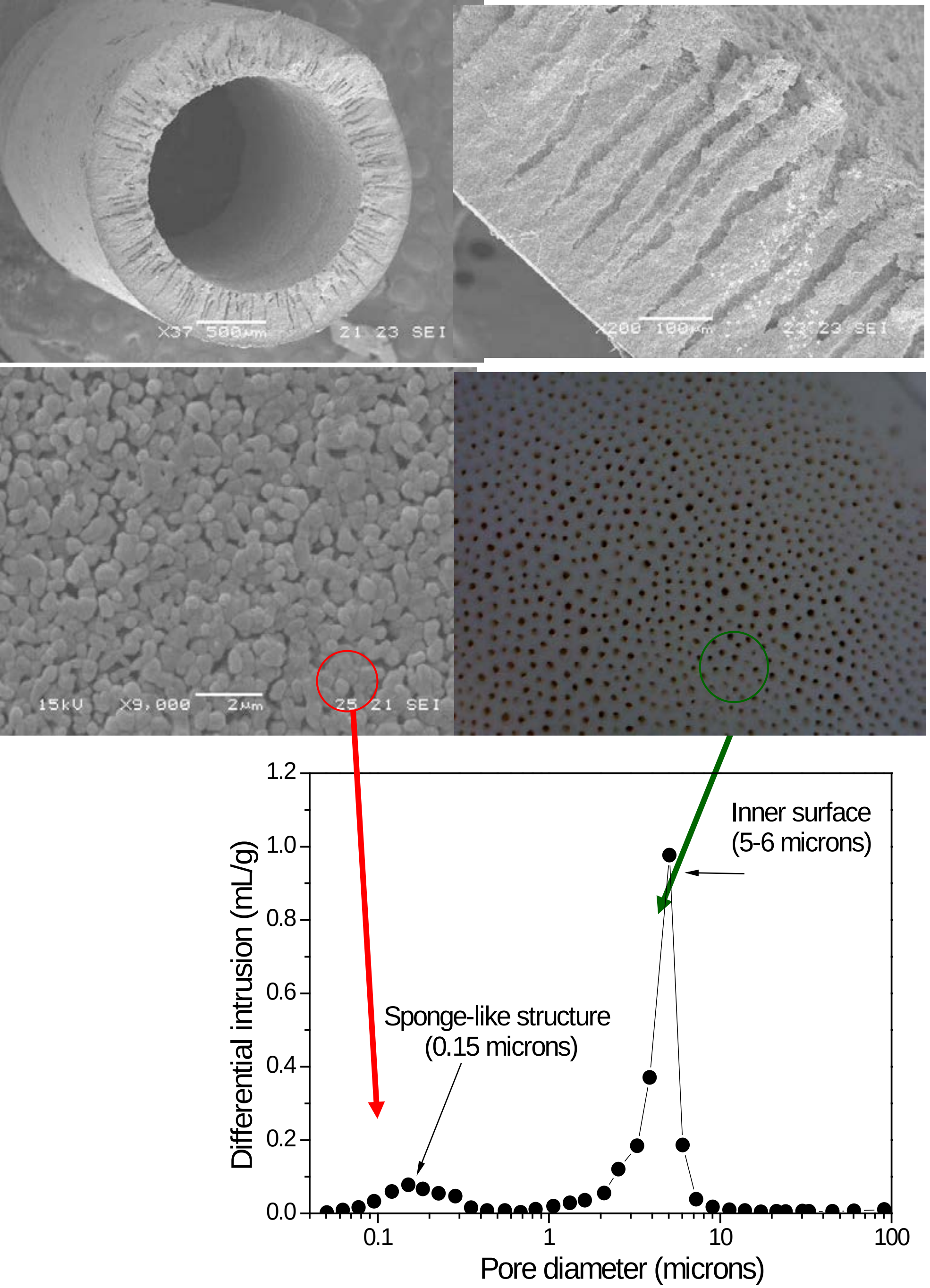
Water permeation data



Mechanical strength (MPa)			
1342 ° C	58.3	41.8	39.7
1455 ° C	116.5	96.3	88.2

Water permeation flux (L/(m² h bar))			
1342 °C	1069	1874	997
1455 °C	753	1088	664

Water flux is comparable with commercial membranes (Metawater 1250@0.1μm, Hyflux 1500@0.2μm and 750@0.1μm), using lower sintering temperatures and less fabricating steps.

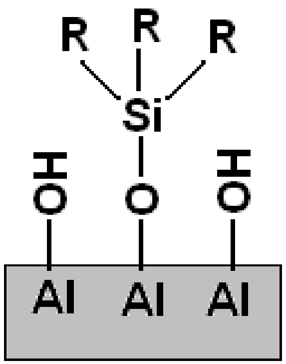


Bi-modal pore size distribution

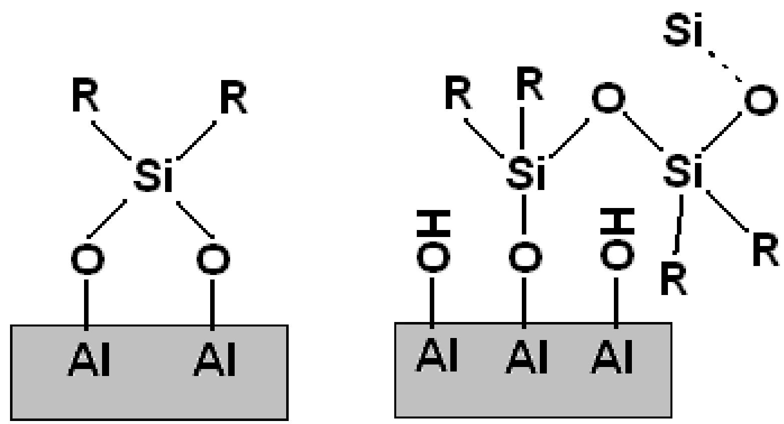
Possible applications

- Warm surfactant/oil /water mixtures usually found in metal cleaning operations,
- Membrane contactor for desalination after surface modification,
- Membrane support for further deposition of nanofiltration or reverse osmosis membranes for desalination,
- The finger-like layer can be used as micro-reactors for enhancement of chemical reactions

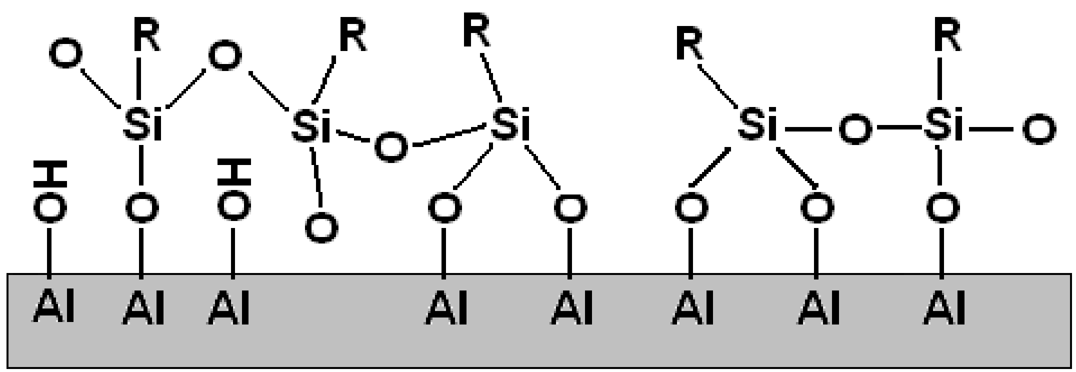
Membrane distillation -surface modification by fluoroalkylsilanes (FAS) grafting



Monofuntional Silanes

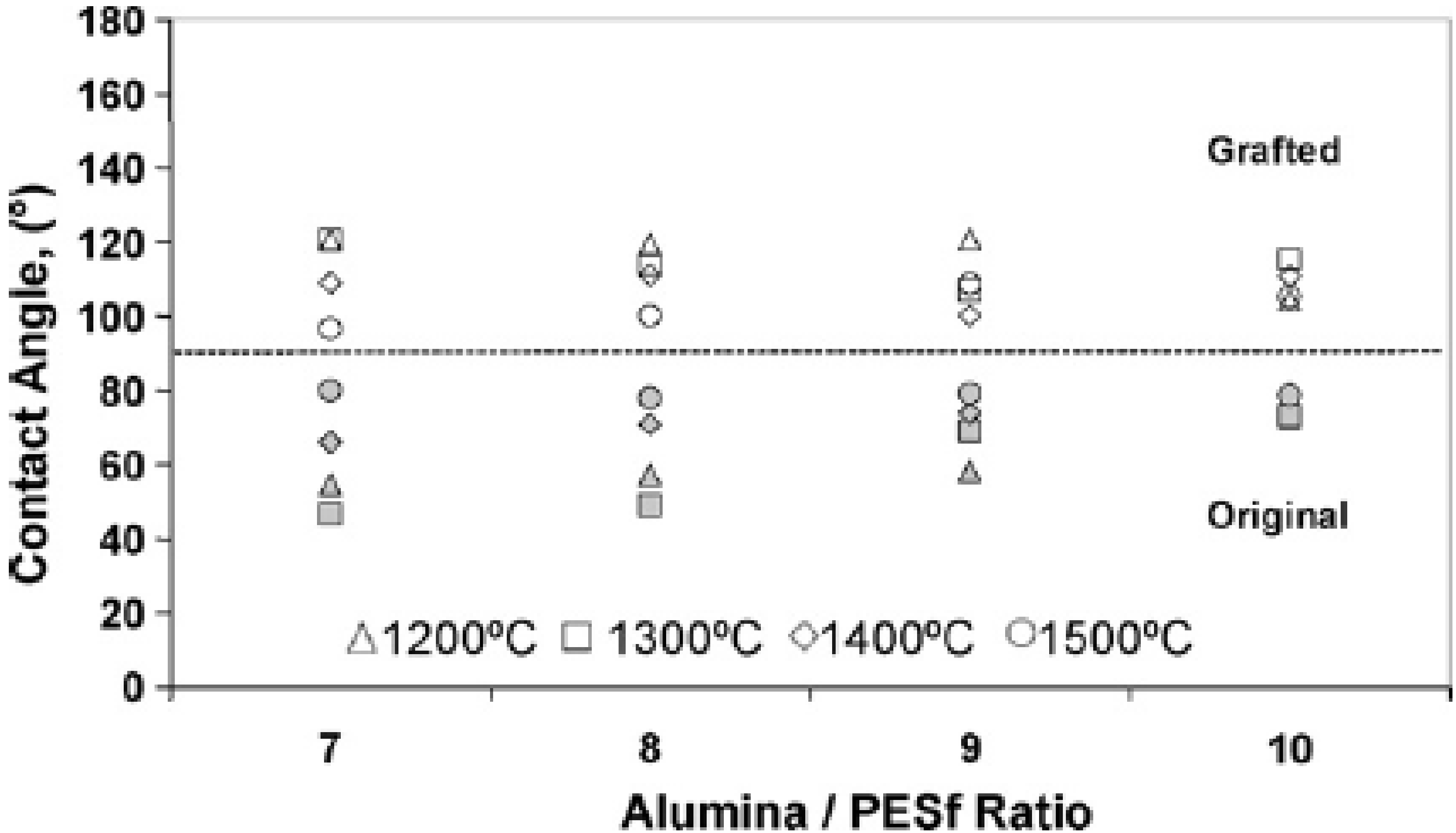


Difunctional Silanes

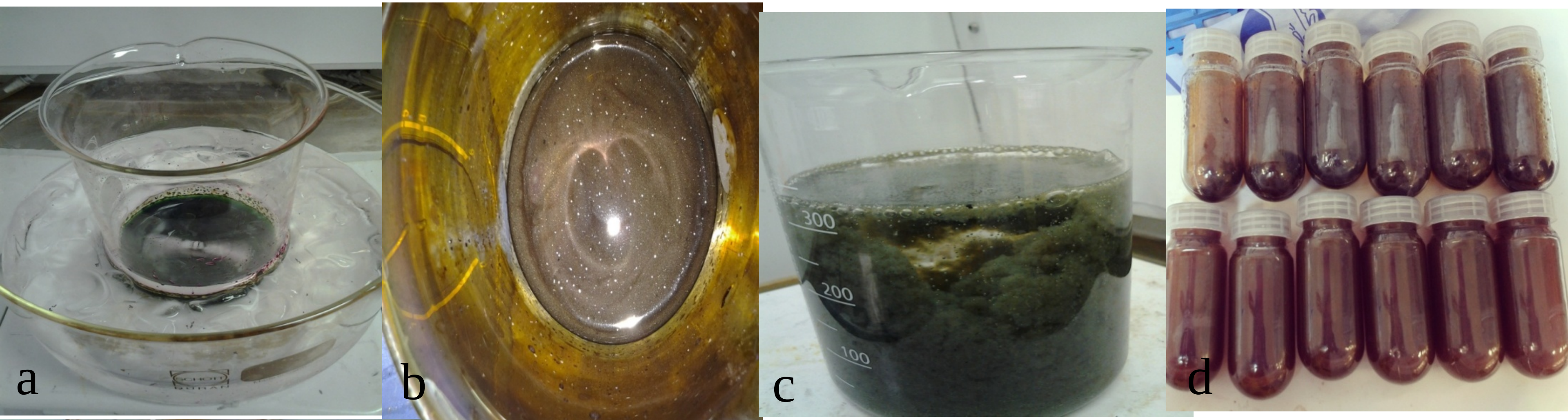


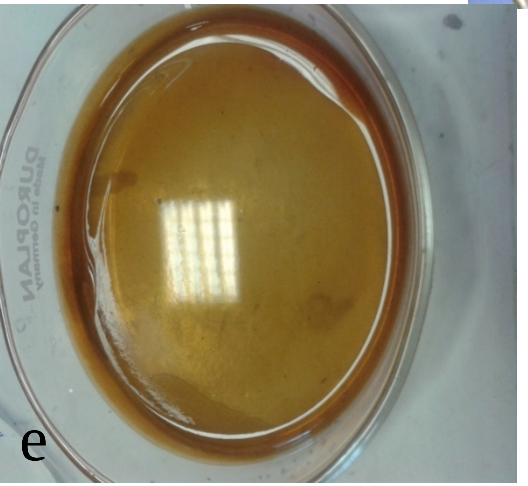
Trifunctional Silanes

The advancing contact angles of the membranes before and after FAS grafting.



3. Graphene based ceramic composite membranes





Synthesis of graphene oxide via Modified Hummer's Method

a) mixture stirred in ice water bath,

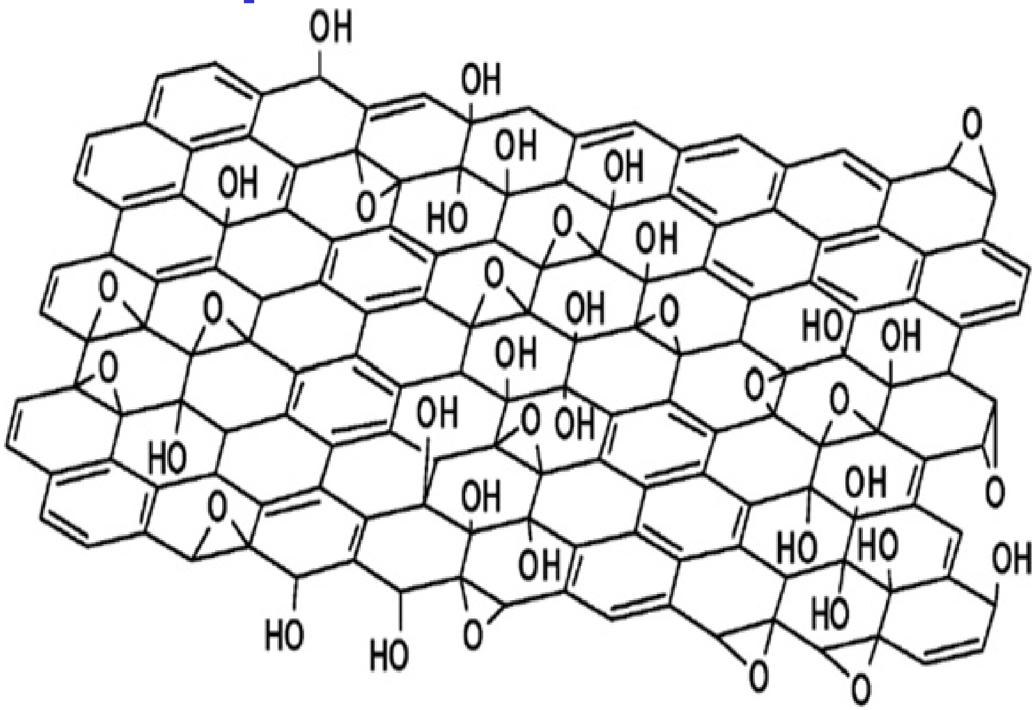
b) mixture stirred after 5 days (turned to dark brown),

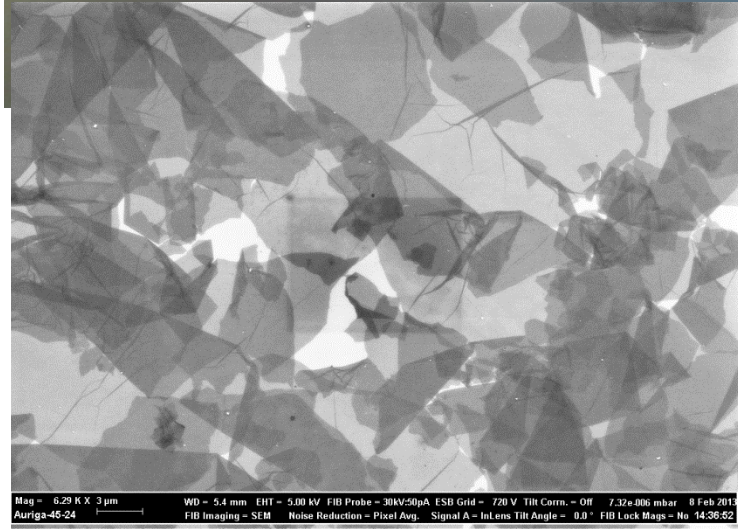
c) addition of water and H_2O_2 into the mixture,

d) purification of mixture by centrifugation,

e) drying process of purified graphene oxide

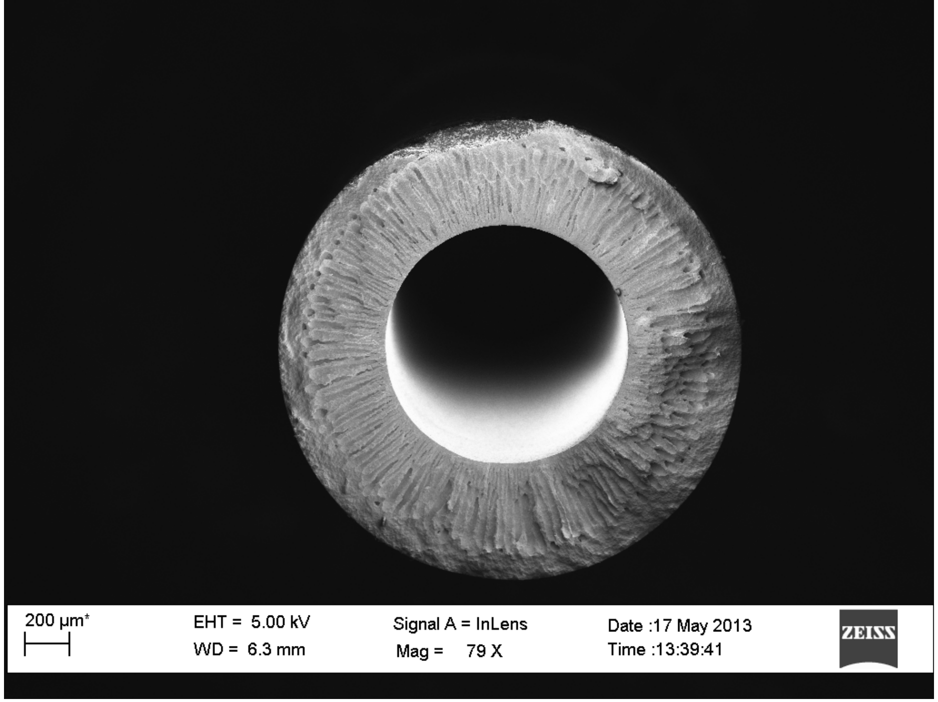
3. Graphene based ceramic composite membranes

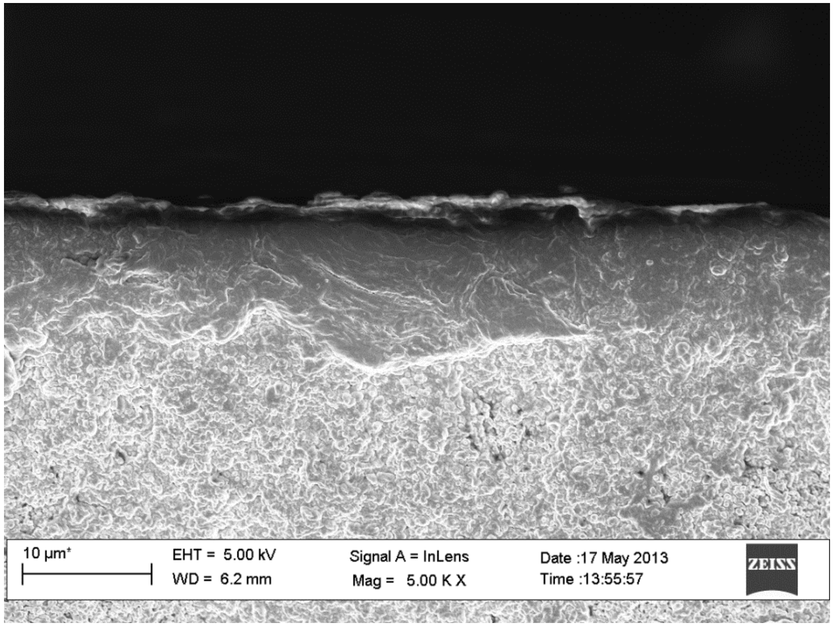




Zeta potential study

•Graphene oxide has highly negative surface charges
•Easily dispersed in water due to ionization of carboxylic acid and the phenolic hydroxyl groups.
•Its colloidal suspension is stable in water, not only because of the hydrophilicity but also by electrostatic repulsion


200 µm*
EHT = 5.00 kV
WD = 6.3 mm
Signal A = InLens
Mag = 79 X
Date :17 May 2013
Time :13:39:41
ZEISS


10 µm*
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WD = 6.2 mm
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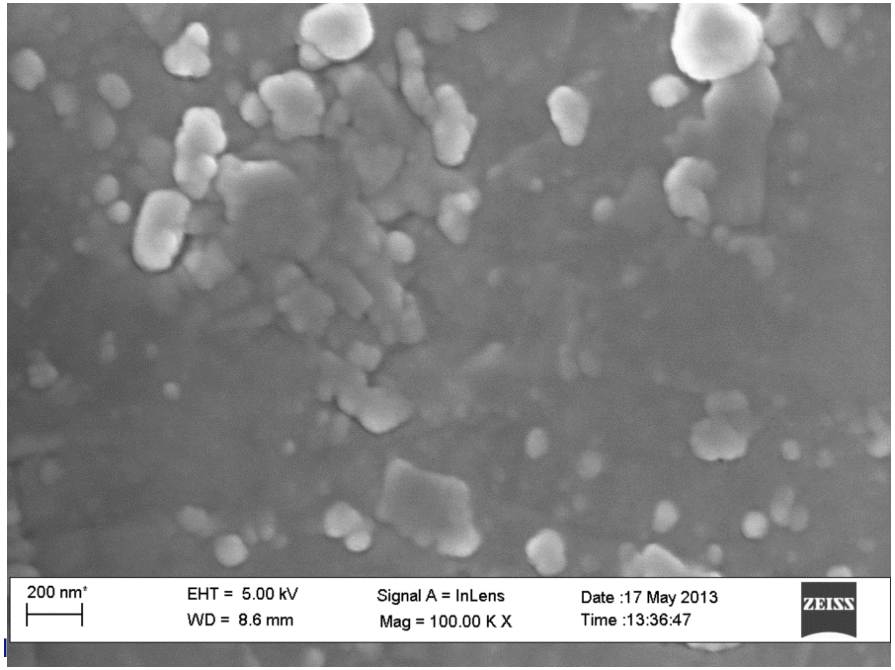
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WD = 8.6 mm
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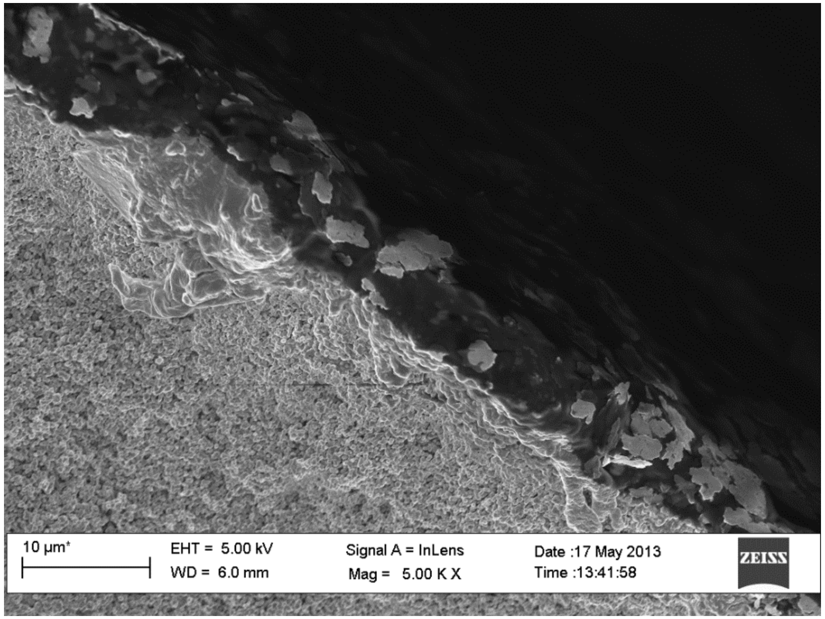
Time :13:36:47
ZEISS


10 µm*
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WD = 6.0 mm
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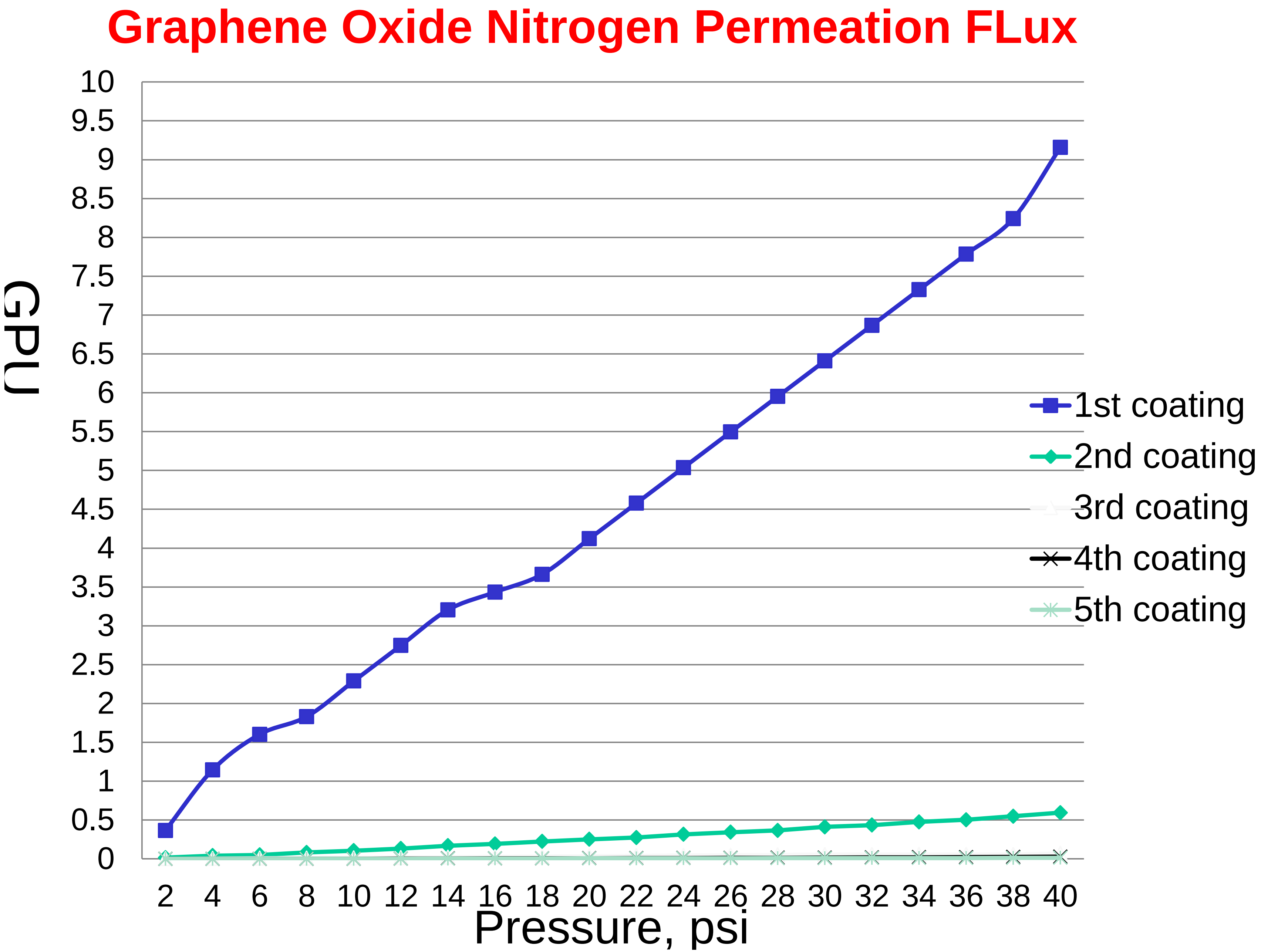
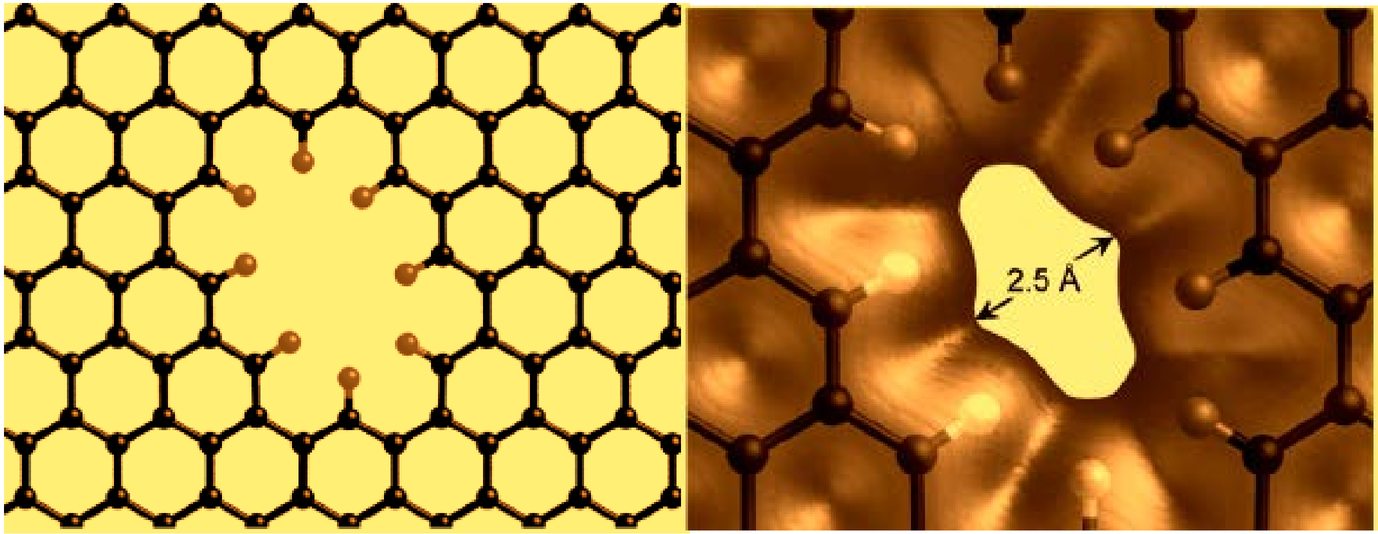


Graphene Oxide Nitrogen Permeation FLux
GPU
Pressure, psi
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
5.5
6
6.5
7
7.5
8
8.5
9
9.5
10
2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34 36 38 40
1st coating
2nd coating
3rd coating
4th coating
5th coating

Functionalization with hydrogen



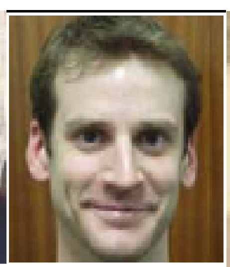
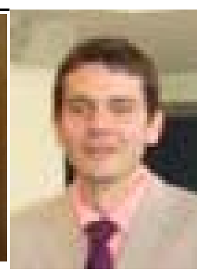
- Created by removing 2 neighboring rings from the graphene sheet and then functionalized with hydrogen
- Dimensions are about 2.5 Angstroms by 3.5 Angstroms

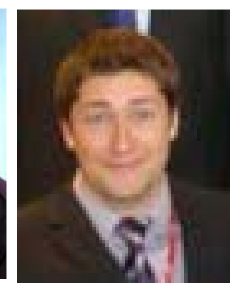
Conclusions

- Micro-structured ceramic hollow fibre membranes consisting of two different pore size distributions with mean pore size of ~0.1 mm (sponge-like layer) and ~8 mm (micro-channels) can be prepared in a single step using a viscous fingering induced phase inversion technique,
- The percentage of the sponge layer (or micro-channels) over whole fibre cross section can be varied by controlling the composition of spinning suspension or other spinning parameters such as air-gap and take up velocities, etc.
- The outer sponge layer (~0.1 mm) may serves as a substrate for deposition of nanofiltration or RO membranes for seawater desalination, while micro-channels reduces mass transfer resistances considerably and can also be used as micro-reactors once an appropriate catalyst is deposited.

Acknowledgements

The research funding provided by EPSRC in the United Kingdom (grant Nos: GR/N38640, GR/R5717, GR/S12203, GR/S87553, etc) is gratefully acknowledged.

Thank You

Questions?