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Preparation and characterization of multiwall carbon nanotubes (MWCNT) mixed matrix membranes for the treatment of aqueous solutions and desalination

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KACST

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Suggested Outlines

Part 1

- Synthesis and purification of CNT.
- Functionalization of CNT.
- CNT orientation
- Preparation of CNT for membrane application

Part 2

- Polymeric materials used in membrane preparation.
- Mixed matrix membranes (MMM).
- Effect of the membrane preparation conditions on the morphology and transport properties of the MMM.
- Conclusion
- Team work
- Acknowledgment

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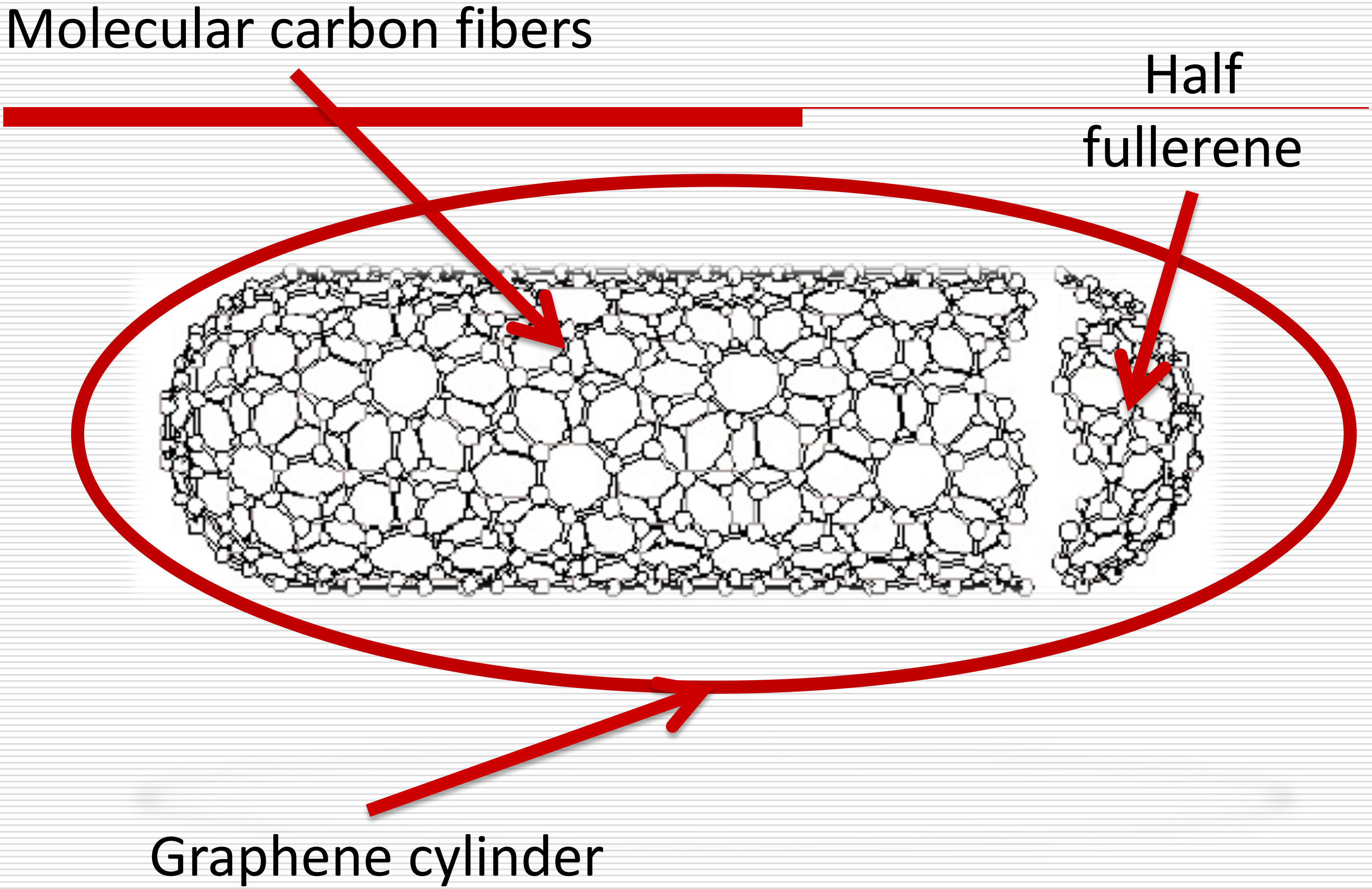
e il Territorio e Ingegneria Chimica

Part 1

Synthesis, purification and functionalisation of Multiwalled carbon nanotubes

Carbon nanotubes



Different kinds of CNTs observed by Ijima in 1991

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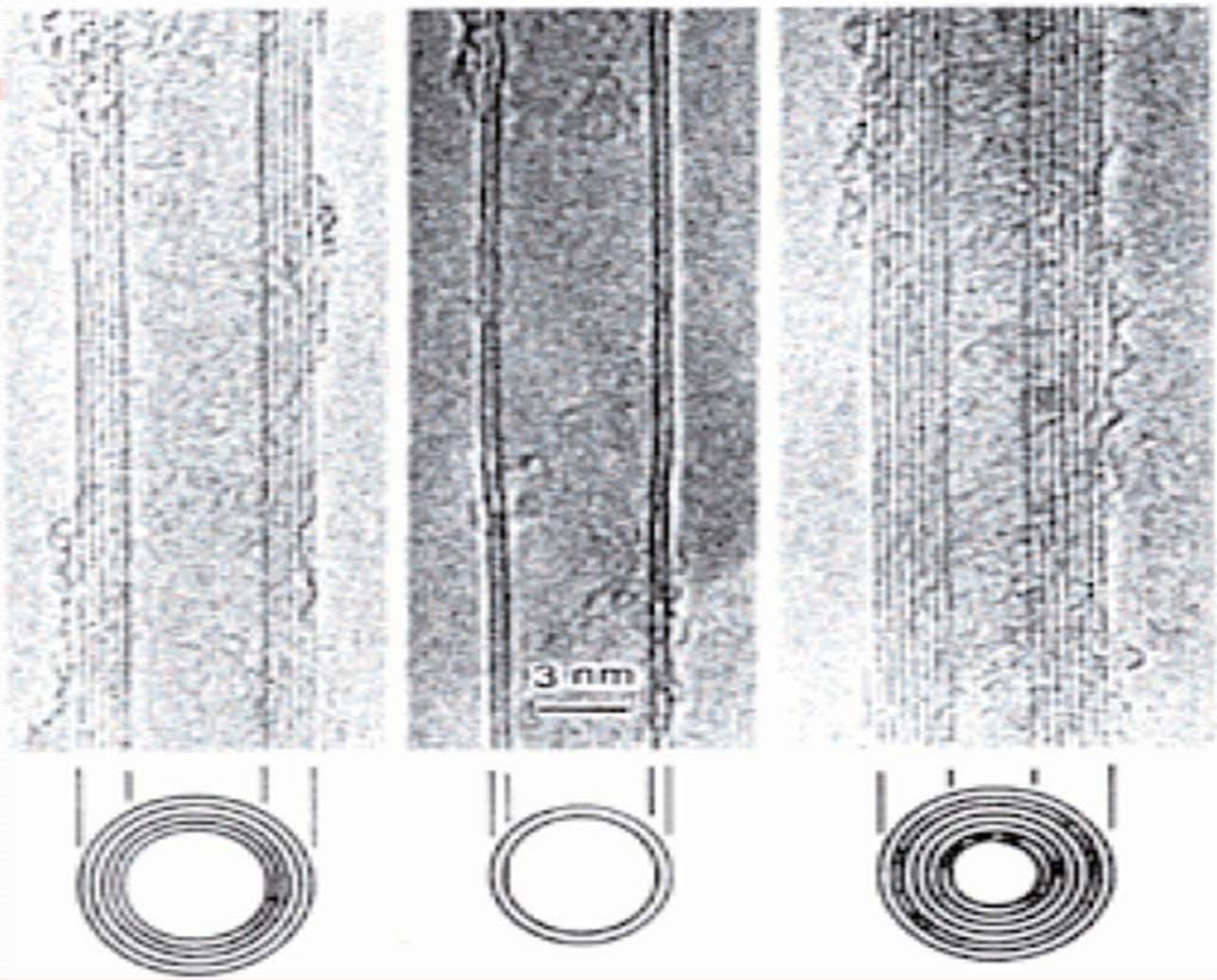
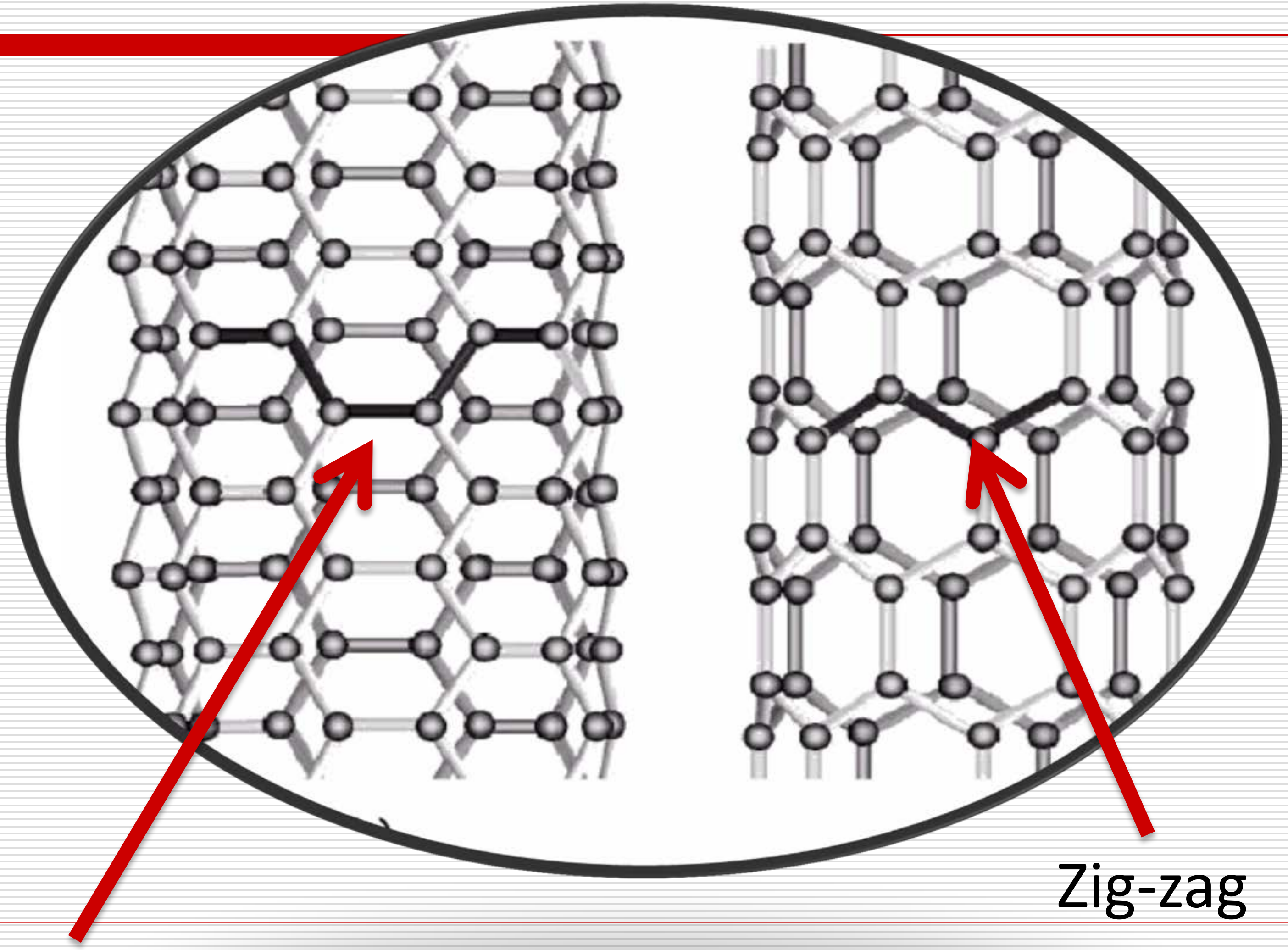
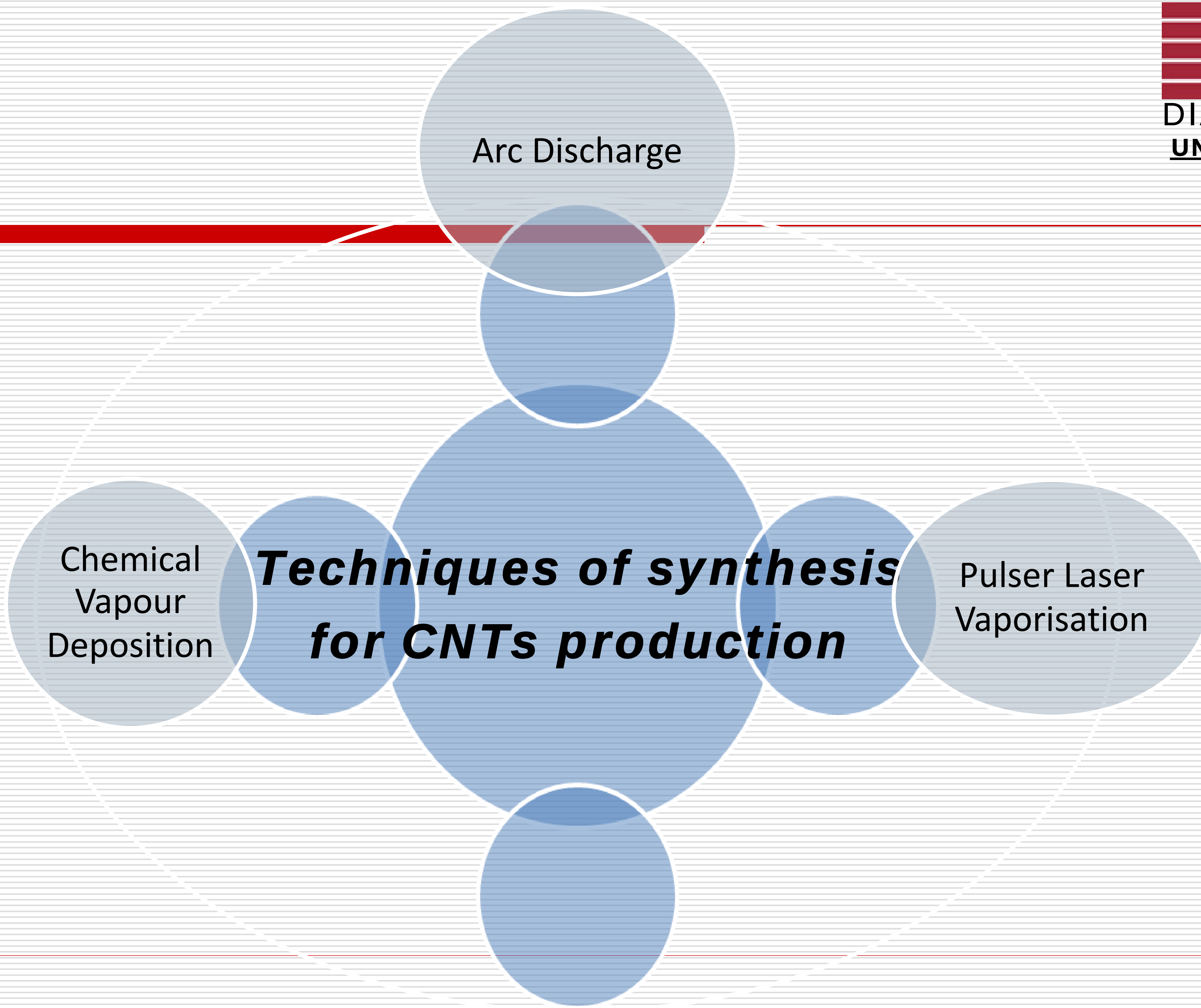


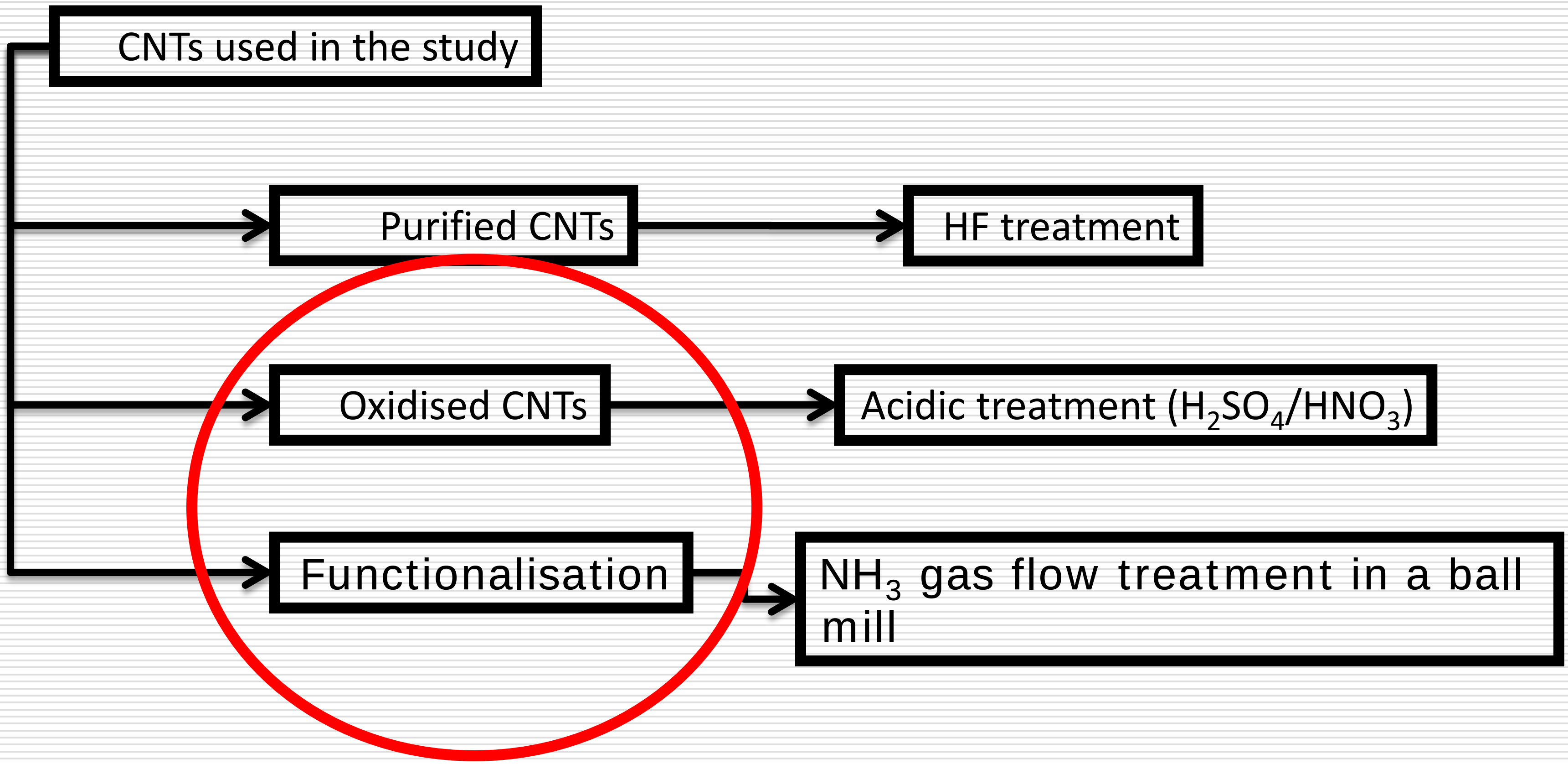
Different structure configurations



Zig-zag

Armchair


Arc Discharge
Chemical Vapour Deposition
Techniques of synthesis for CNTs production
Pulser Laser Vaporisation


CNTs used in the study
Purified CNTs
HF treatment
Oxidised CNTs
Acidic treatment (H_2SO_4/HNO_3)
Functionalisation
NH_3 gas flow treatment in a ball mill

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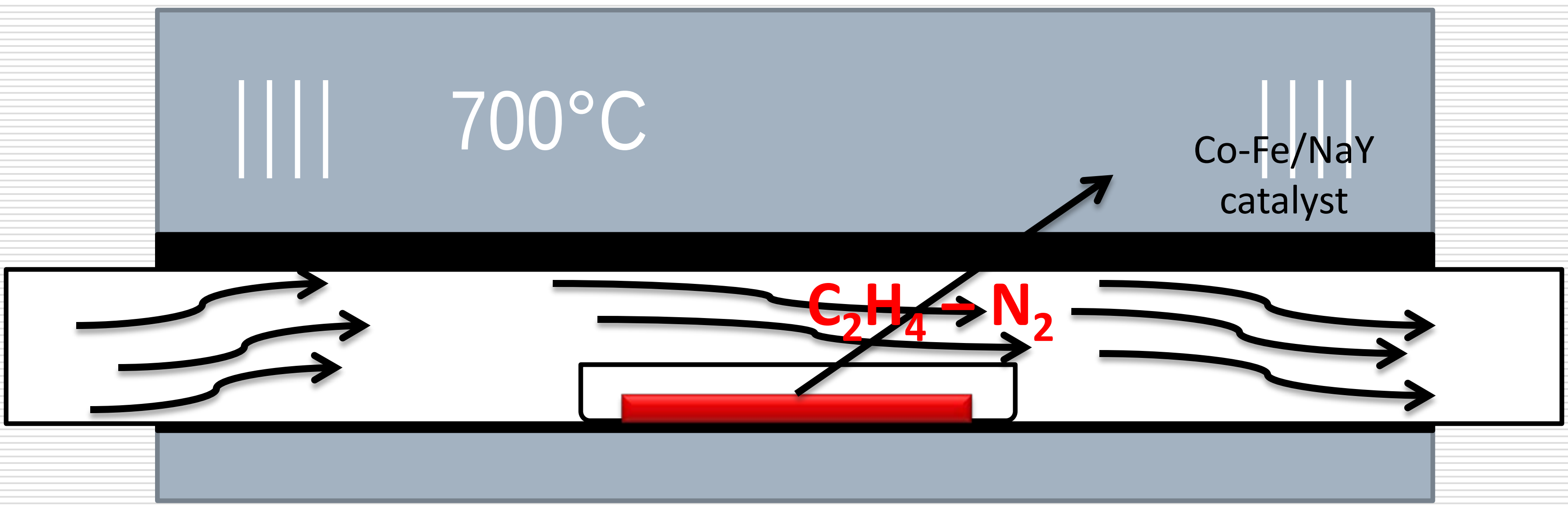
- Synthesis of MWCNTs
- Purification process of MWCNTs

Synthesis of MWCNT



120 min
20 min
5 min

Summary of synthesis conditions

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- ✓ Synthesis temperature: 700°C
- ✓ Amount of catalyst: 0.25 g
- ✓ Gas flow: C_2H_4 800ml/min, N_2 416 ml/min (optimal conditions)
- ✓ Synthesis time: 20 min

The CNTs production

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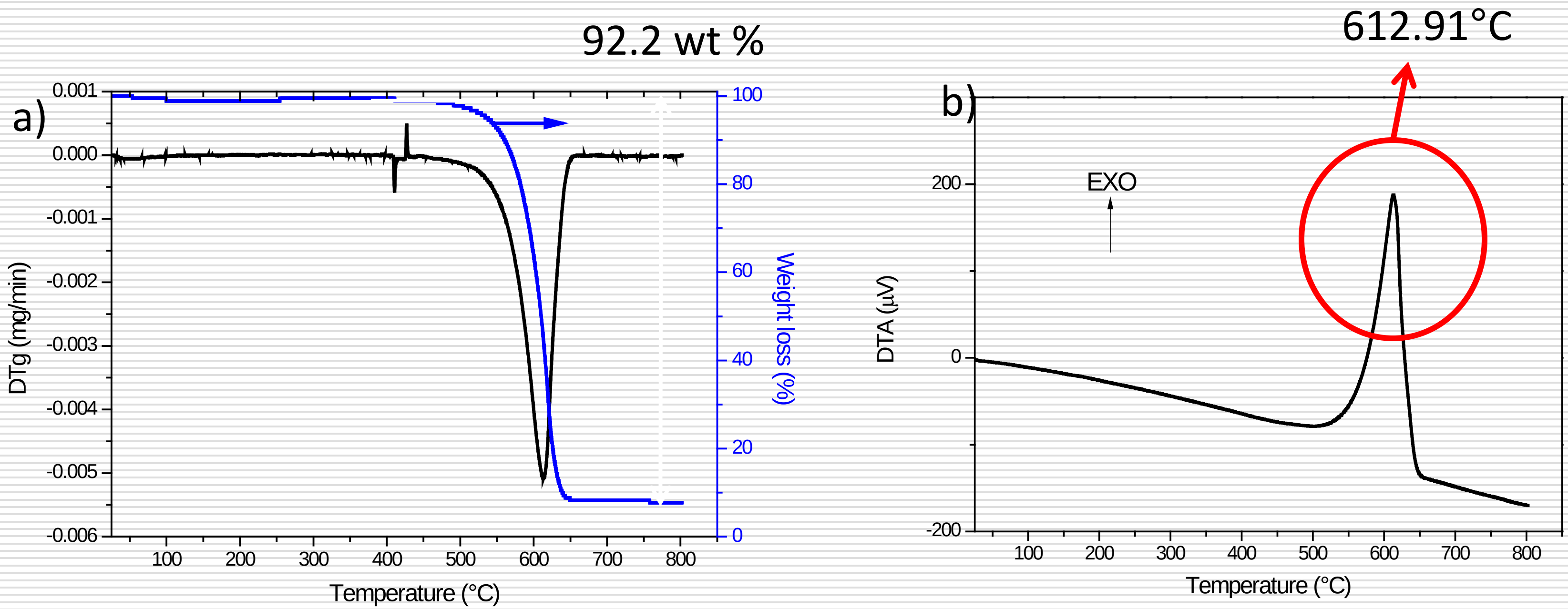
Carbon deposit (Cd) and Carbon yield (Cy) obtained from syntheses as a function of gas flows using constant amount of catalyst and 20 min of reaction time.

C_2H_4 flow (ml/min)	N_2 flow (ml/min)	Cd* (%)	Cy (%)
1,534.00	798.00	1,205.26	6.97
1,000.00	520.00	1,329.41	10.55
800.00	416.00	1,447.06	14.35
600.00	312.00	1,204.76	19.68
400.00	208.00	1,065.22	28.58
100.00	52.00	452.00	52.73

- •Cd = (CNTs weight/Weight dried cat)*100
- •*Cy = (CNTs weight/$C_{hydrocarbon}$)*100

The CNTs production



(a) Tg and DTg curves and (b) DTA curve of the CNTs obtained from the synthesis.

The CNTs production

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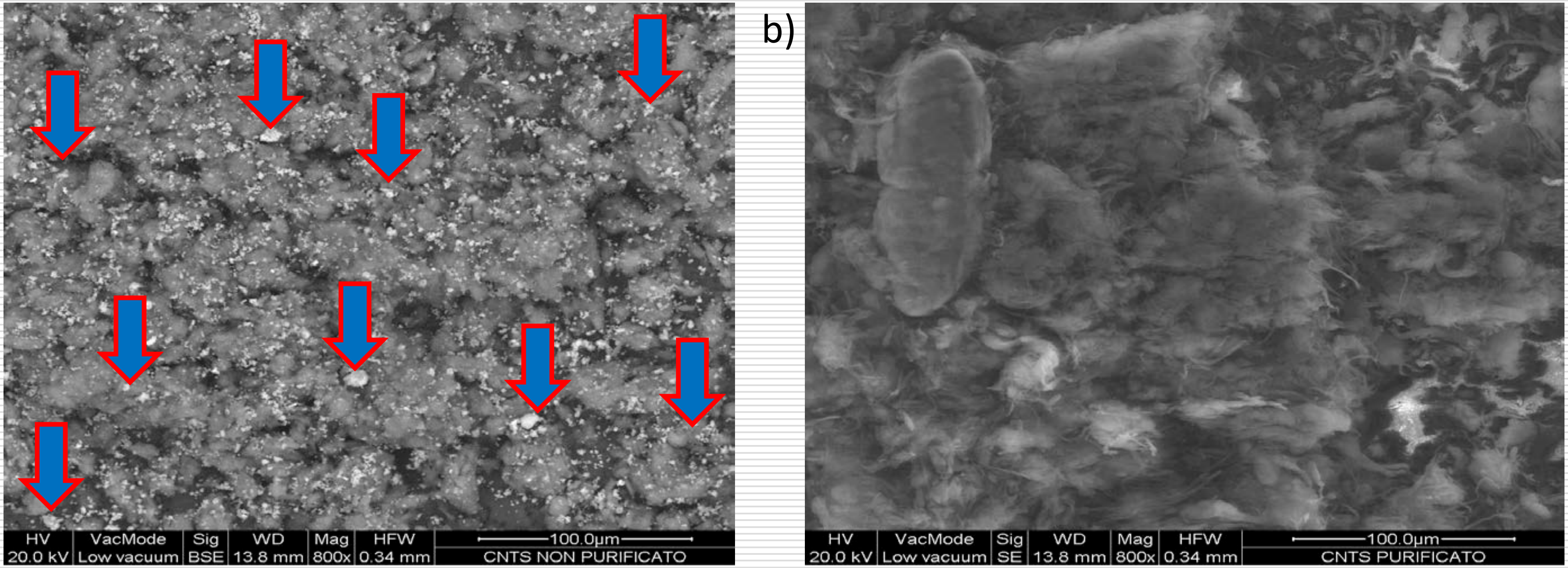
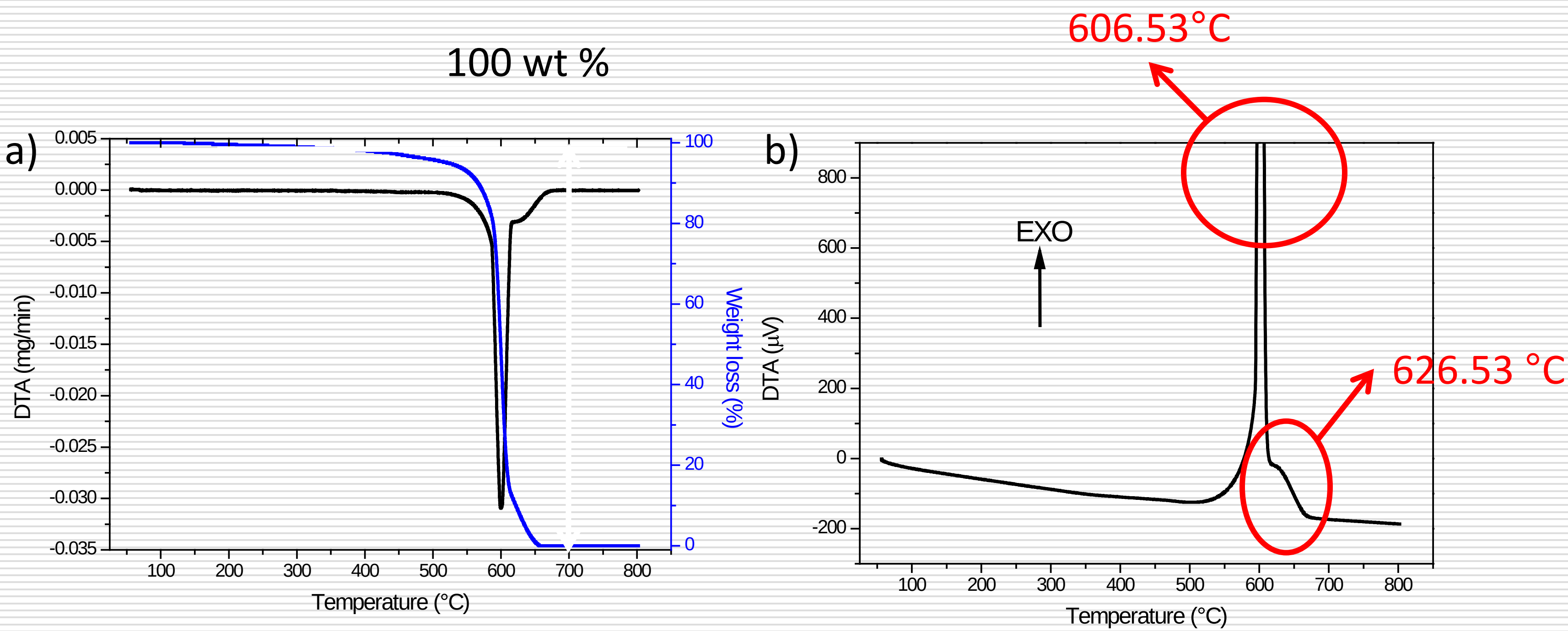
a) b)



SEM images of the as made (a) and purified samples (b).

The CNTs production

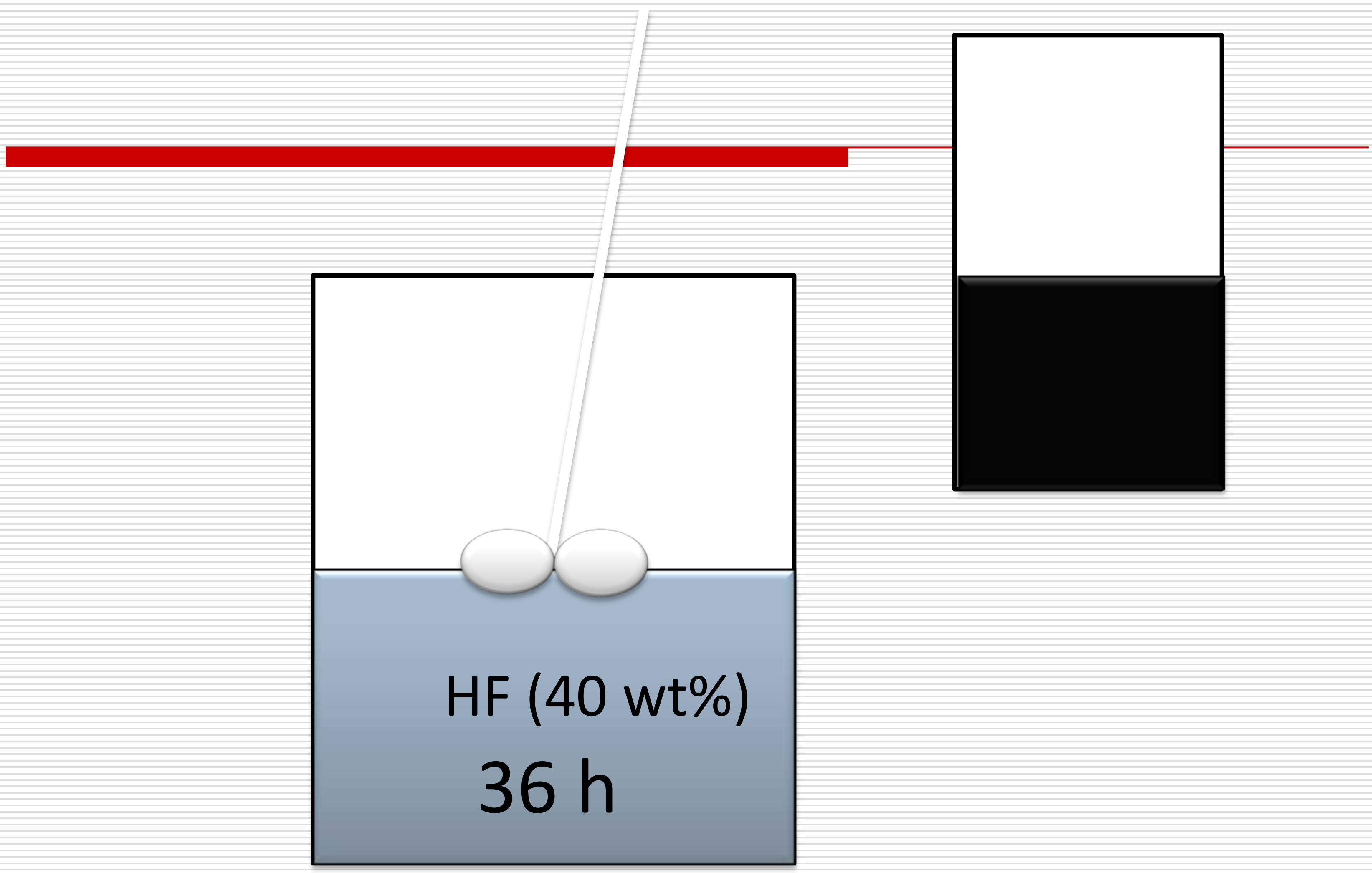
100 wt %



(a) Tg and DTg curves and (b) DTA curve of the purified sample.

- Synthesis of MWCNTs
- Purification process of MWCNTs

Purification process of MWCNTs

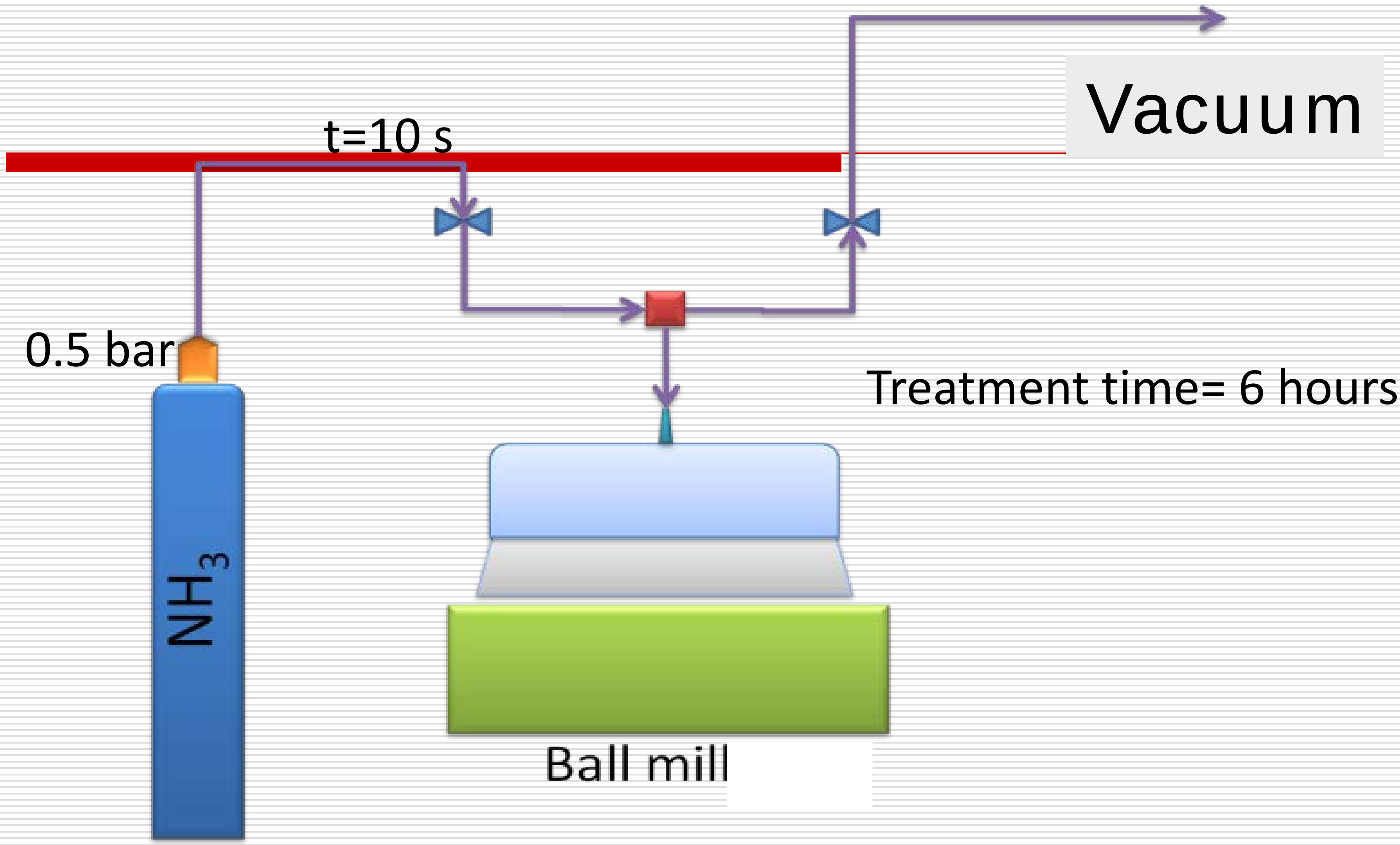


Functionalisation

a. NH_3 gas treatment

b. Oxidation

NH_3 gas treatment



Functionalisation

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a. NH_3 gas treatment

b. Oxidation

Oxidation

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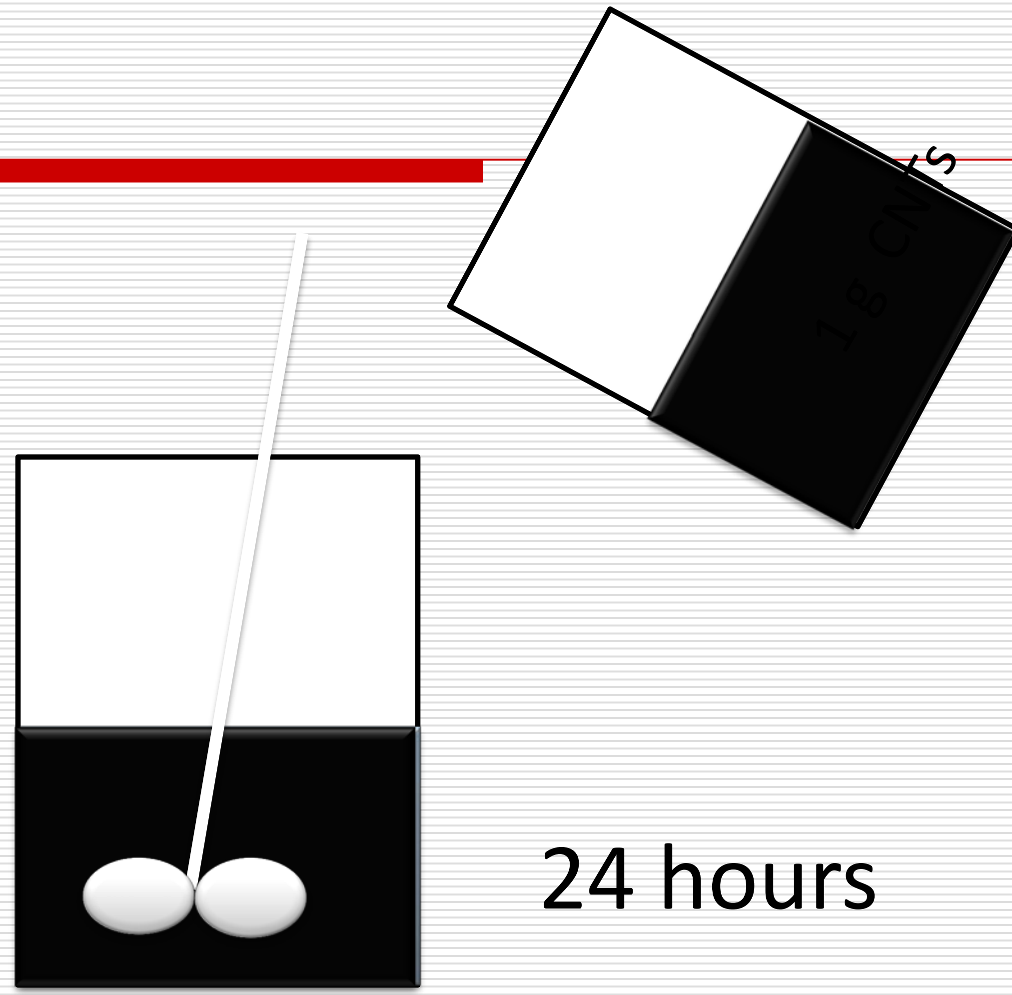

24 hours

Oxidation

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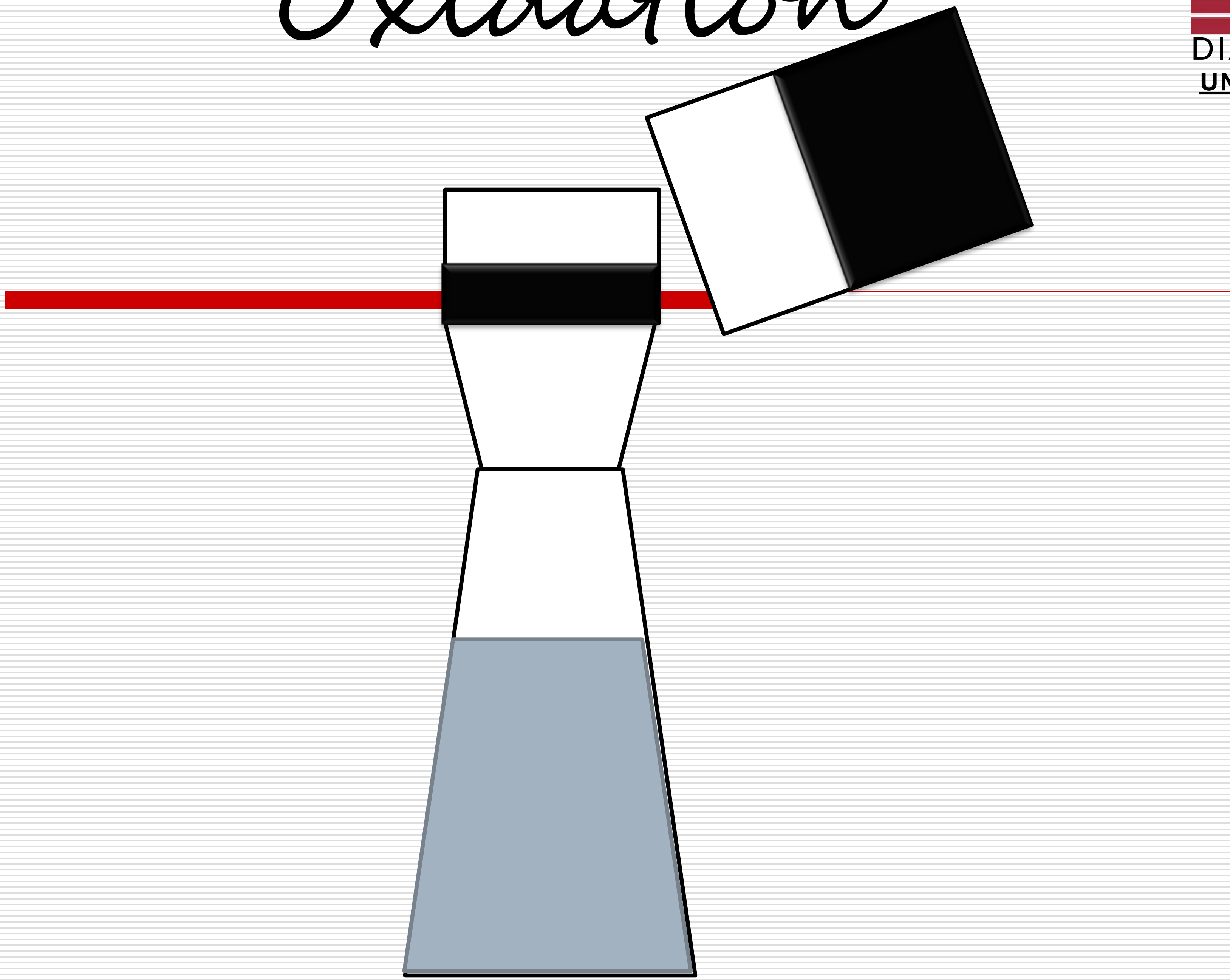

The CNTs production

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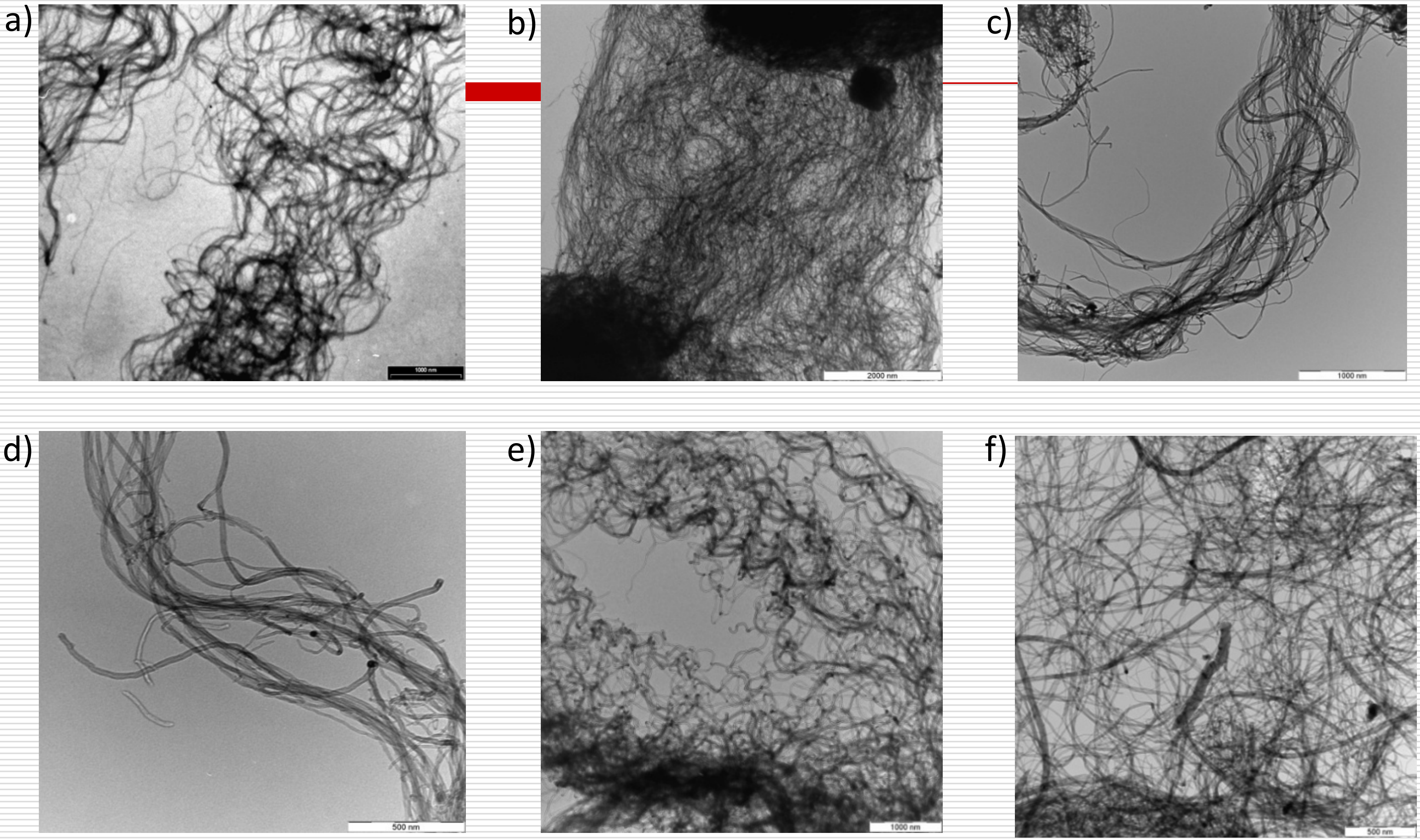

TEM images of CNTs with different functional groups: (a) purified product; (b) and (c) Oxidised; (d), (e) and (f) functionalised with NH_2 groups.

The CNTs production

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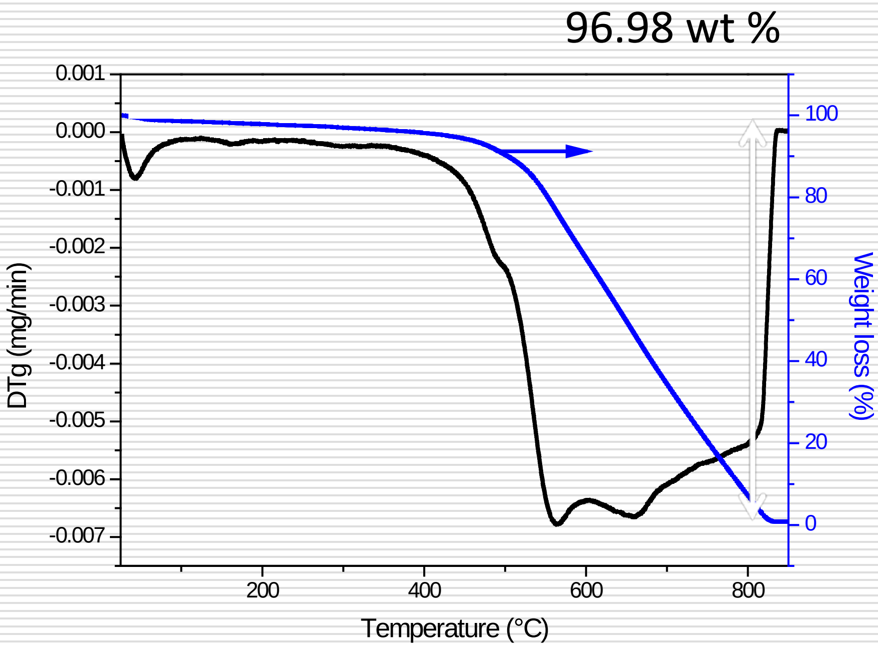
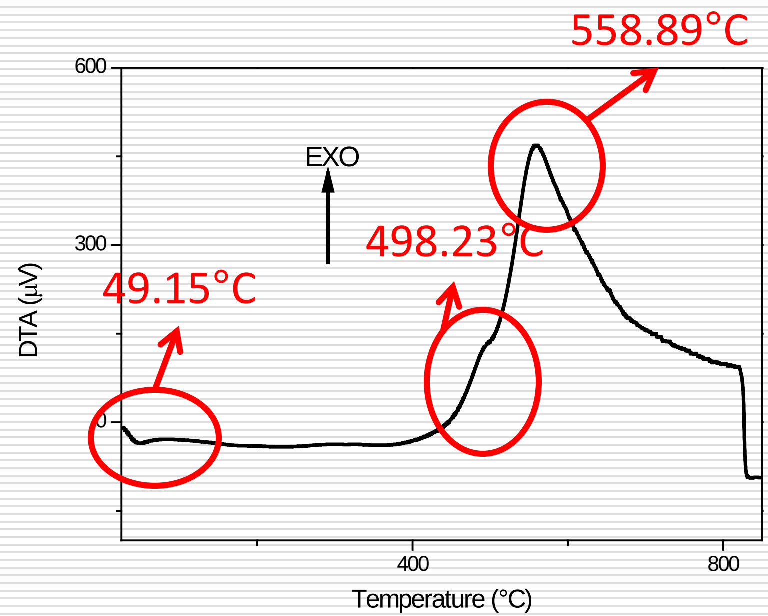
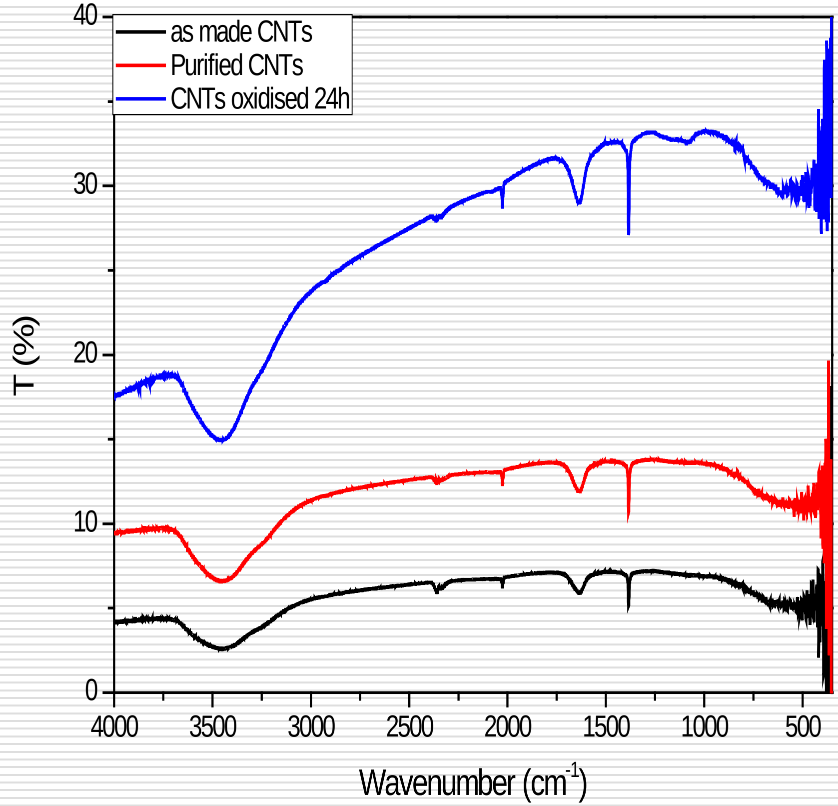




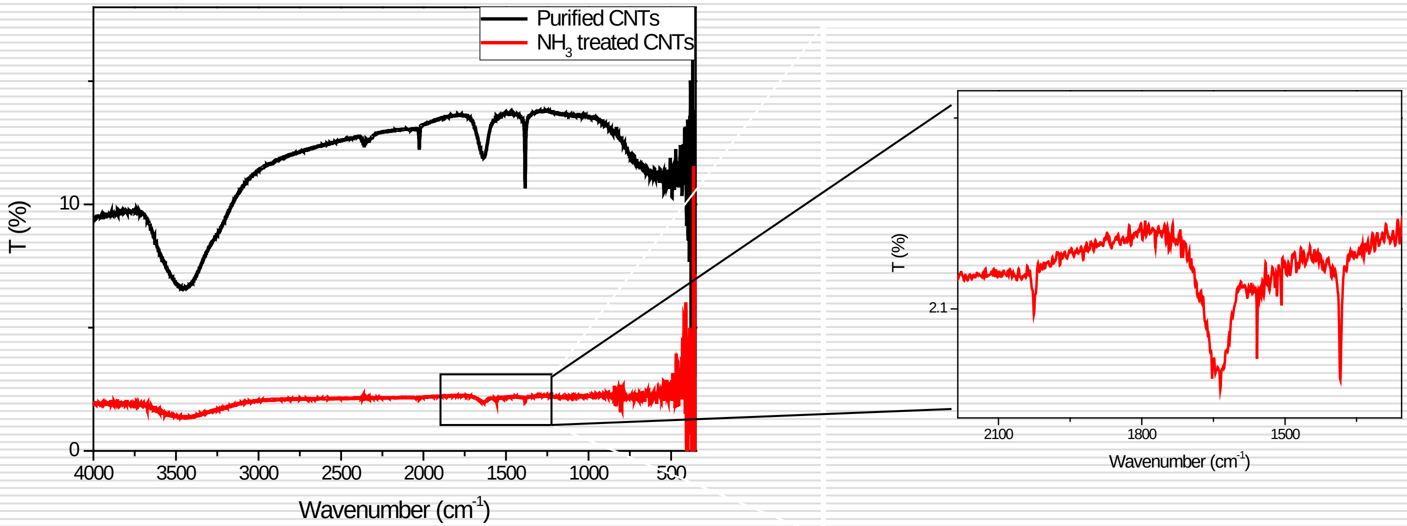
(a) Tg and DTg curves and (b) DTA curve of CNTs functionalised with NH_3 gas.

The CNTs production



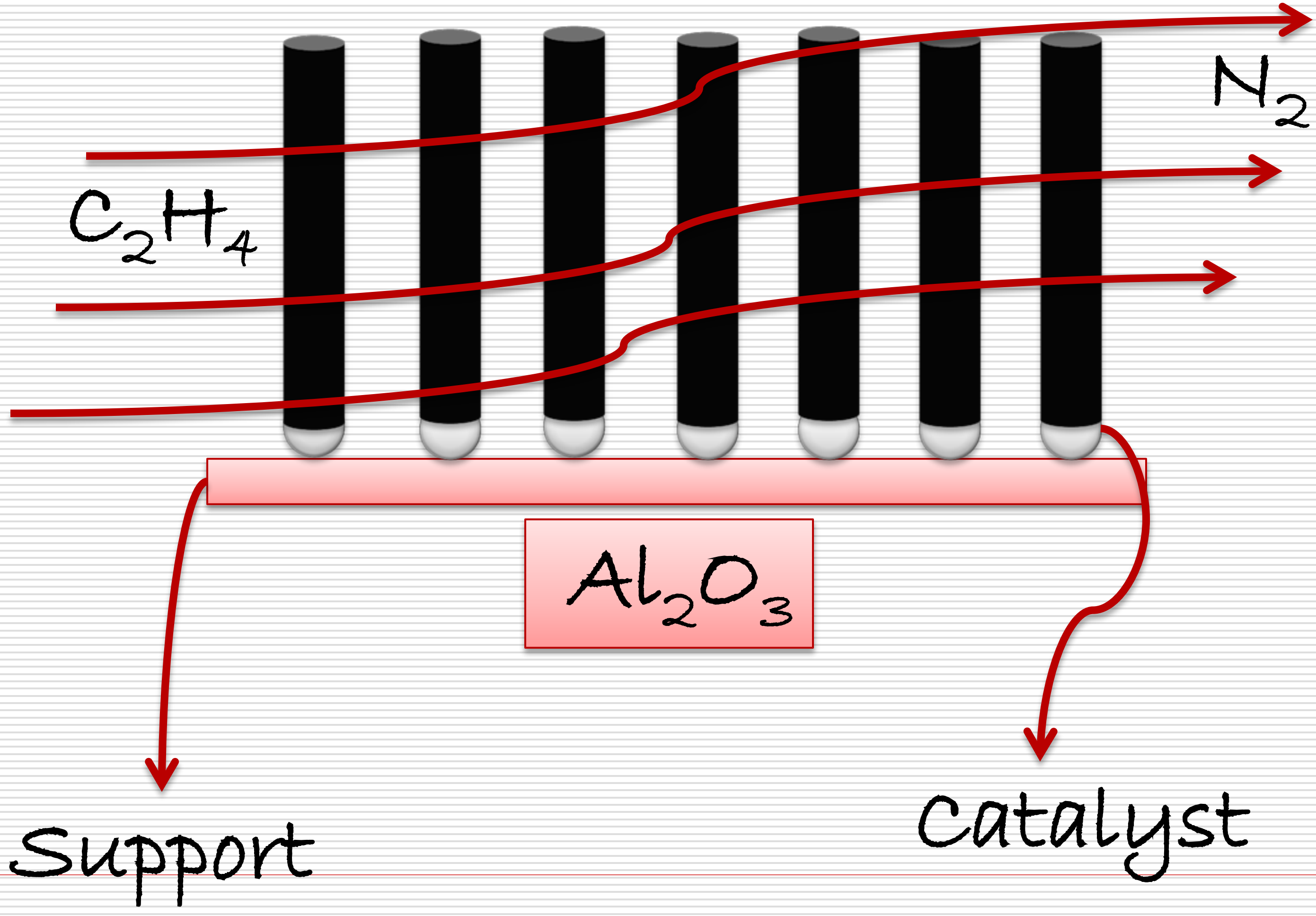
FTIR spectra of different CNTs products

The CNTs production

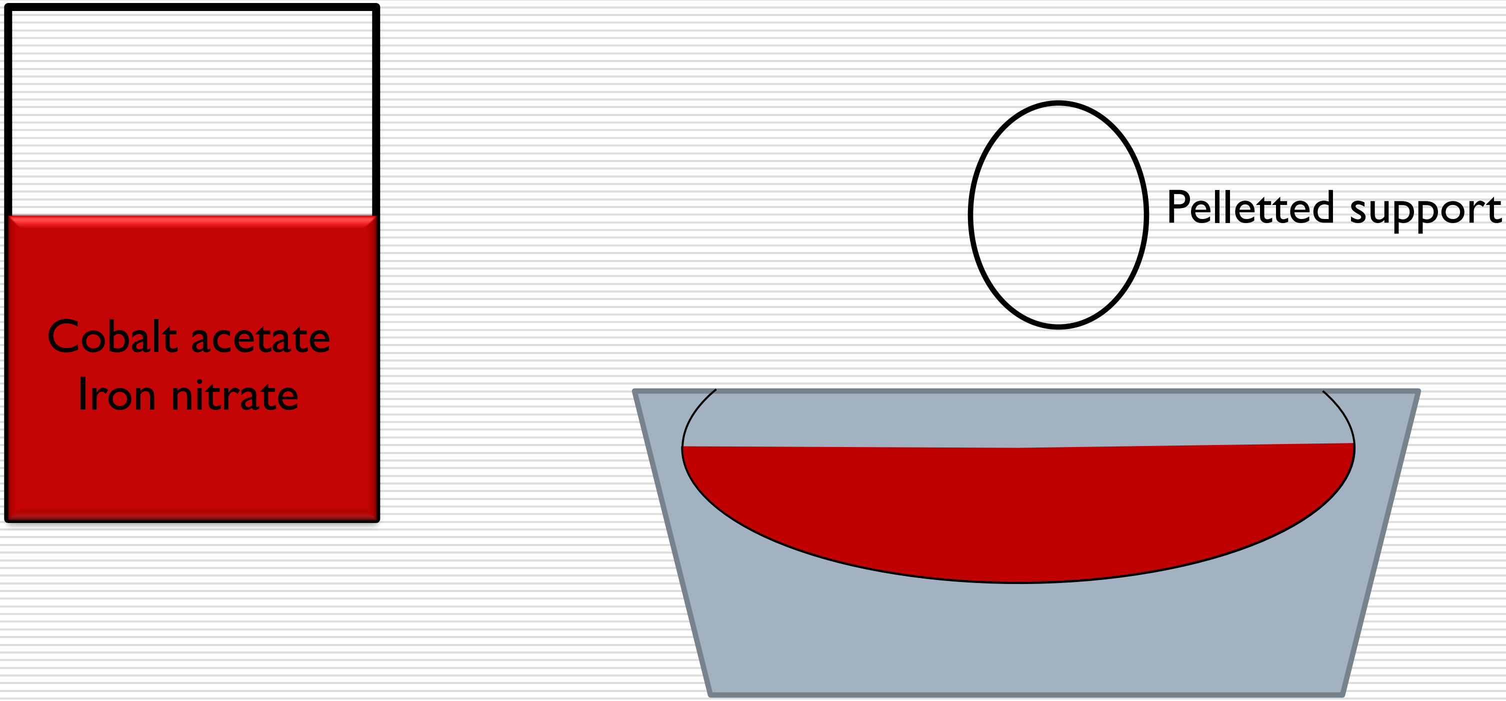


FTIR spectra of the purified and NH_3 treated CNTs.

- Synthesis of aligned MWCNTs


C_2H_4
N_2
Al_2O_3
Support
Catalyst

Preparation method of the catalyst



Impregnation method

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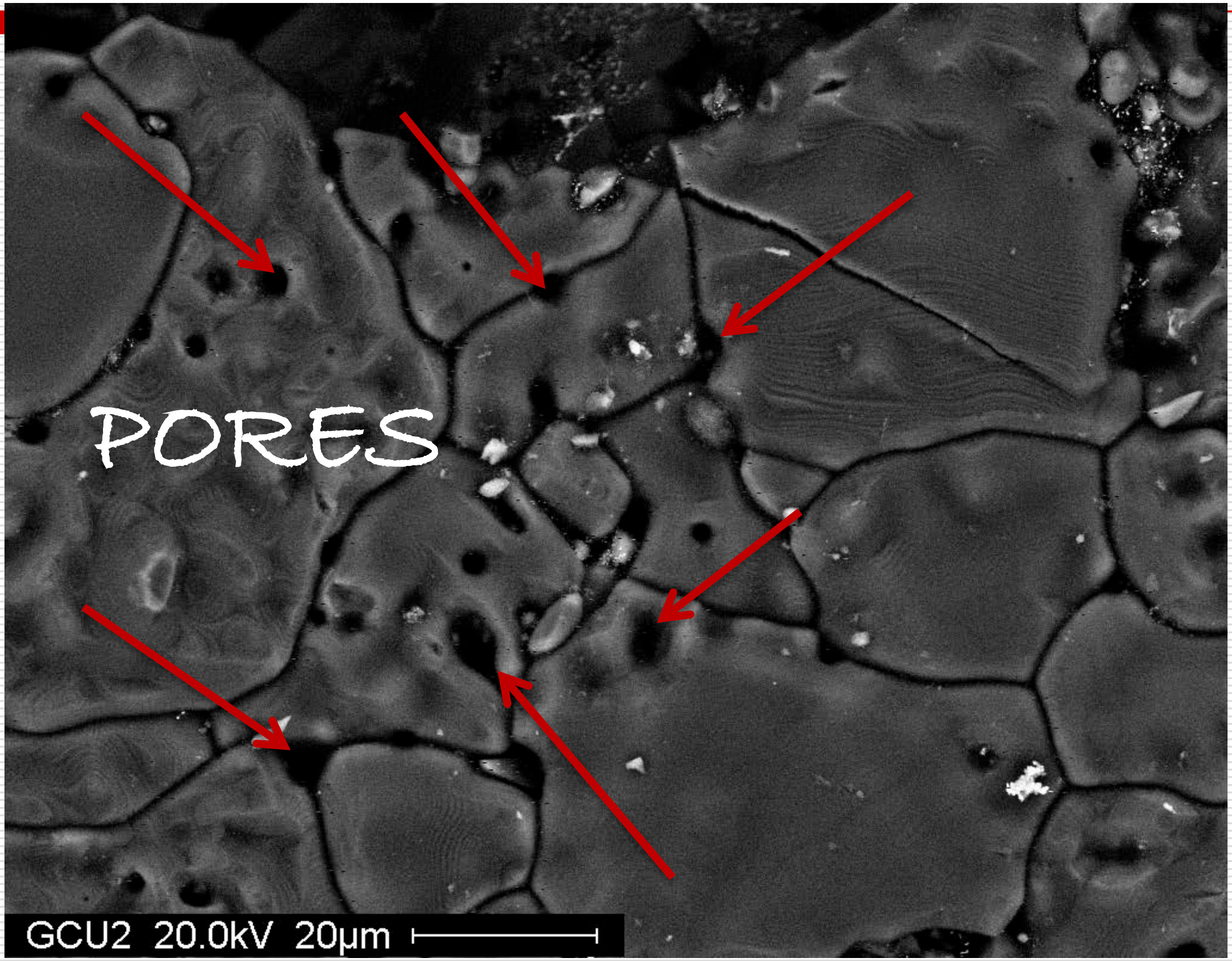
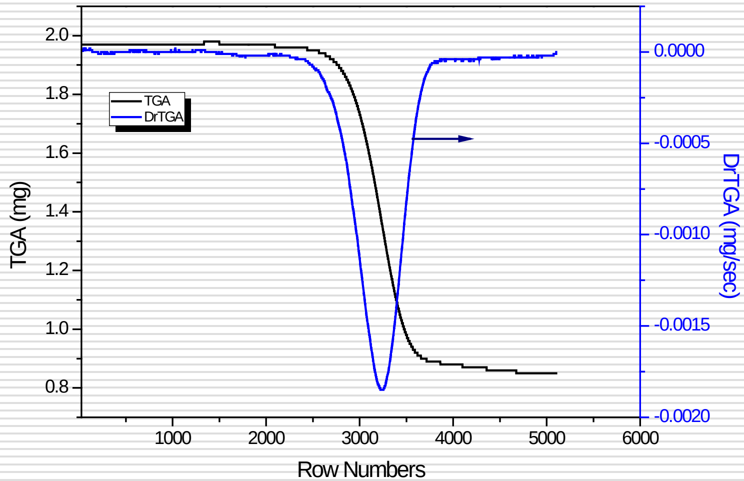
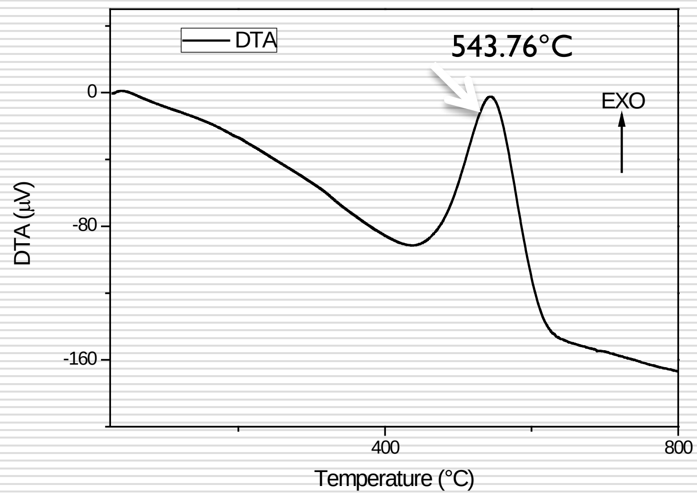


SEM image of alumina pellet

Thermal characterisation of CNTs produced at 20 min (reaction time).

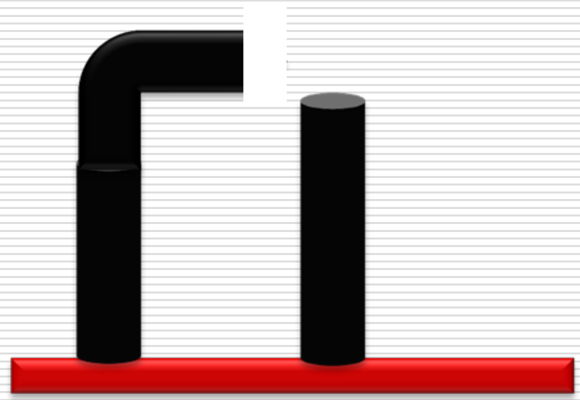




Gas flow: 800 ml/min C_2H_4, 416 ml/min N_2

Short reaction times (lower than 19 min)

Long reaction times (20 min)



Degeneration of the morphology at high reaction times.

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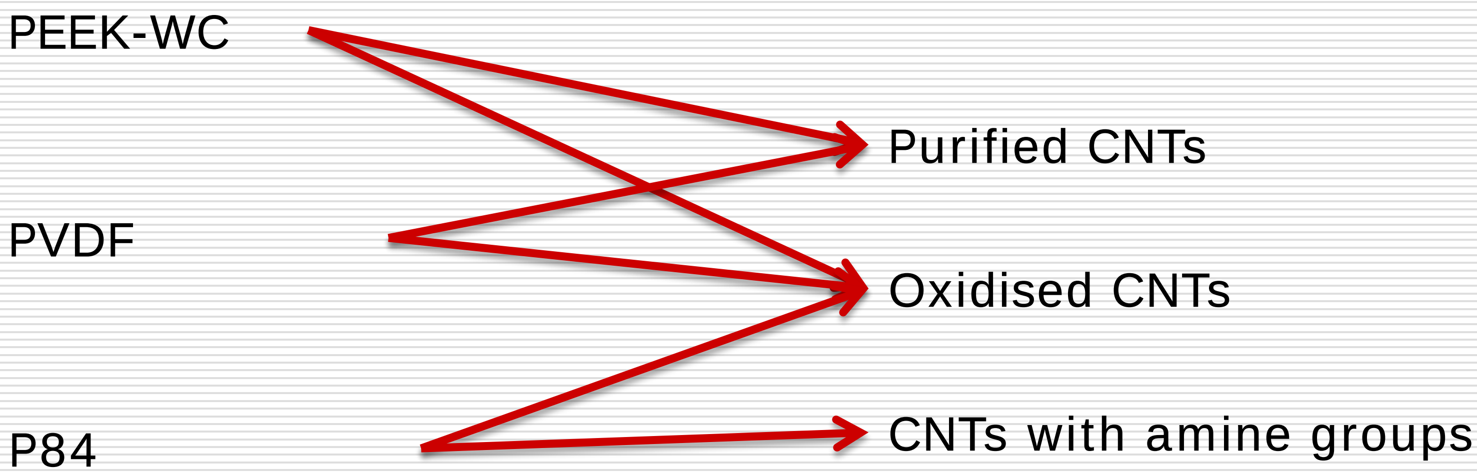
CNTs preparation for membrane applications



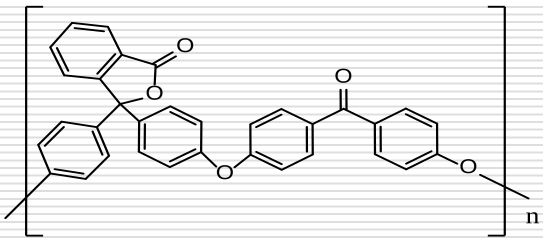
THANK YOU

Part 2

Preparation and Testing Membranes

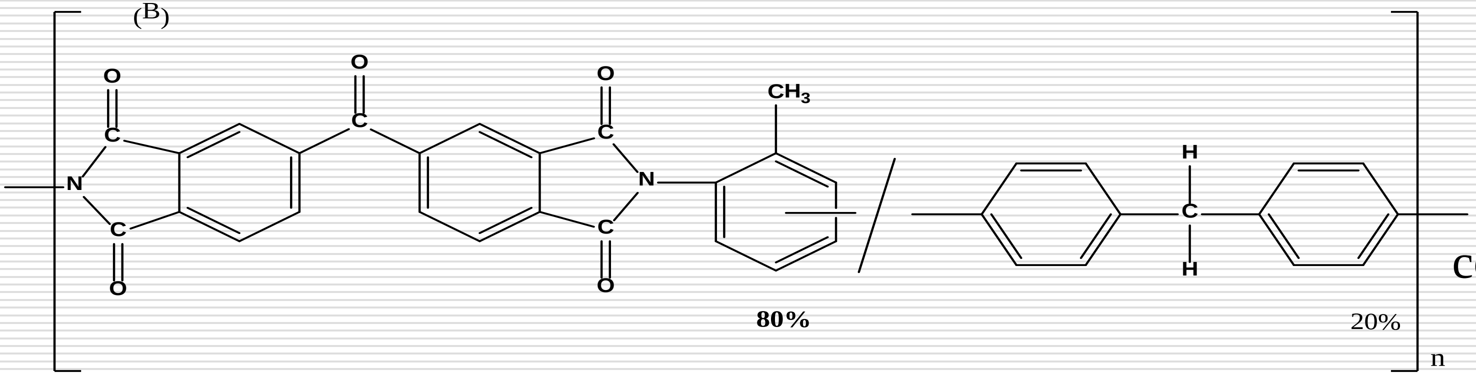
Powermatic material used for membrane preparation

(A)



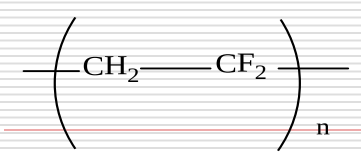
PEEK-WC (A)

(B)



co-polyimde P84 (B)

(C)

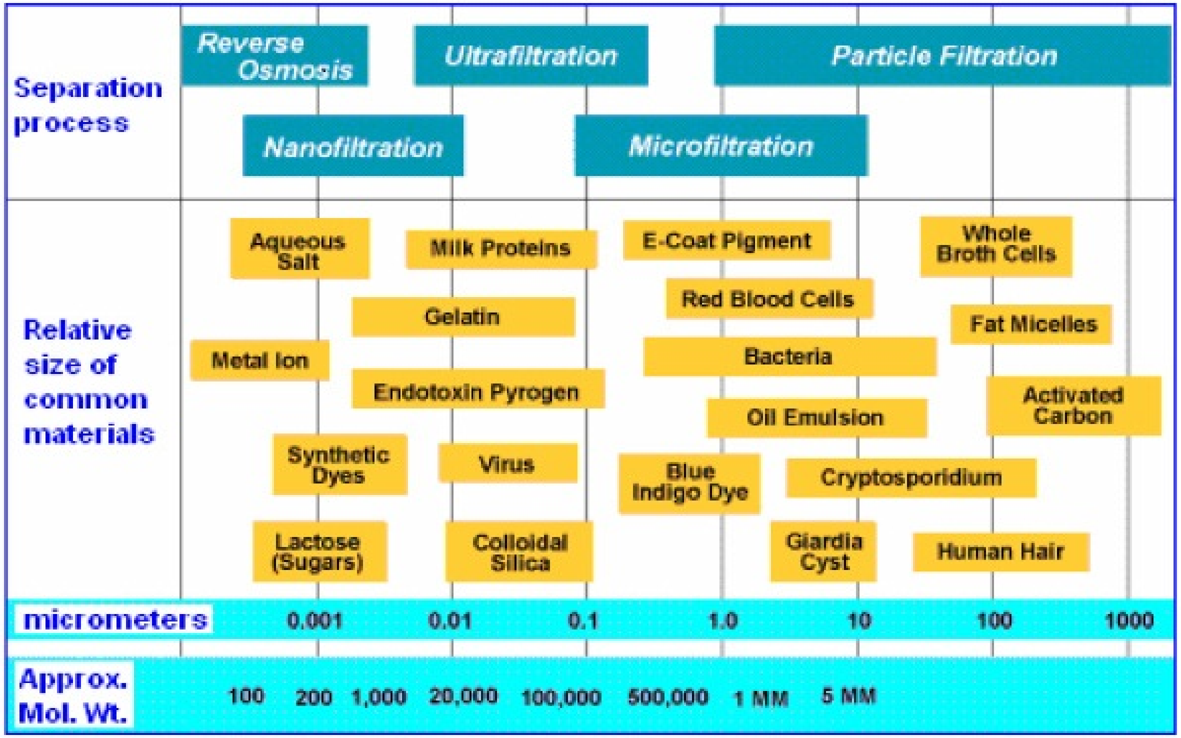


polyvinylidene fluoride (PVDF) (c)

Synthetic Membranes Importance's

- Potable water starting from sea water.
- Treat the waste water in industrial processes.
- Purify the air.
- Application in biomedical fields.

Filtration ranges of membranes separation processes



Membranes classification

Structure classification

Symmetric membrane vs Asymmetric membrane

Material classification

Polymeric membranes vs. the inorganic membranes

Advantages of both polymeric and inorganic membranes

Disperse CNTs fillers into polymer

Characteristic parameters of a membrane

Flux decline due to concentration polarization and fouling,

To limit this problem by

Reduction of TMP

Increasing feed velocity

Use of turbulence promoters

Solution pre-treatment

Composite organic-inorganic membranes

Composite organic-inorganic membranes

Increase Hydrophilicity

High permselectivity

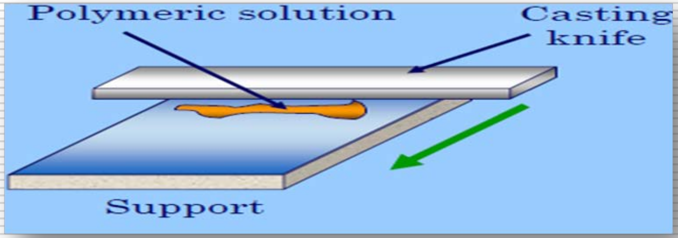
Fouling resistance

Macrovoids-free structure

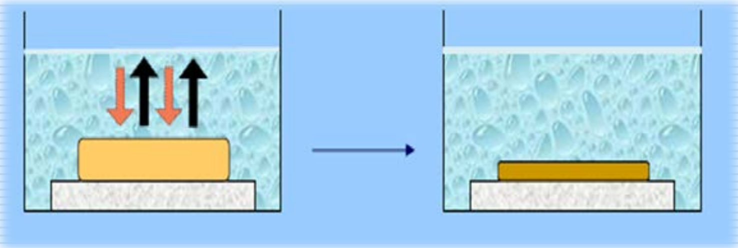
General Steps to Prepare Polymers Membranes

STEP1: **Preparation of membrane polymer solution**

STEP 2: **Casting the solution**



STEP 3: **Immersion of the film in the water bath**



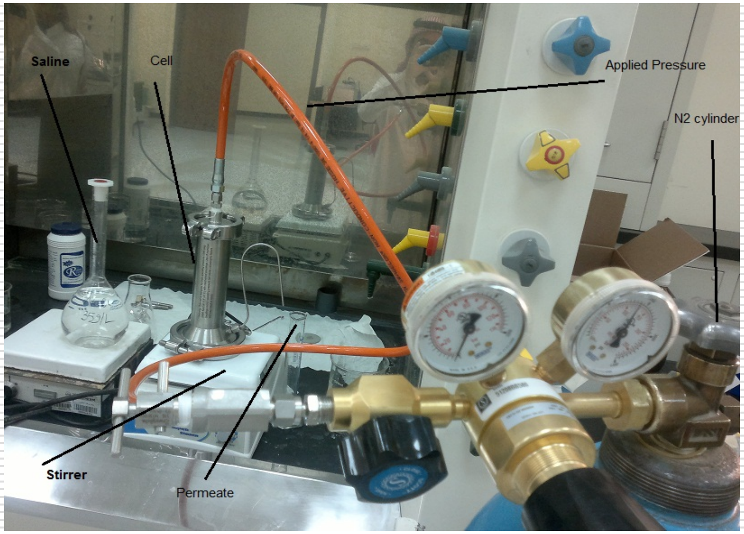
Membrane permeation and Retention Experiments

Dead-end mode with SteriltechTM HP4570 stirred cell having an active membrane area of 14.6 cm²

Flux (J) $$J = \frac{Vp}{t * A}$$

Permeance (Pe) $$Pe = \frac{J}{TMP}$$

The membrane rejection (R) $$R\% = \left(1 - \frac{C_p}{C_r}\right) * 100$$



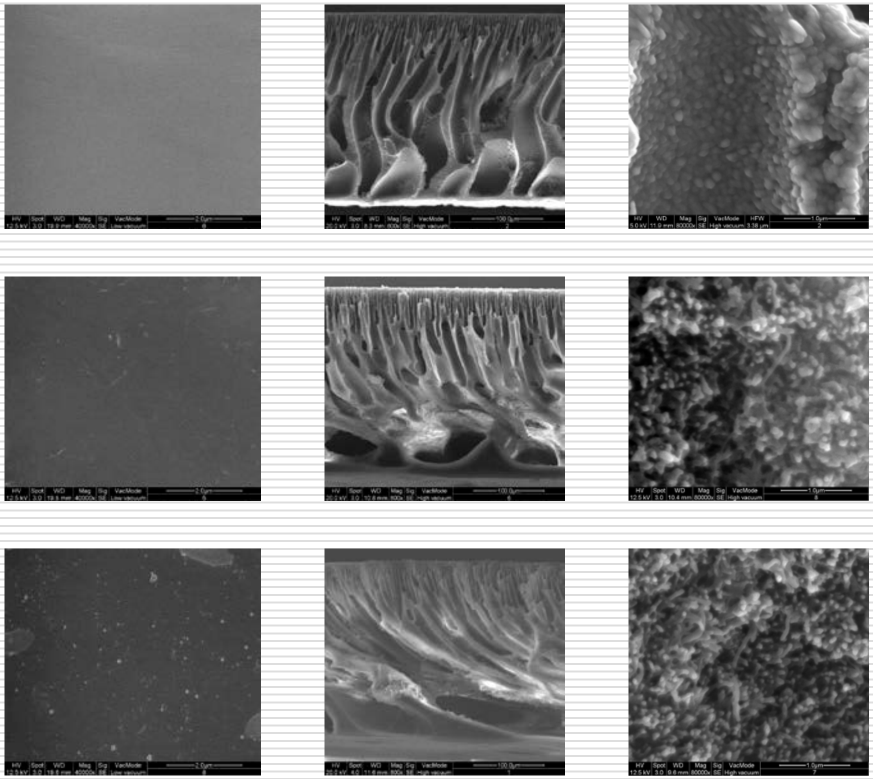
SEM images of P84 membranes

Up surface | Cross section | Particular cross section

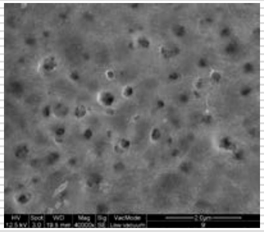
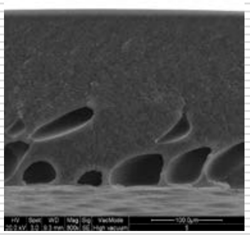
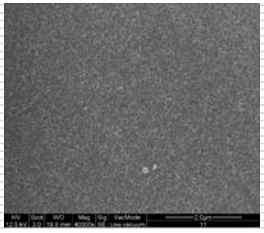
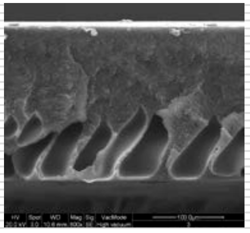
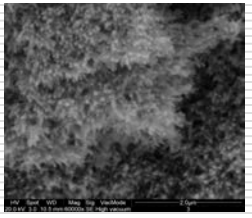
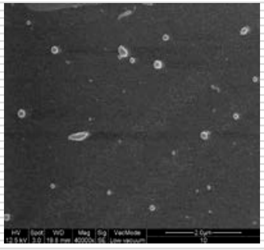
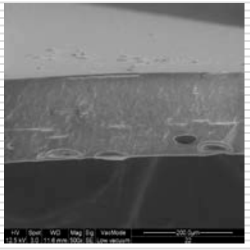
P84 (N)

P84 (N) + MWCNTs(OX-1)

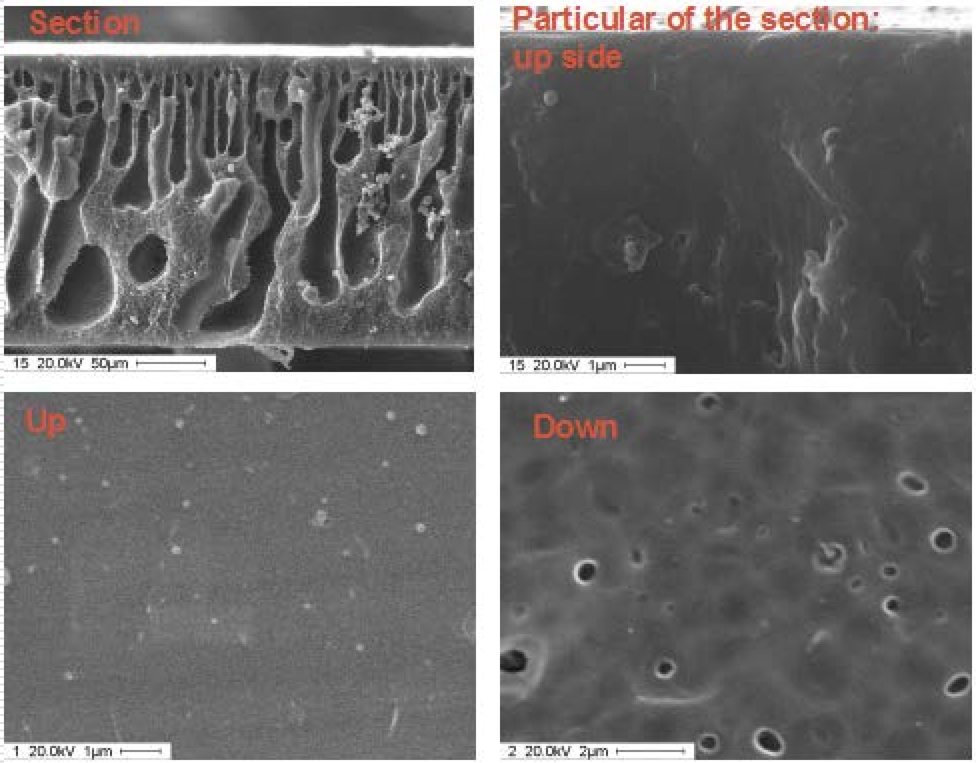
P84 (N) + MWCNTs(NH_2-1)



SEM images of P84 membranes

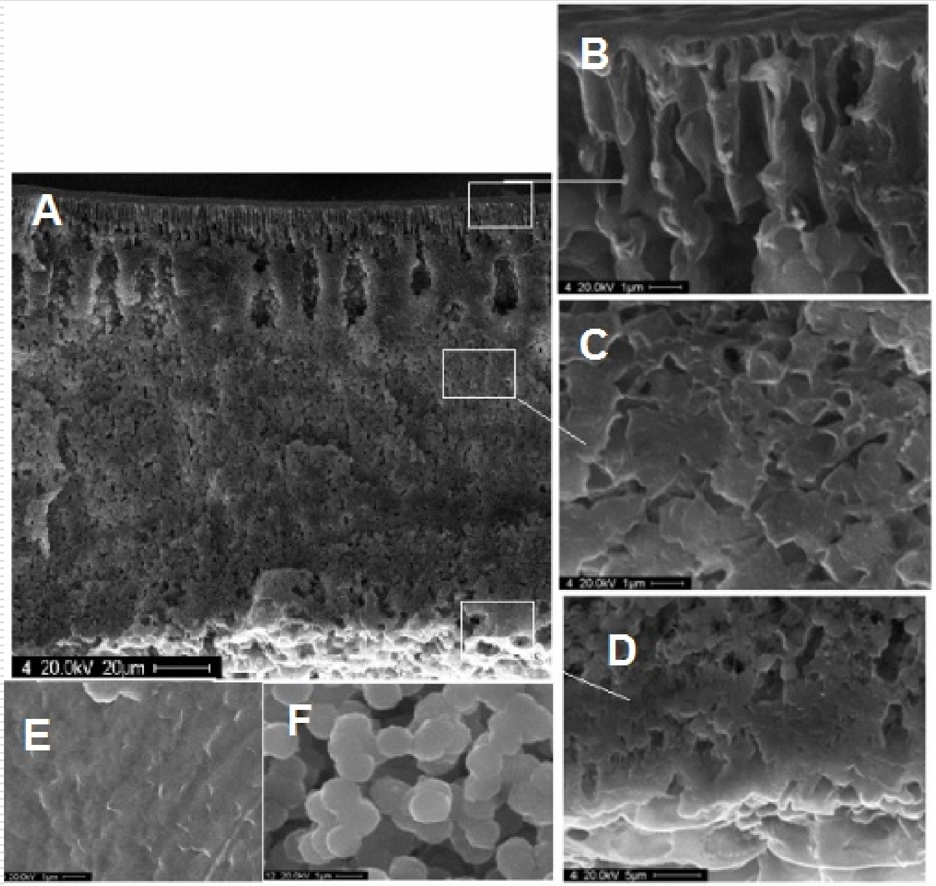
	Up surface	Cross section	Particular cross section
P84 (D)			
P84 (N) + MWCNTs(OX-1)			
P84 (N) + MWCNTs(NH_2-1)			

SEM images of PEEK-WC hybrid members

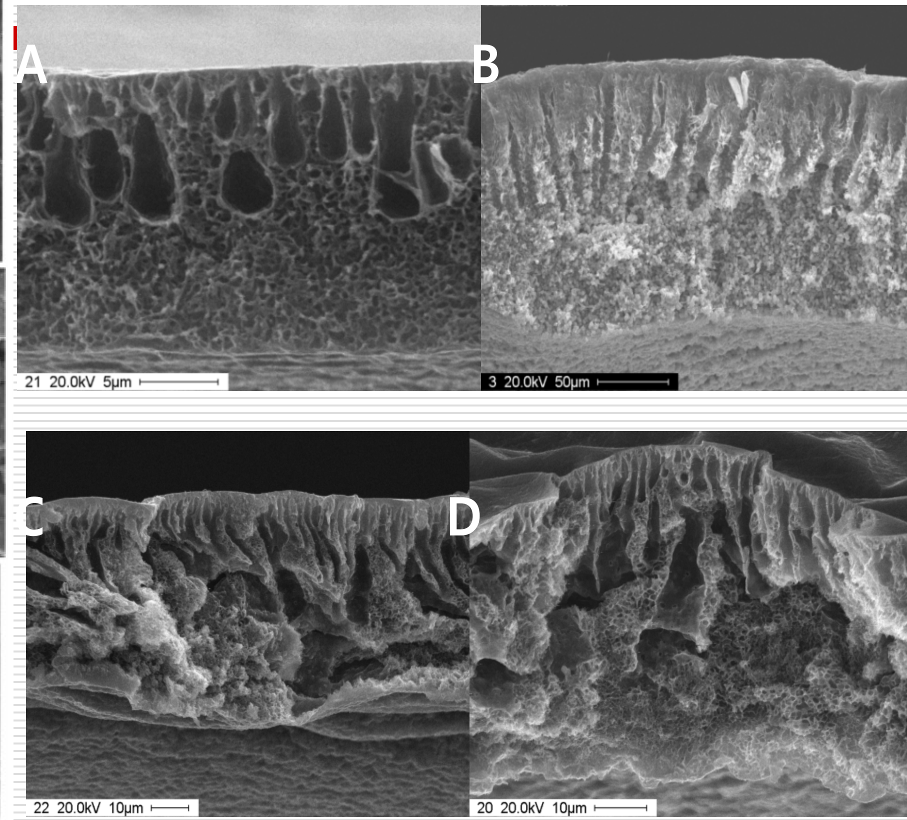


SEM images of the of the PEEK-WC hybrid membrane
(loading MWCNTs: 2 wt%) prepared from a DMF:THF 60:40 wt% solution

SEM Images of PVDF Membranes

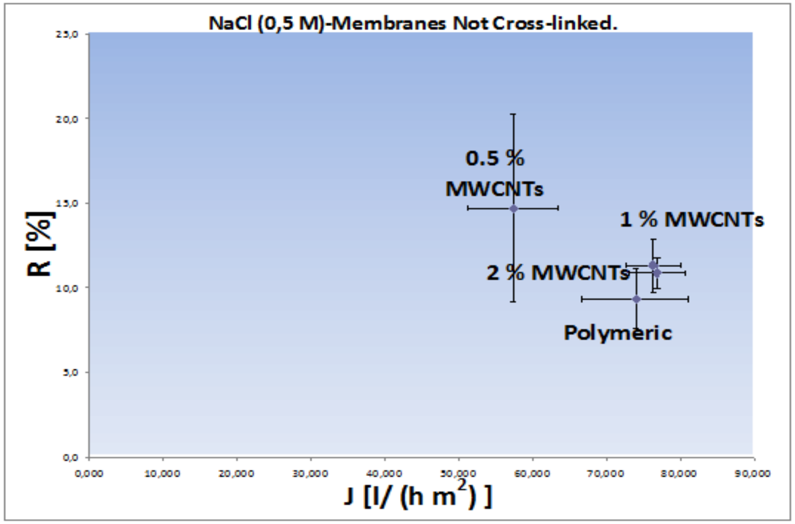


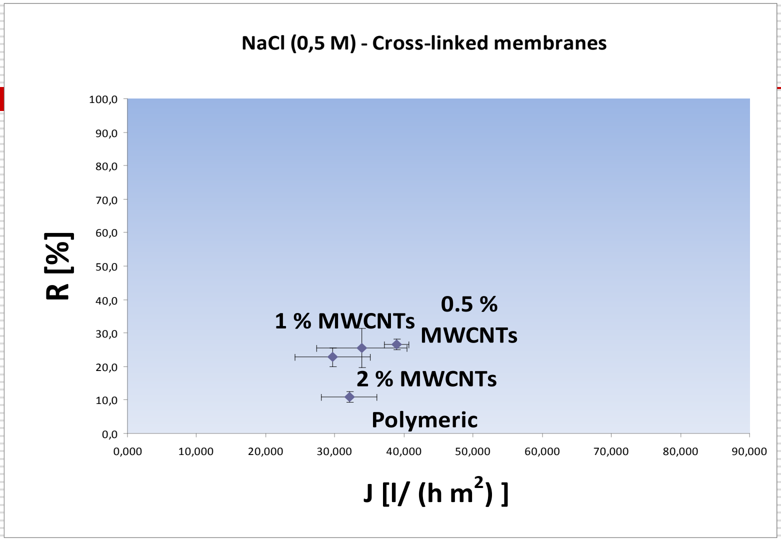
SEM images of the polymeric PVDF membrane prepared without LiCl (similar to protocol A, but without the MWCNTs) : cross-section (A) particulars of the cross sections (B, C, D), up surface (E) and down surface (F)

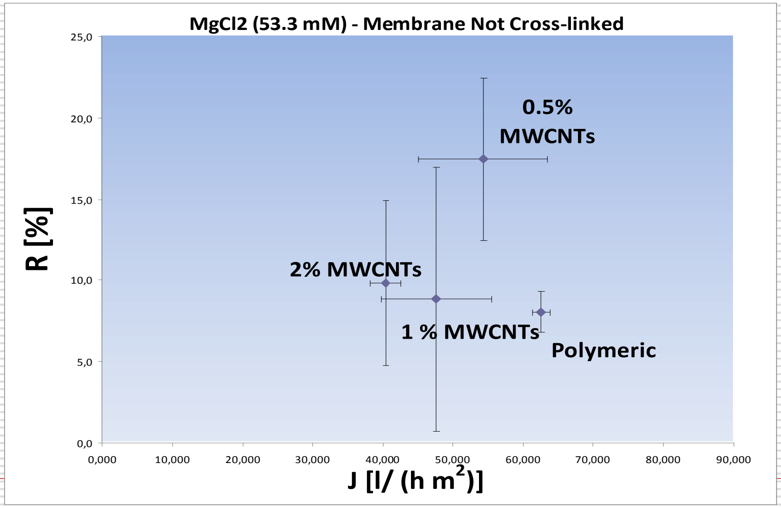


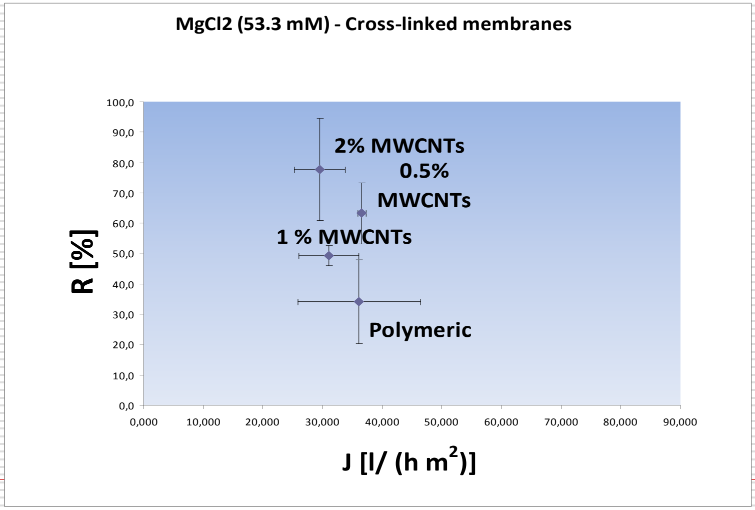
SEM images of the polymeric PVDF membrane prepared with LiCl (similar to protocol B, but without the MWCNTs) and the hybrid membranes prepared following the protocol B with 0.5wt% (B), 1wt%(C) and 2 wt% of MWCNTS loading.

Transport properties of the MMM (Rejection and Flux of P84 membranes)





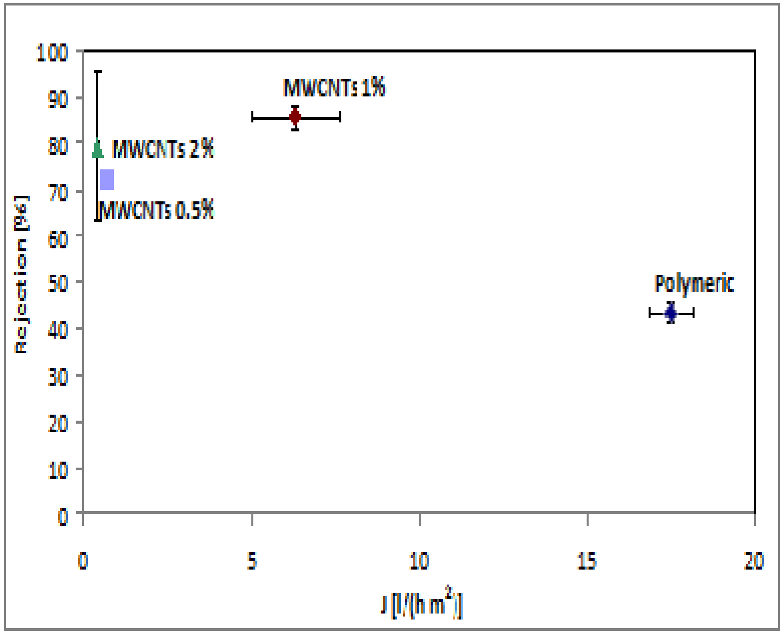


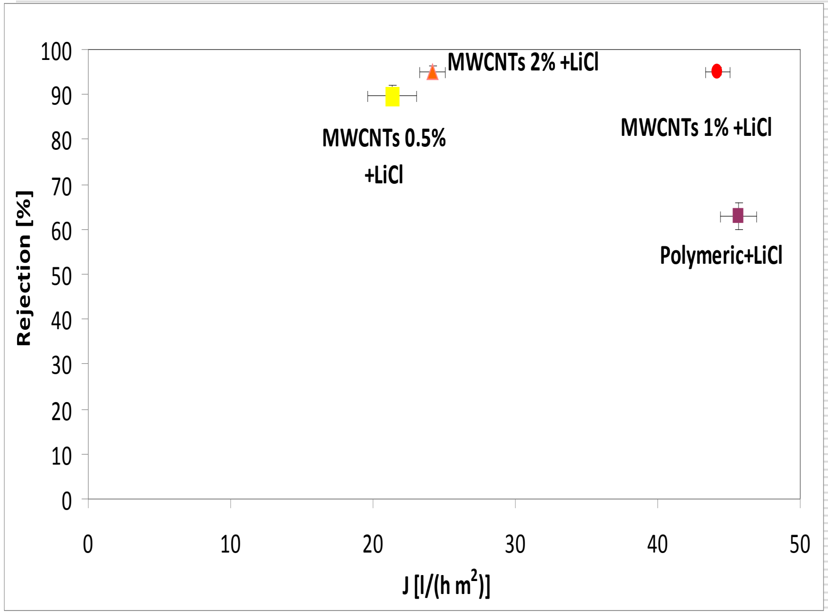


Flux and rejection of the not-cross-linked polymeric and hybrid PI membranes.. TMP 20 bar

Flux and rejection of the cross-linked polymeric and hybrid PI membranes. TMP 20 bar

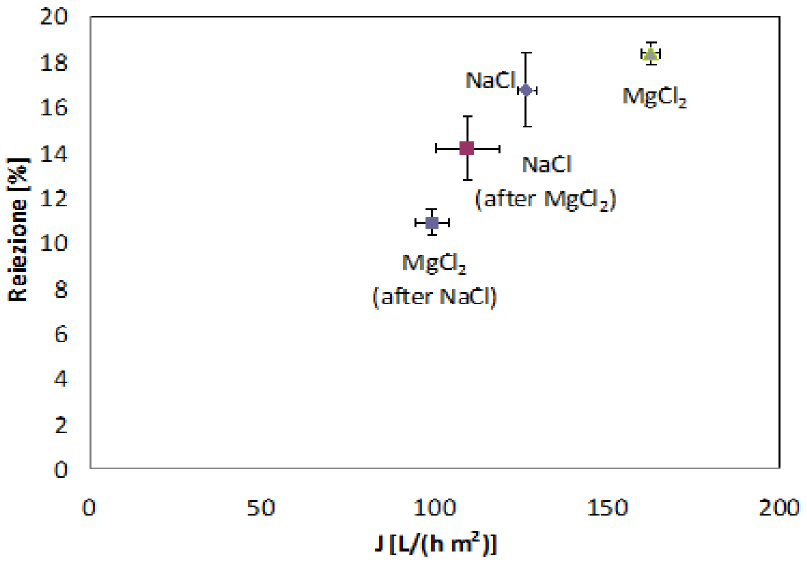
Transport properties of the MMM (Rejection and Flux of PVDF membranes)



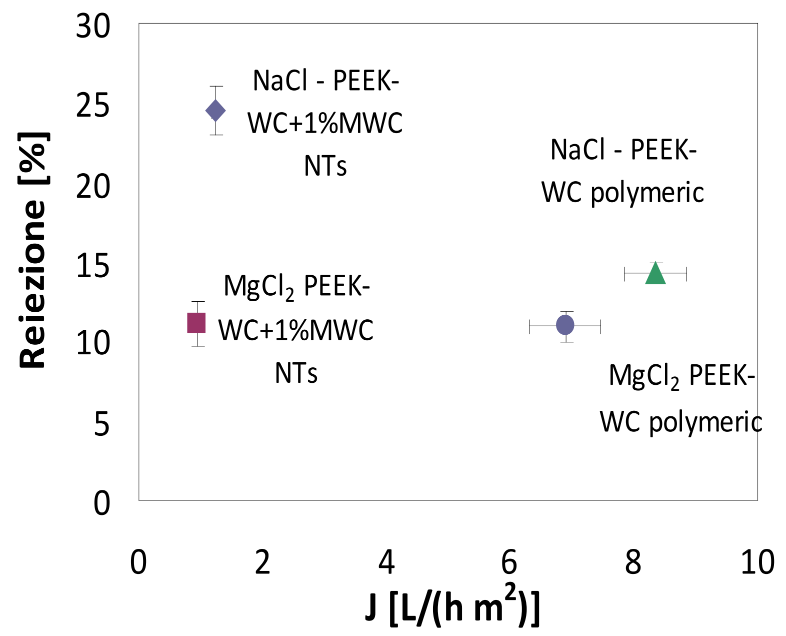


Flux and rejection of the PVDF membranes prepared following the protocol A (a) and B (b)

Transport properties of the MMM (Rejection and Flux of PEEK-WC membranes)



Flux and rejection of the PEEK-WC polymeric membrane prepared from a DMF:THF 60:40 wt% solution. TMP 10 bar



Flux and rejection of the PEEK-WC membranes, polymeric and composite (1% wt of MWCNTs) prepared from a DMF:THF 50:50 wt% solution. TMP 20 bar

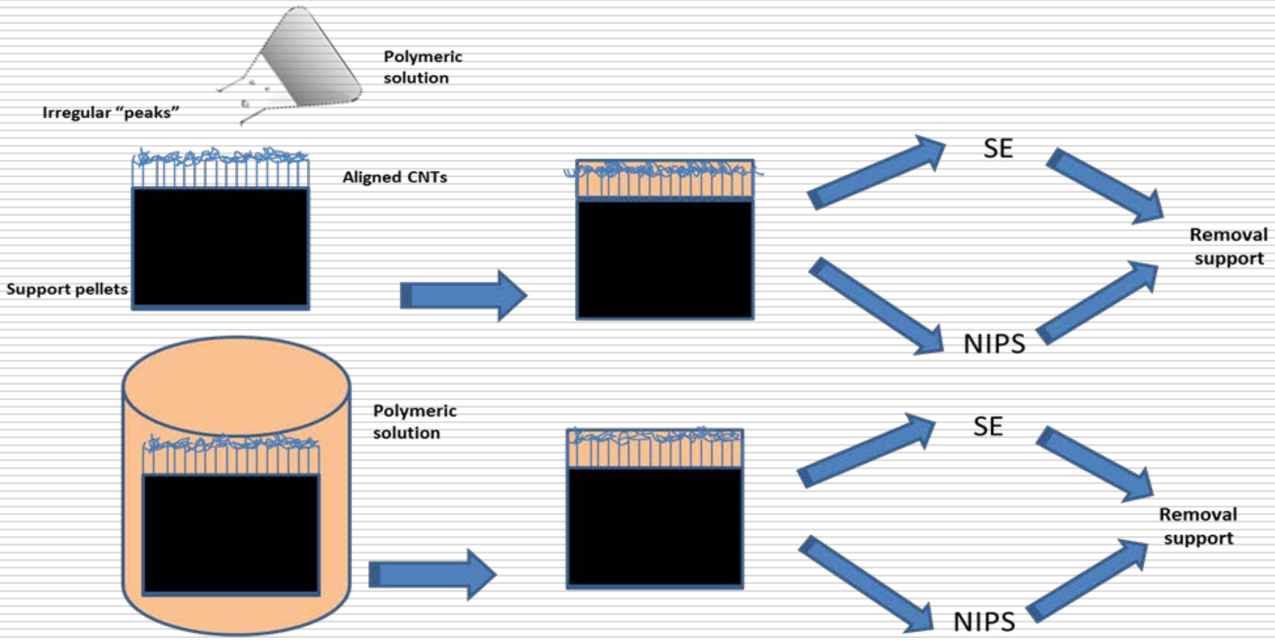
Membrane code	Water Permeance (L/hm²bar)
P84(N)	254
P84(N)+MWCNTs(OX-1)	359
P84(N)+MWCNTs(NH_2-1)	295
P84(N)+MWCNTs(NH2-2)	175
Matrimid	18.4
Torlon	0.25
P84(D)	207
P84(D)+MWCNT(OX-1)	157
P84(D)+MWCNT(NH2-1)	211
P84(D)+MWCNT(NH2-2)	233
P84(D)+MWCNT(NH2-3)	290
UTC-20	4.26
MPF-44	1.43
DESAL-5	7.6
DESAL-DR	5.2
PSH-100	(what type this membrane why it is high) 402
RC-100	537(what type this membrane why it is high)

Membrane code	Orange II sodium salt Permeance solution (L/hm^2bar)	Rejection %
P84(N)	254	55.84
P84(N)+MWCNTs(OX-1)	359	31.43
P84(N)+MWCNTs(NH_2-1)	295	49.08
Matrimid	18.4	60.57
Torlon	0.25	55.71
UTC-20	3.5	Why high here100
MPF-44	0.8	what type of material 100
DESAL-5	4.8	95Why high here
DESAL-DR	3.6	Why high here97

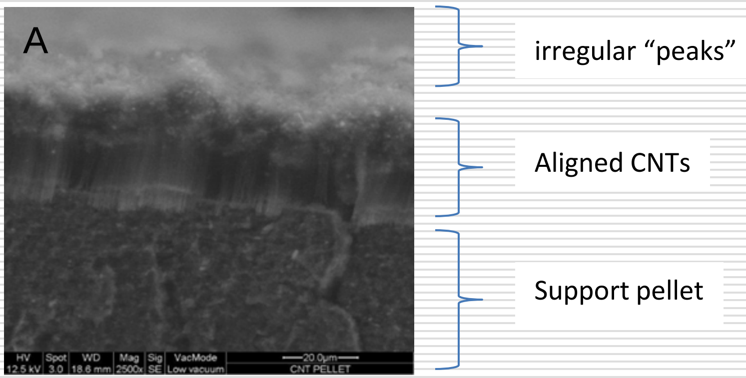
Mechanical results of some membranes

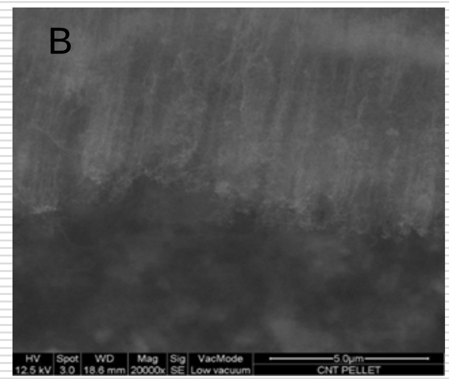
Membrane code	Tensile Strength (MPa)	Ultimate Elongation %	Toughness (Mpa)
PVDF	0.06	97.4	0.045
PVDF 0.5% LiCl	0.2	24.9	1.1
PVDF 0.5% MWCNTs 0.5% LiCl	5.91	32.8	1.6
PVDF 0.5% MWCNTs 2% LiCl	4.3	22.0	1.5
PVDF 1% MWCNTs 2% LiCl	1.4	18.4	1.5

Preparation of Oriented CNT Membrane



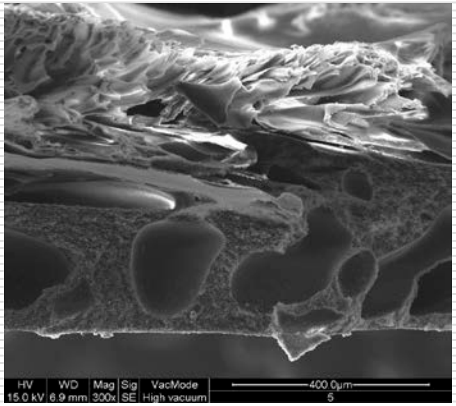
SEM images of the aligned CNTs growth on the support pellet (A-CNT): (A) Cross-section of A-CNT;(B) Particular of the interface between the support and the aligned CNTs.



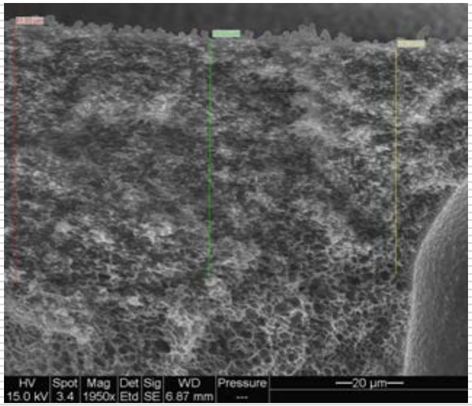


SEM images of the PEEK-WC membrane prepared by Dip coating + NIPS: (A) Cross-section; (B) Particular of the "lower surface"; (C) Particular of the "lower surface" at higher magnification.

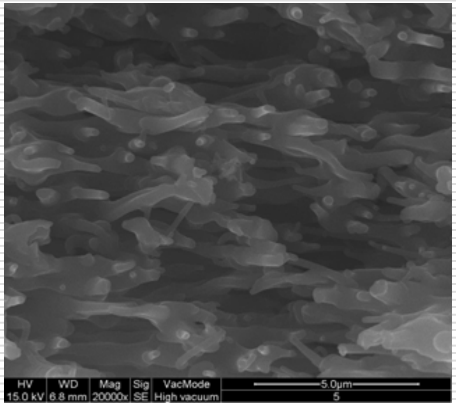
A



B



C



Preparation difficulty: compatibility between the carbon nanotubes and the polymeric matrices

Difficulty of removing the support from the membrane

Future work

Increase the dimension of the samples to approach practical use

Examine the dispersion of carbon nanotubes within the membranes

Conclusions

The CNT membrane reduced fouling and improved transport properties
The CNT membrane improved the mechanical properties of the membrane
Carbon nanotubes increased the retention of salts

Future work
Prepare MMM containing aligned carbon nanotubes
Examine the influence of the various functions on the carbon nanotubes

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