NTNU

Norwegian University of Science and Technology

TMT4320 Nanomaterials
October 26th, 2016

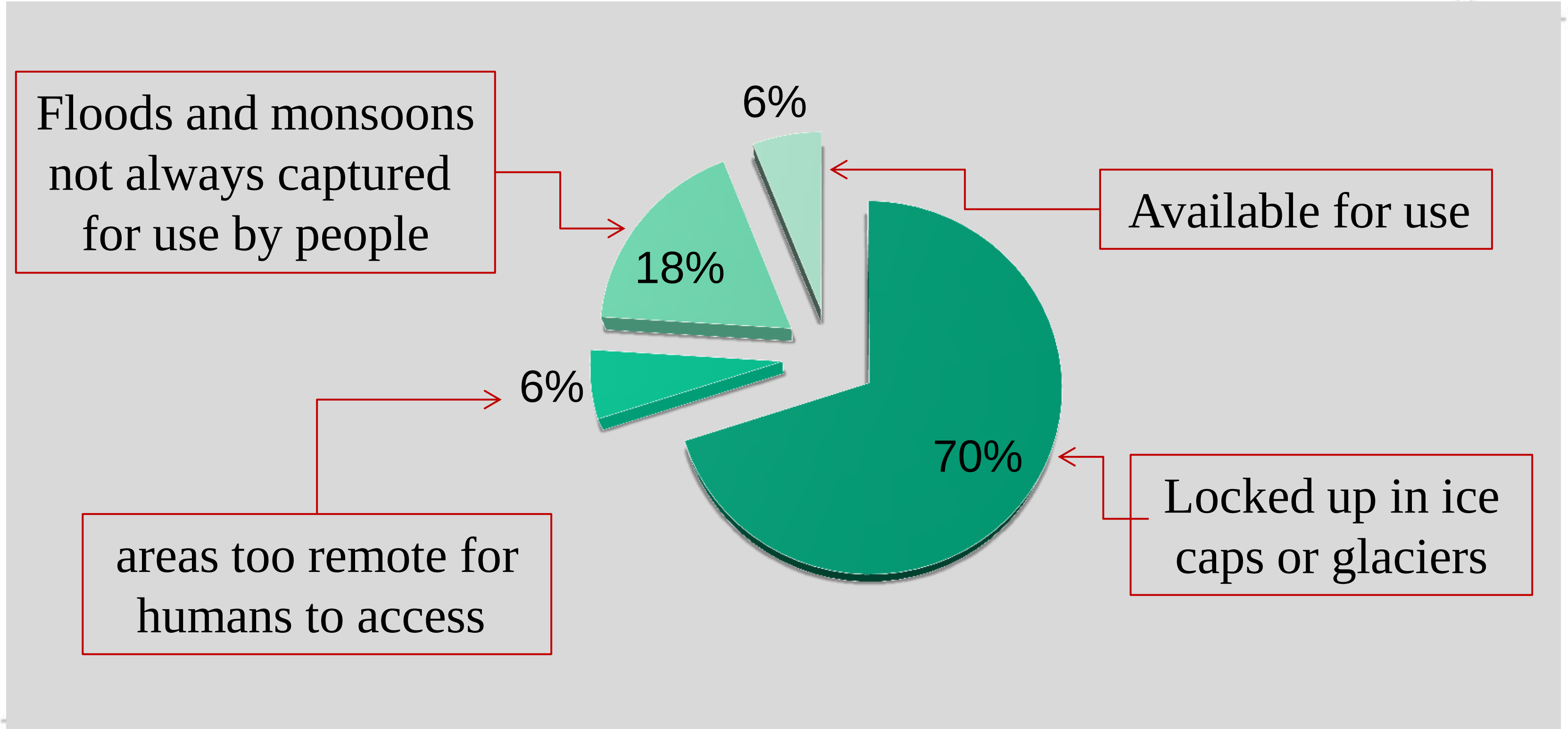
- Application of nanomaterials: Environment

Outline

- Overview on freshwater in our planet
- Nanomaterials and water remediation:
  - Disinfection
  - Decontamination
  - Desalination

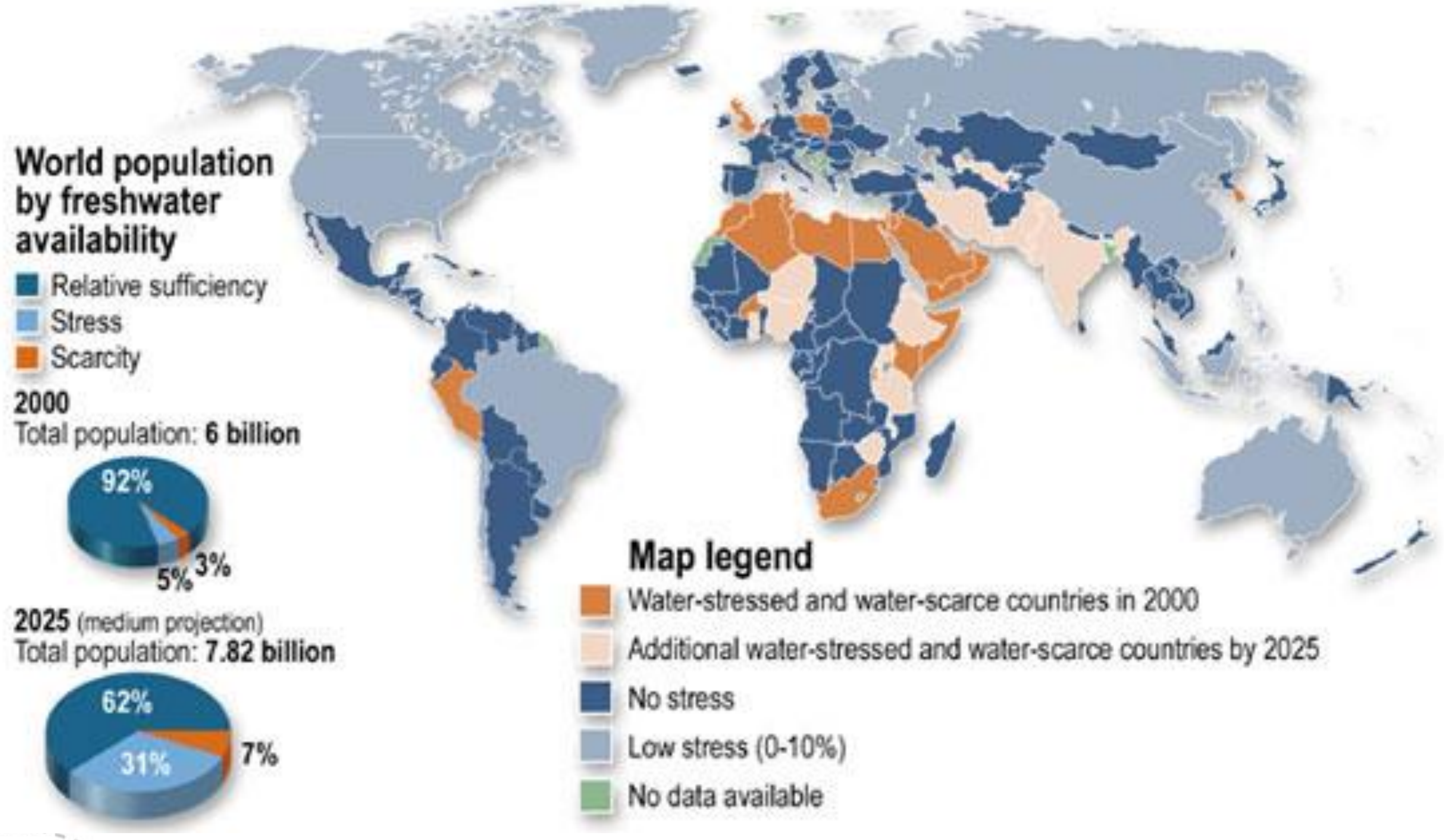
Freshwater distribution on our planet

- ~70% of earth's surface is covered with water
- ~97% of the earth's water supply is composed of salt water
- ~3% of the earth's water supply is fresh water



Source: World Water council, February 2008, http://www.worldwatercouncil.org/

- **2000** ~600 Million people of the total population (6 billion) face water deficiency
- **2025** between 2.7 billion and 3.2 billion people may be living in either water deficiency or water stressed conditions



Source: World Water council February 2008, http://www.worldwatercouncil.org/

The role that nanomaterials could play in resolving issues relating to water-quality

To NOT contaminate!

Disinfection

Ag and Cu Nanoparticles embedded in paper filter

Clean/Fresh water

Decontamination

Porous magnetic nanocomposites

Desalination

VA-CNT Nanomembrane Fabrication and performance

Definition

Water Purification is the process of removing chemicals, materials, and contaminants to produce clean, fresh drinking water

Conventional methods for water purification

Filtration: Separation of solids from fluids

Sedimentation: Particle settling out of liquids against a barrier

Desalination: Removing salts and other minerals

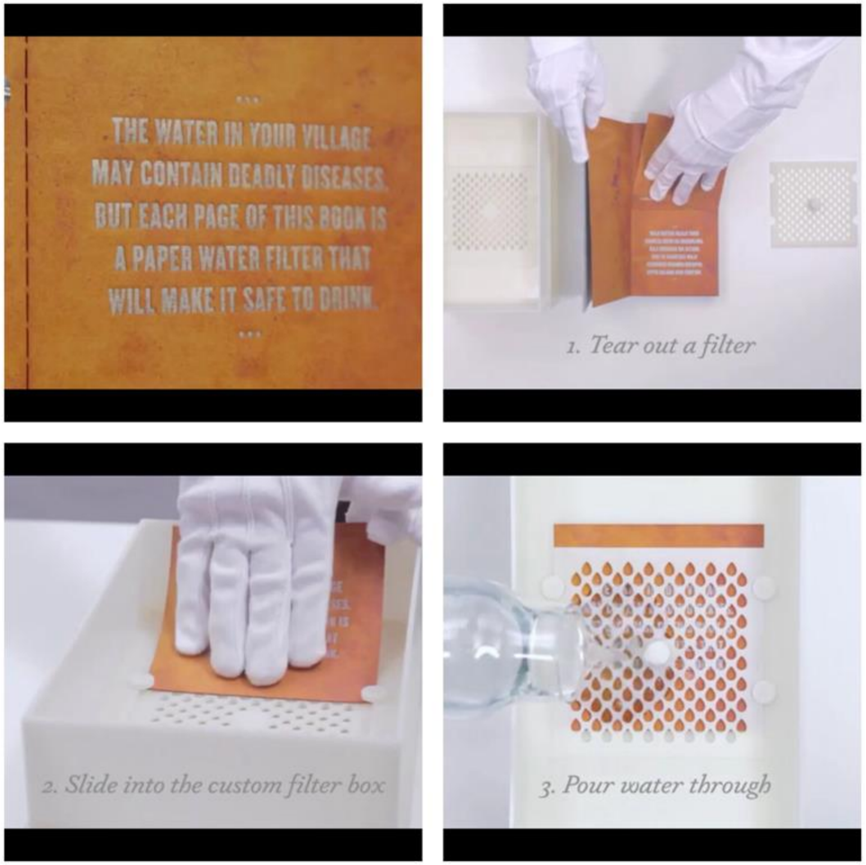
Biological Processes: Removing living organisms

Chemical Processes: removing chemicals and/or chemical compounds

Nanomaterials and water disinfestation

“Drinkable Book ™ ”

Water is Life & University of Virginia



"All you need to do is tear out a paper, put it in a simple filter holder and pour water into it from rivers, streams, wells etc and out comes clean water, and dead bacteria as well"

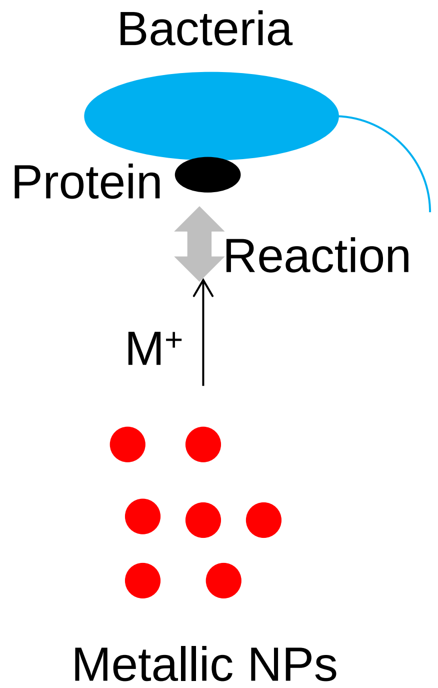
Source: BBC News, Science and Environment, Boston, 16th August 2015
http://www.bbc.com/news/science-environment-33954763

"Drinkable Book ^{TM} *"* How it works?

- A "Drinkable Book^{TM}" that combines treated paper with printed information on how and why water should be filtered
- The pages consist of sheets of thick filter paper embedded with Ag or Cu NPs which kill bacteria in water as it passes through
- The paper removes more than 99% of bacteria
- Resulting levels of contamination are similar to US tap water
- Ag and Cu NPs leaching into the water are below safety level
- One page can clean up to 100 litres of water.

Metallic NPs as antibacterial agents

- Metal ions react with protein (enzyme) on the surface of the cell membrane
- Enzyme's activity is inhibited
- Then, the cell collapses

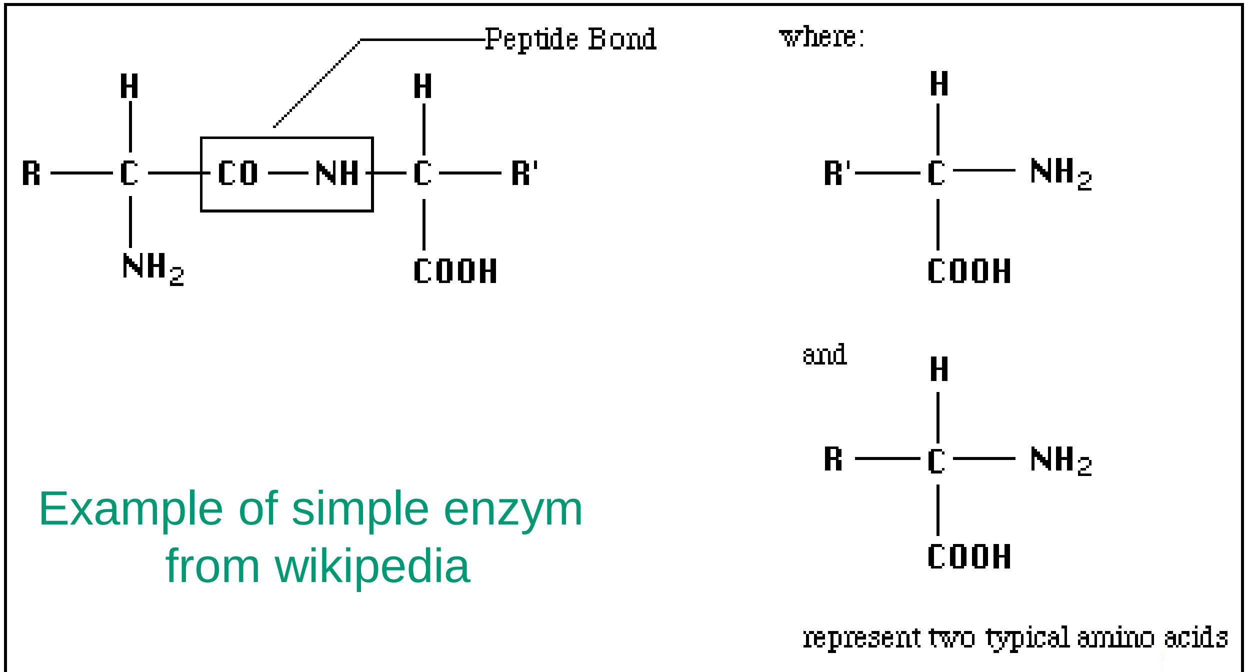


Suggested mechanism of antibacterial effect by metals

Handbook of nanoceramic and nanocomposite coatings and materials 1st Ed. Chap 23 (2015)

Metallic NPs as antibacterial agents

Ag ions tend to react with function groups containing C, N, O inducing the inhibition of the enzyme function

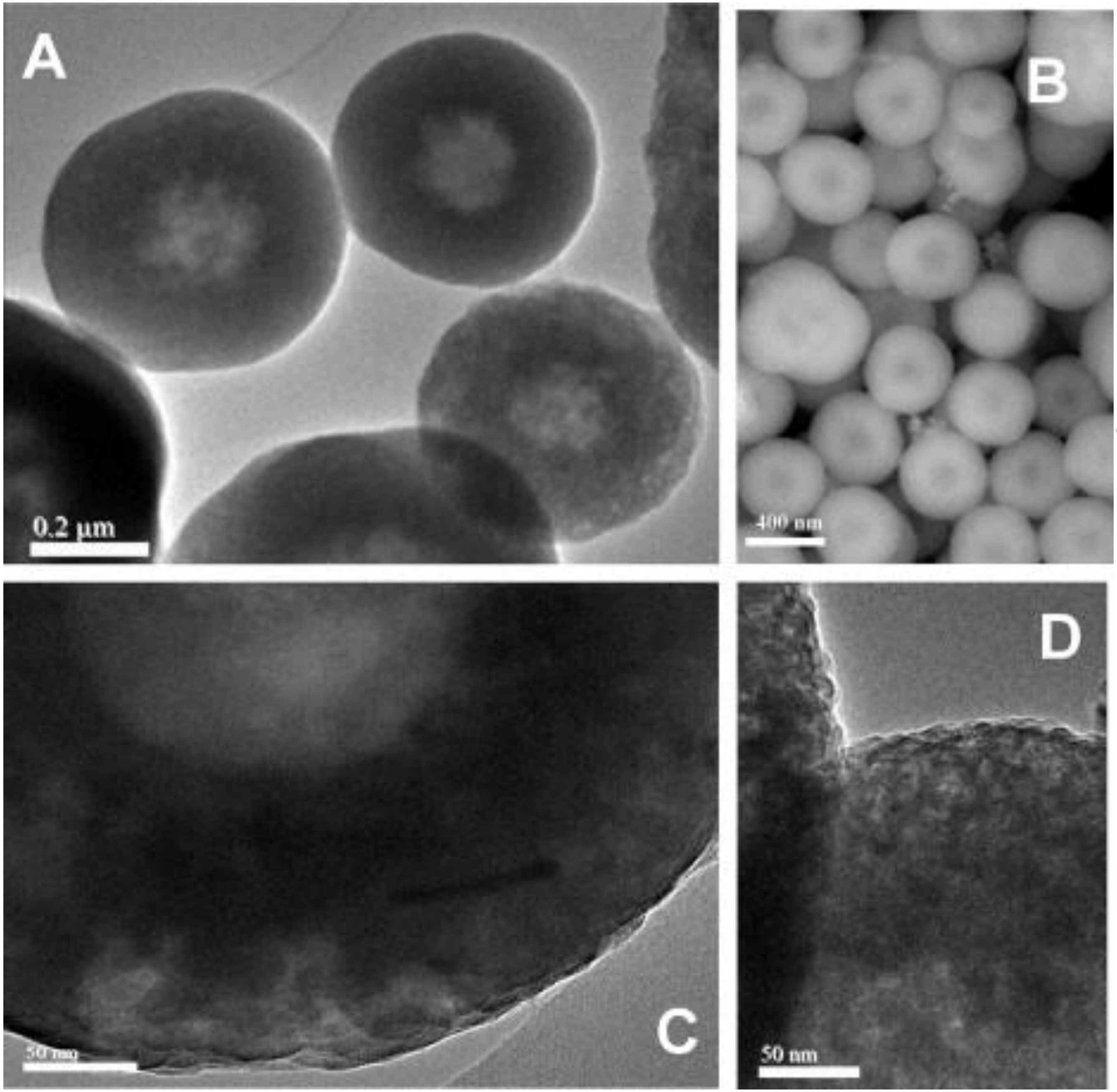


Example of simple enzym from wikipedia

FIGURE 1
Typical protein structure - two amino acids joined by a peptide bond.

Nanomaterials and water decontamination

Hydrothermal assisted synthesis of iron oxide-based magnetic silica spheres and their performance in water decontamination



J. Colloids and interface science, 365. 2012 156-162

Synthesis of iron oxide-based magnetic silica spheres: materials and methods

Ethanol
Water
CTAB
MNPs

Fe_2O_3
10 nm

Over night

Sol-gel
Reaction
Ultrasons
And shaker

TEOS
addition

The mixture was transferred to an autoclave and was hydrothermally treated at 120 C for 48 h.

Hydrothermal treatment

Calcination

400 C during 8 h.

TEOS: Tetraethylorthosilicate $Si(OC_2H_5)_4$
CTAB: cetyltrimethylammonium bromide

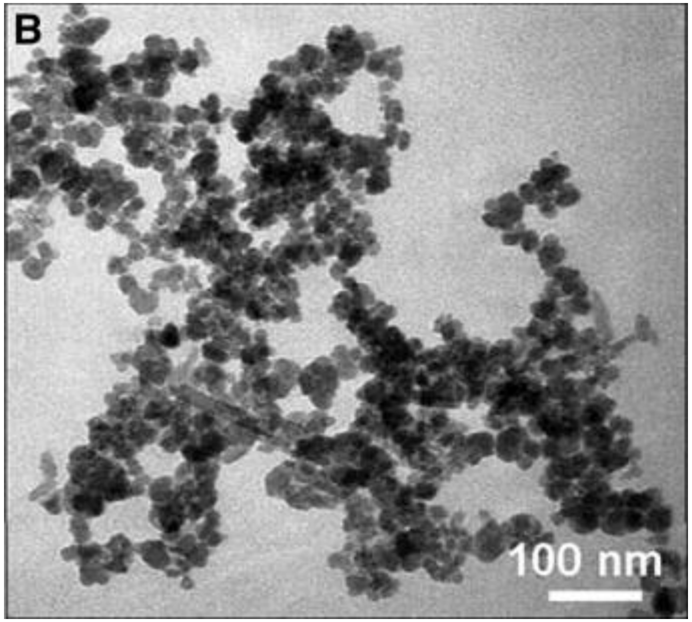
J. Colloids and interface science, 365. 2012 156-162

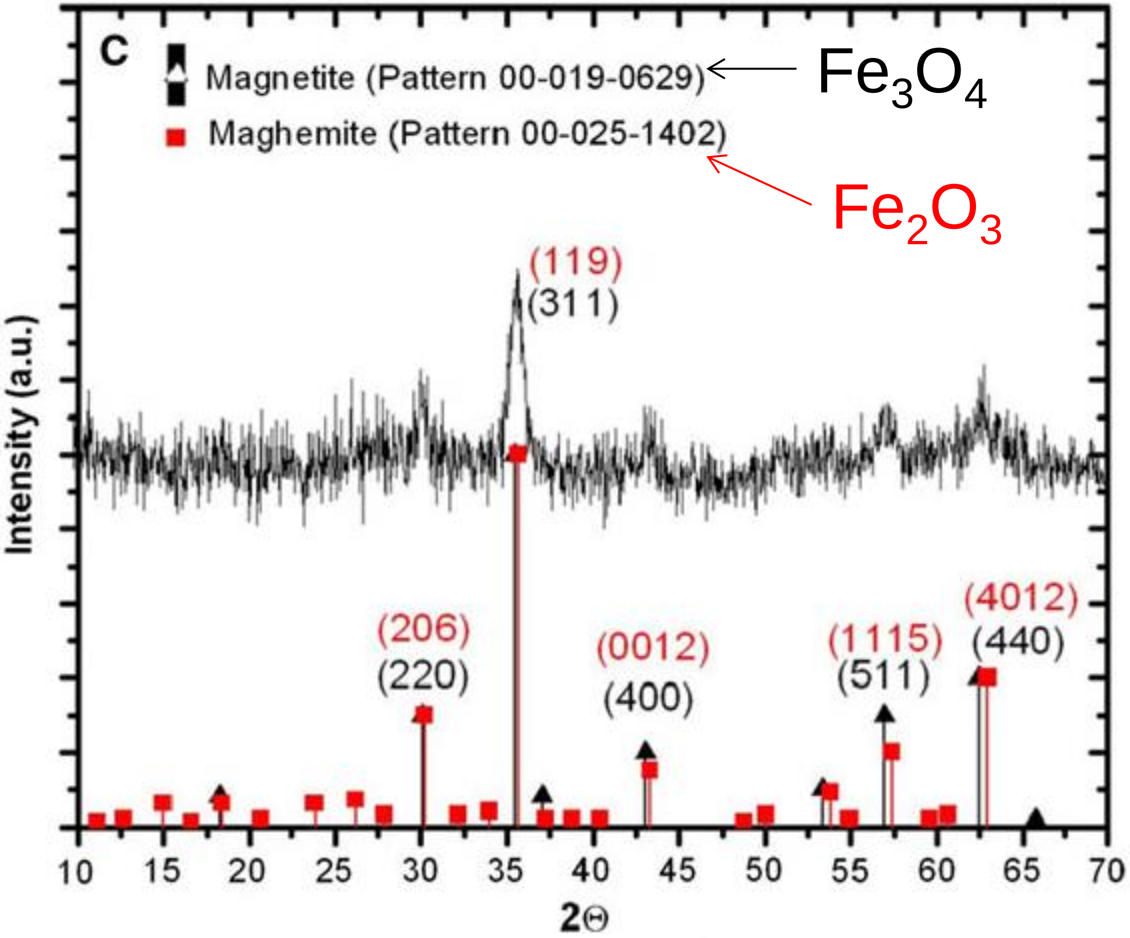
Co-Precipitation of iron oxide (MNPs)

- Aqueous mixture of $FeSO_4$ and $FeCl_3$ (1:2 molar ratio) NH_4OH was used as a precipitation agent.
- $FeSO_4.7H_2O$ (0.67 M, 9.3 g in 50 mL) and $FeCl_3$ (1.27 M, 10.8 g in 50 mL) were mixed and heated to 80 ºC.
- In order to precipitate the iron hydroxides, the pH value was raised and maintained to 10 for 30 min.
- The solution was rigorously stirred at a constant temperature during all the process. Then, the pH value was increased to 10.5–11.
- The resultant solid magnetite materials were dried in a vacuum oven at 60 ºC during 24h. And the powder was collected and stored in a glass container

J Nanopart Res (2011) 13:3199–3206

TEM image and XRD pattern of the as-synthesized NPs

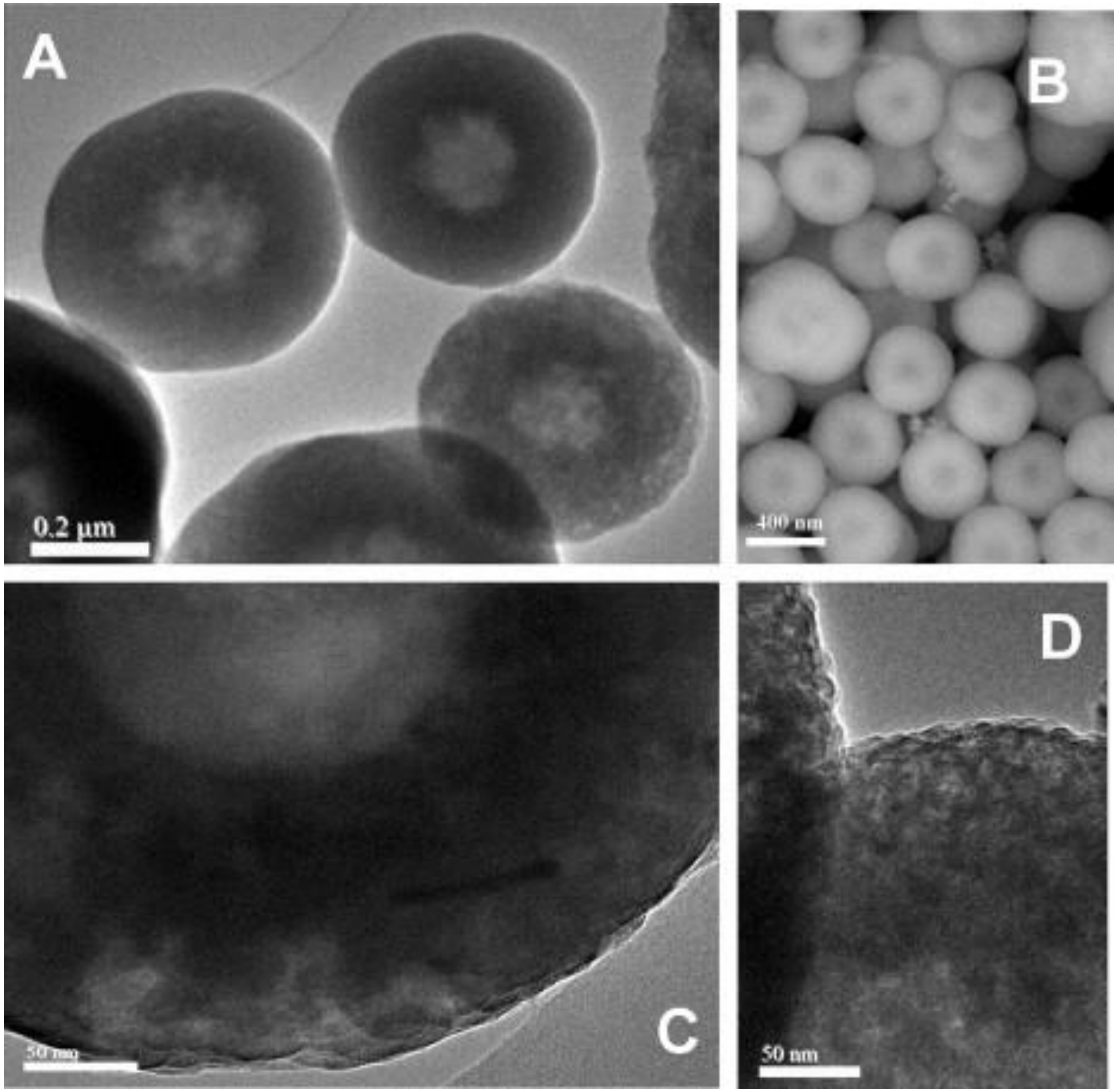




Synthesis of the Porous Magnetic Silica (PMS) spheres

- 14 mL of aqueous solution of cetyltrimethylammonium bromide (CTAB) 0.8 wt% and 4.5 mL of ammonium solution were mixed with 60 mL of ethanol containing 15 mg of MNPs at 25 ºC at a pH of 10.
- The concentration of the CTAB corresponds to 3.875 times the CTAB critical micelle concentration (CMC) [*].
- After stirring for 5 min, 800 µL of tetraethylorthosilicate (TEOS) were slowly added to the solution. The mixture was maintained under shaking bath overnight.
- The obtained suspension was transferred to a Teflon-lined stainless steel autoclave and was maintained at 120 ºC for 48 h.
- The resulting solid material was collected by magnetic separation and washed with distilled water. The dried powder was calcined at 400 ºC during 8 h.

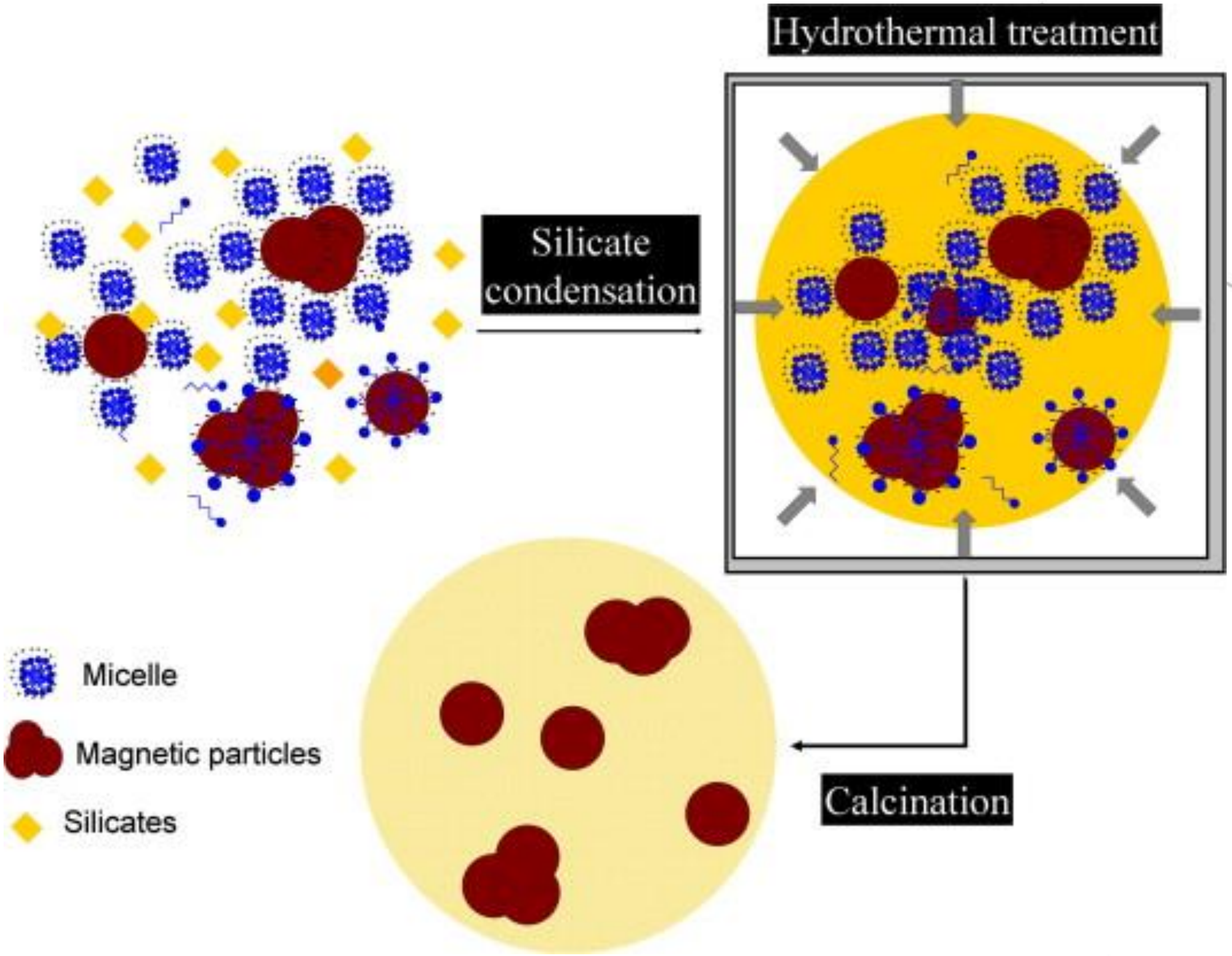
* Colloids and Surfaces A: Physicochemical and Engineering Aspects 296 (2007) 104e108



TEM (A, C, D) and SEM (B) images of the obtained “hollow-like” porous Fe_2O_3/SiO_2 spheres synthesized by the one-step hydrothermal-assisted modified-Stöber method.

J. Colloids and interface science, 365. 2012 156-162

Mechanism of formation of iron oxide-based magnetic silica spheres



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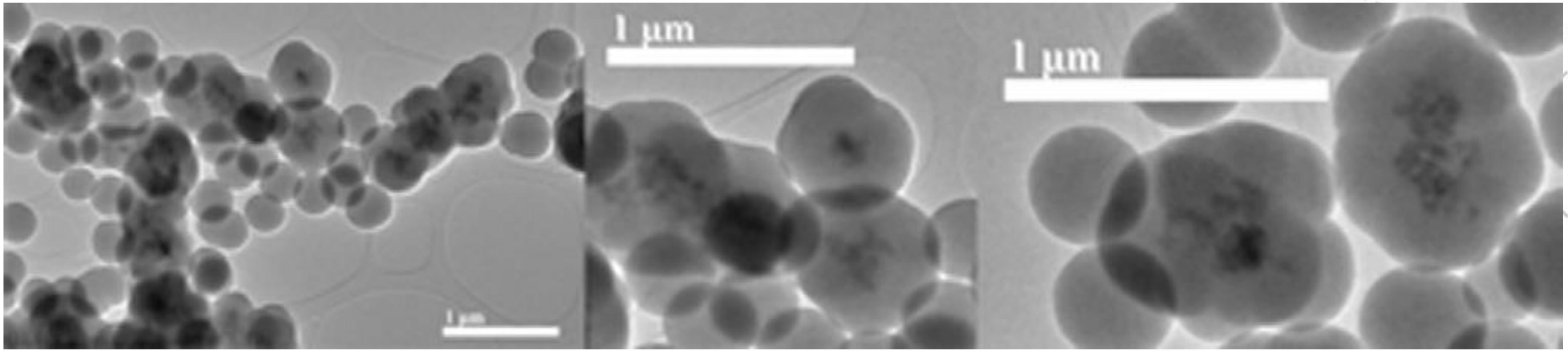
P2 reference sample (no porous sample)
No hydrothermal treatment



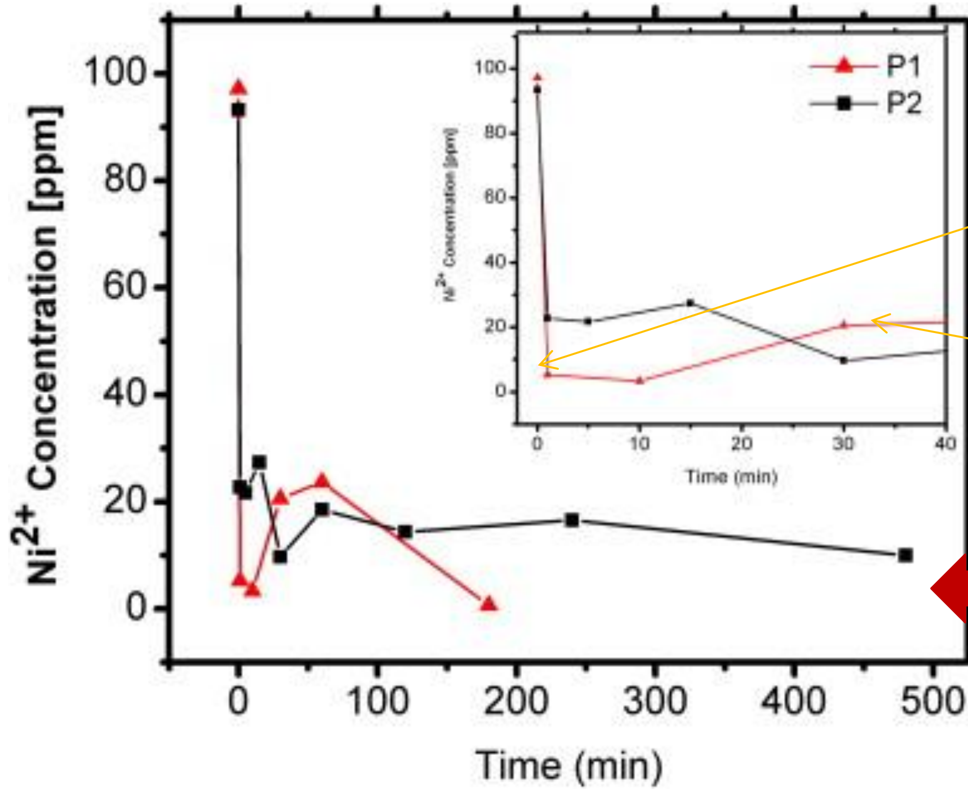
Removal of Ni^{2+} from an aqueous solution

- 20 mg of the PMS spheres were mixed with 15 mL of nickel chloride aqueous solution at a concentration of 100 mg L^{-1}
- 5 samples were prepared in the same conditions
- Each solution was stirred during a fixed time at 150 rpm at room temperature.
- At the end of the stirring process, the PMS spheres were magnetically separated from the suspension, and the solutions were filtered with a 0.200 mm pore filter.

Definitions of sorption

- Adsorption
  - Accumulation of atoms or molecules on the surface of a material
  - Chemisorption: Strong interaction between an adsorbate and a substrate surface (ionic or covalent bonds)
  - Physisorption: Weak Van der Waals force between an adsorbate and a substrate surface, or electrostatic interactions
- Absorption
  - A substance diffuses into a liquid or solid to form a solution
- Desorption is the reverse process of both adsorption and absorption

Evolution of the Ni^{2+} concentration in the aqueous solution.



Adsorption

Adsorption-Desorption equilibrium

100% of the Ni^{2+} was removed after 3 hours

P1 is the sample prepared
P2 is a reference sample (without hydrothermal process)

Materials Chemistry and Physics 135 (2012) 510-517

Desalination of sea water and membrane technologies

Water Desalination Process

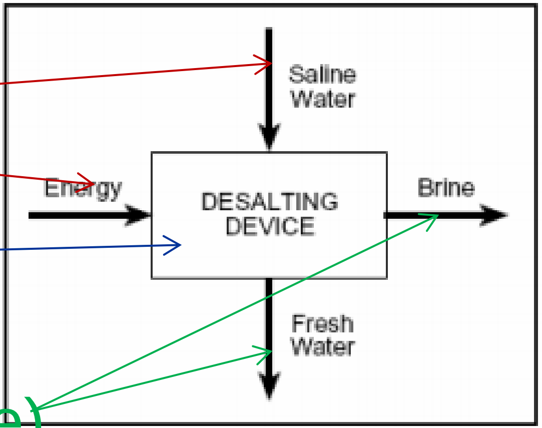
A wide variety of desalination technologies effectively remove salts from salty water (or extract fresh water from salty water), producing a water stream with a low concentration of salt (the product stream) and another with a high concentration of remaining salts (the brine or concentrate).

Most of these technologies rely on either distillation (thermal processes) or membranes to separate salts from the product water.

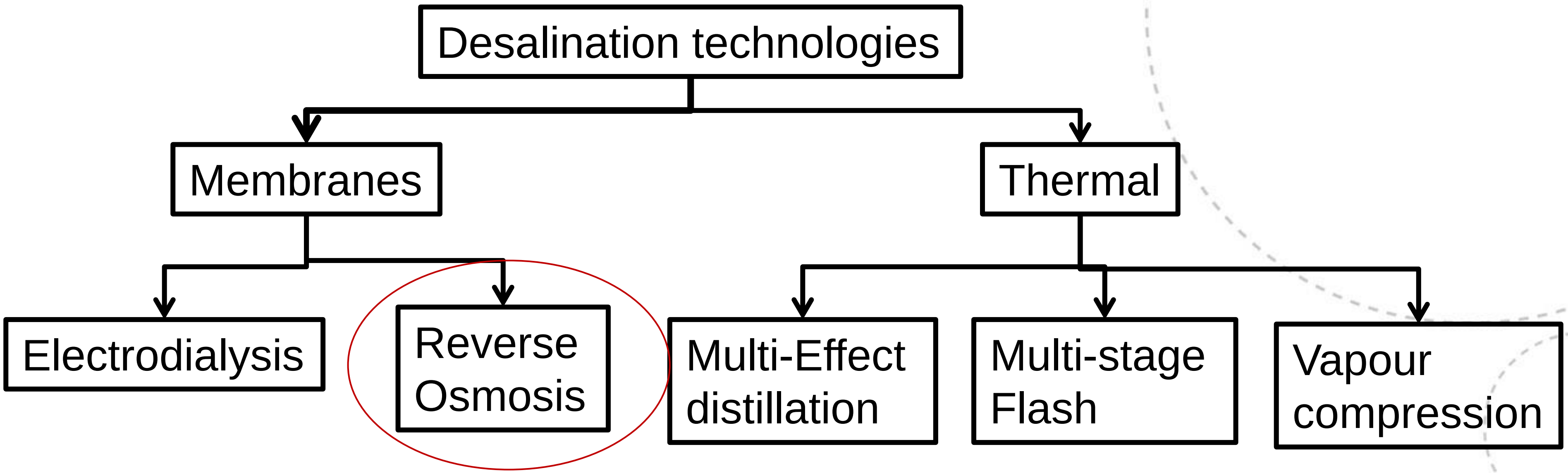
Inputs: Energy + Saline water

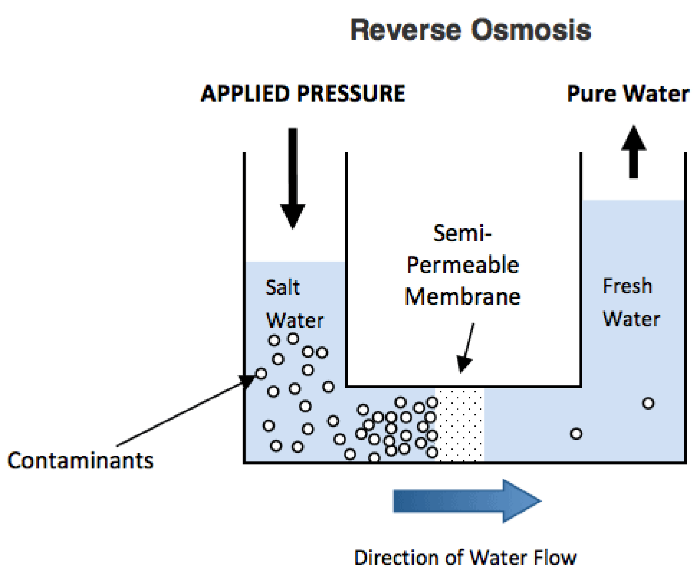
Desalting device

Outputs: Fresh water + Brine (concentrate)



General classification of desalination processes



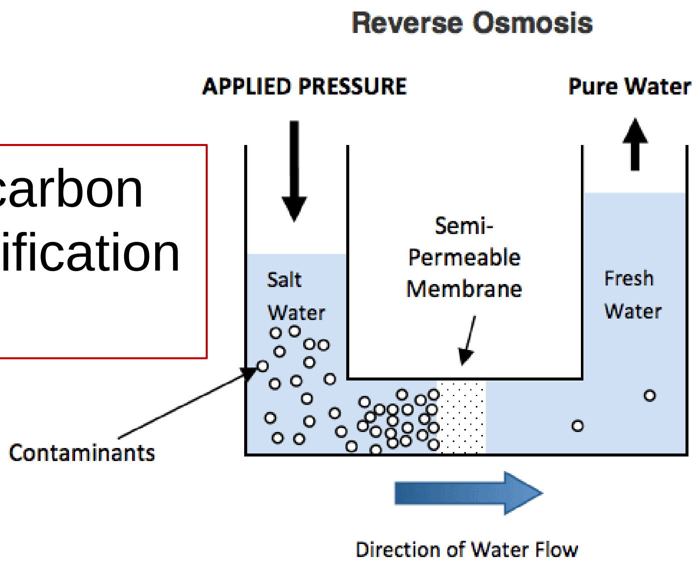


http://www.theseus.fi/xmlui/bitstream/handle/10024/112289/hietanen_jani.pdf?sequence=1

Reverse osmosis membranes

- Need of high pressure input (energy)
- Pollutant precipitation reduces the lifetime of the membrane
- Fouling and pore blocking
- Need of chemical treatments for cleaning and recycling

Investigation of novel membranes such as carbon Nanotubes (CNTs) for cost-effective water purification and desalination



Membrane-based on Vertically Aligned CNTs (VA-CNT) for water desalination

- Growing VA-CNTs
- Preparation of the membrane
- Performances

General classification of Bottom-Up methods

Lecture 21st September

Bottom-Up methods

Chemical methods

Physical methods

- Wet chemistry
- Sol gel
- Colloids
- …..

Chemical Vapour Deposition (CVD) :

- Spray pyrolysis
- ALD
- ….

Physical Vapour Deposition (PVD)

- Sputtering
- PLD
- MBE
- ….

Today's focus: Vapour phase synthesis!

Bottom-up methods

Lecture 21st September

TNN 67-75 pp

Vapour phase synthesis

Spray conversion processing

Atomization of chemical precursors into aerosol droplets that are dispersed in a gas medium

Example:
Flame spray pyrolysis

Chemical Vapour Deposition (CVD)

Gaseous species react or decompose on a hot surface to form a stable solid product

Example:
Plasma Enhanced CVD (PE-CVD)

Physical Vapour Deposition (PVD)

Generation of vapour phase from solid materials (sputtering, lased ablation, evaporation….)

Example:
PLD
Sputtering

Plasma Enhanced Chemical Vapour Deposition (PECVD)

TNN 185-189 pp

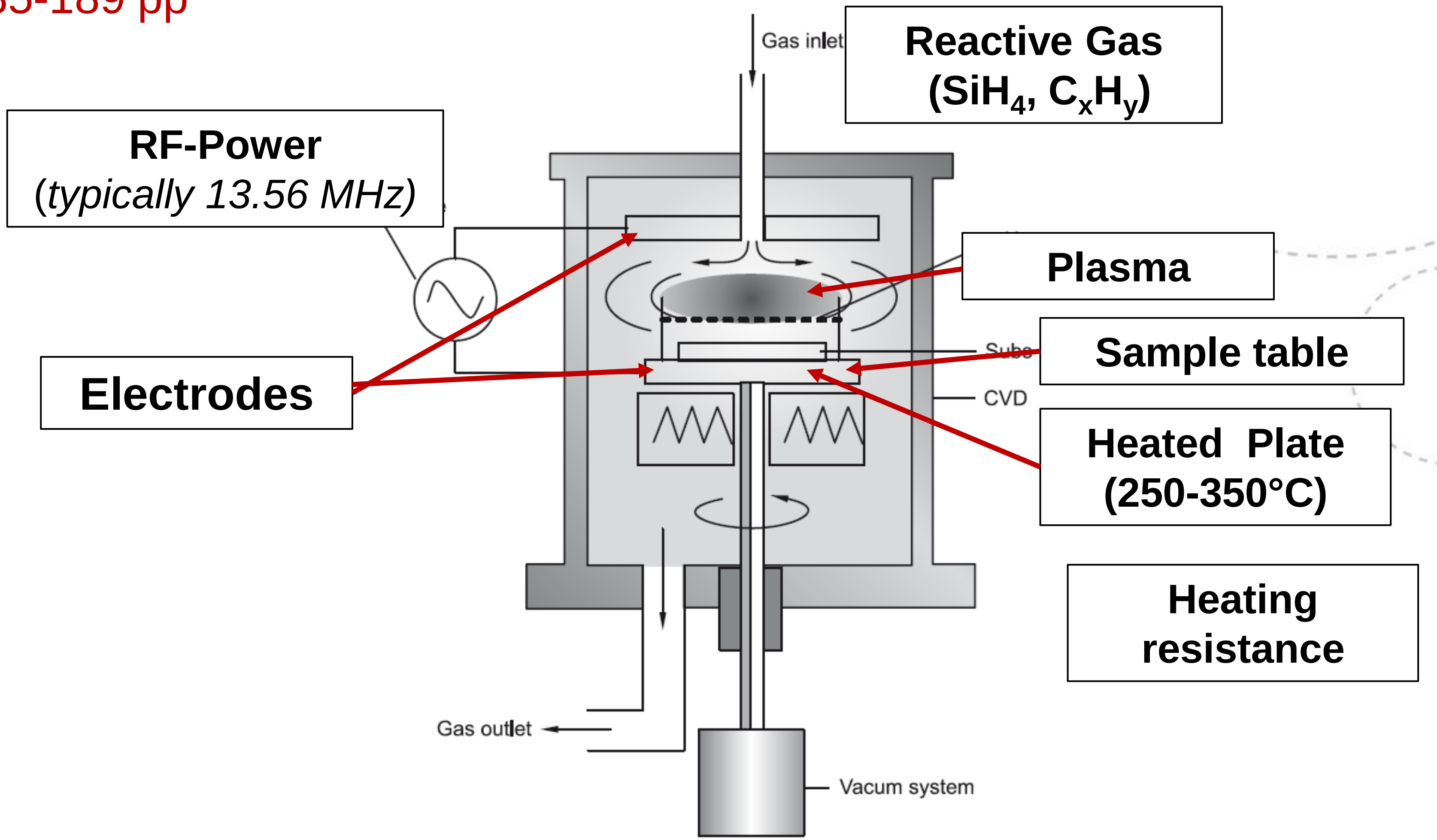


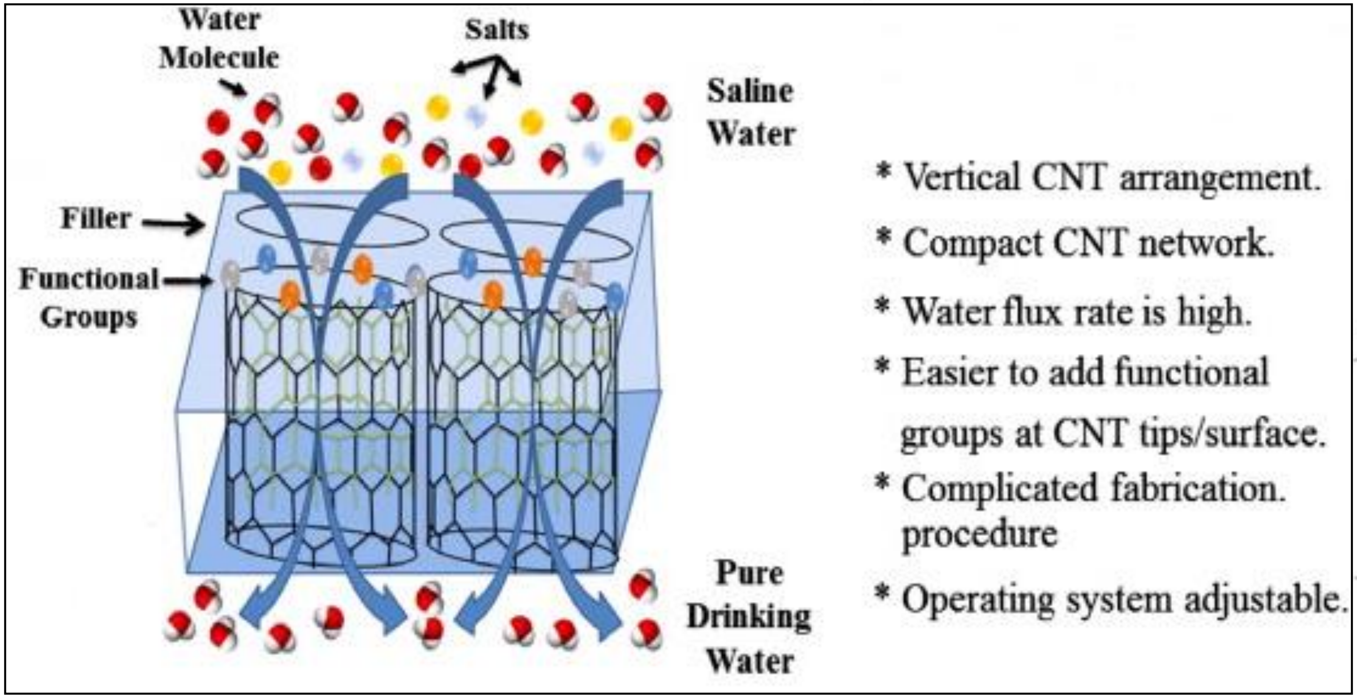
Fig. 6.10 Schematic diagram of a typical plasma CVD apparatus with a parallel plate electrode structure.

SiH_4 = Silane, C_xH_y = Hydrocarbon

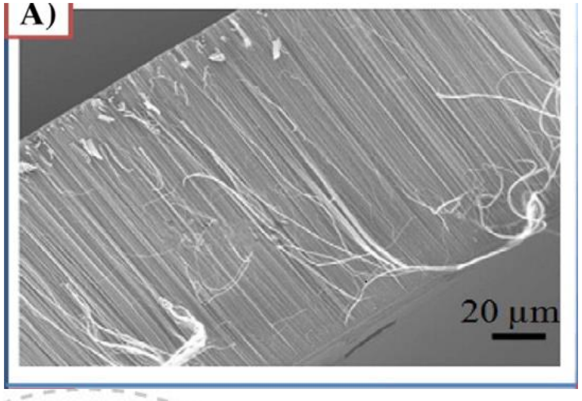
Plasma Enhanced Chemical Vapour Deposition (PECVD)

- PECVD is a process used to deposit thin films from a gas state to a solid state on a substrate.
- In comparison to standard CVD techniques that require 600°C to 800°C, PECVD operates at lower temperatures
- The space between the electrodes is filled with the reacting gases, and a plasma is created between the electrodes.
- The Plasma is generally created by Radio Frequency (RF). (Alternative Current (AC))
- For metallic films, the plasma can be created by Direct Current (DC) discharge between two electrodes
- Operating pressure: 0.13 mbar to 1.59 mbar

Membrane-based on Vertically Aligned CNTs (VA-CNT) for water desalination



Cross sectional SEM image of a CNT membrane

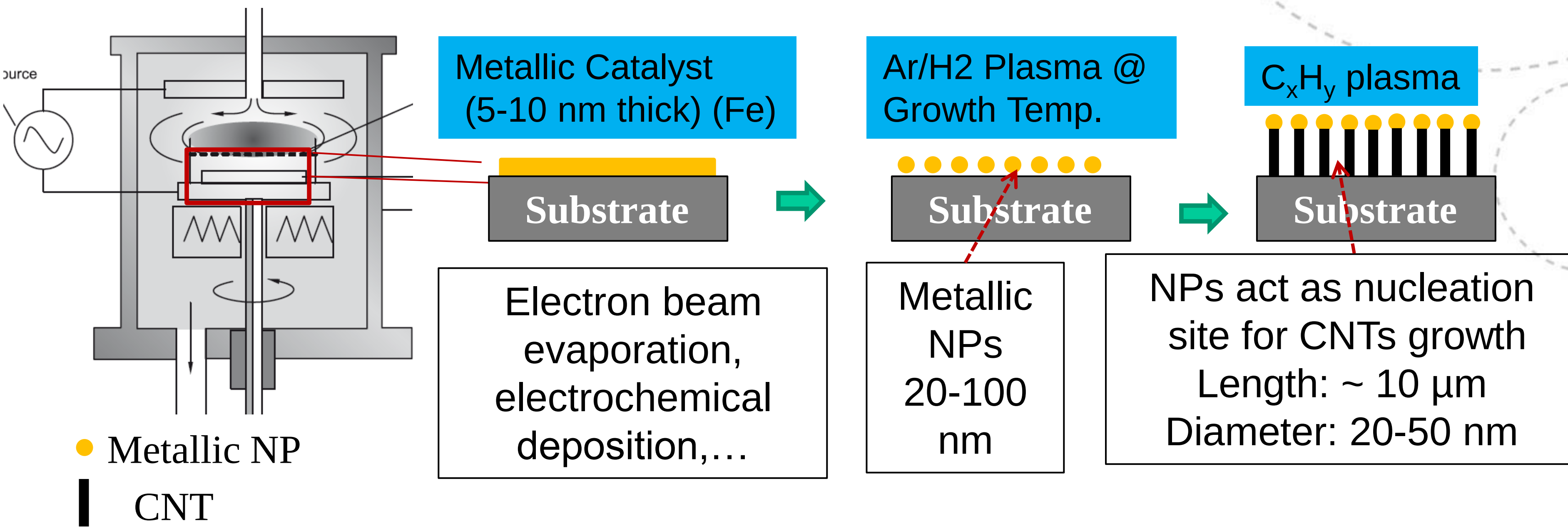


Prototype of CNT membrane showing water molecules movement from salinated water through CNT channel.
Salts are trapped on CNT tips

R. Das et al. / Desalination 336 (2014) 97–109

Nano-engineering of Vertically Aligned Carbon Nanotube (VA-CNT) membrane

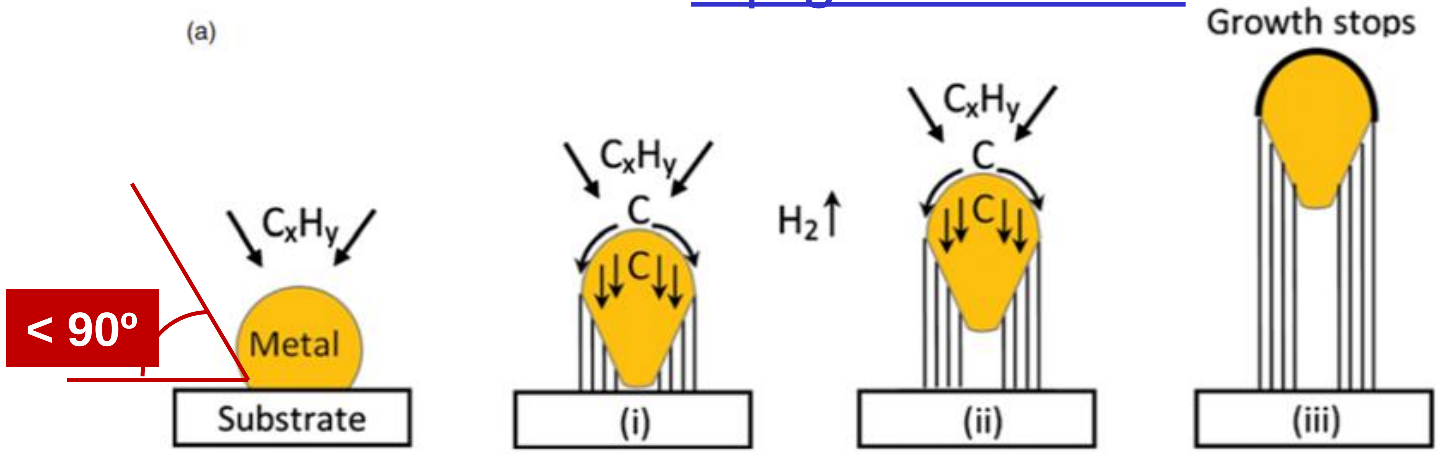
Step 1. Growth of aligned MWCNTs by (PECVD)



- PECVD is an efficient method for the growth of aligned CNTs
- CNT growth directly onto substrate at lower temperatures as compared to T-CVD

Kumar and Ando, J. Nanosci. Nanotechnol. 10, 3739–3758, 2010

Growth mechanism of VA-CNTs: Tip-growth model

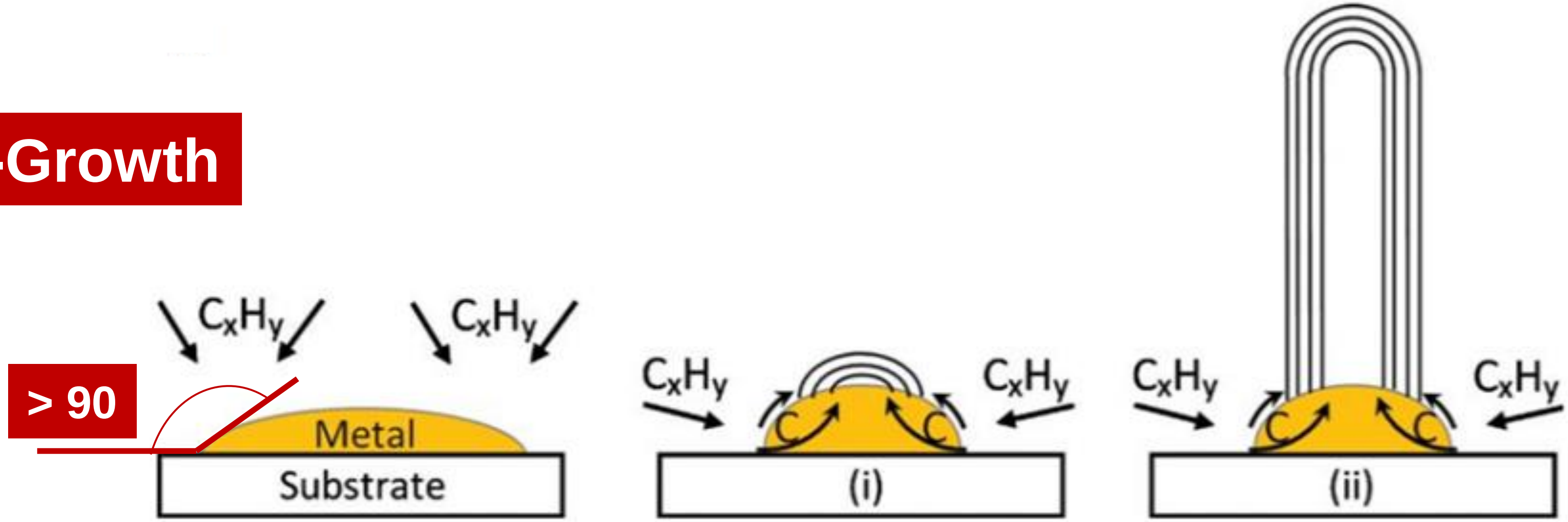


- Weak interaction between the catalyst and the substrate
- Hydrocarbon decomposes on the top surface of the catalyst and diffuses down through the metal particle (supersaturation)
- CNTs precipitate out pushing the whole metal particle off the substrate (i)
- As long as the metal's surface is not covered (*then open for fresh Hydrocarbon decomposition*) , CNT continue to grow (ii)
- Once the metal is fully covered with excess carbon, the CNT growth is stopped

J. Nanosci. Nanotechnol. 10, 3739–3758, ***2010***

Growth mechanism of VA-CNTs: Base-growth model

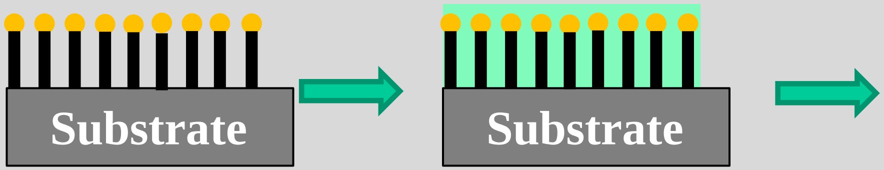
Base-Growth



- Strong interaction between the metallic particle (catalyst) and the substrate
- Hydrocarbon decomposes on the top surface of the catalyst and diffuses down through the metal particle
- CNTs precipitation fails to push the metal particle off the substrate (i)
- Carbon crystallizes out as a hemispherical dome, then extends up in the form of cylinder (i -ii)
- The CNTs continue growing with the catalyst particle rooted on its base

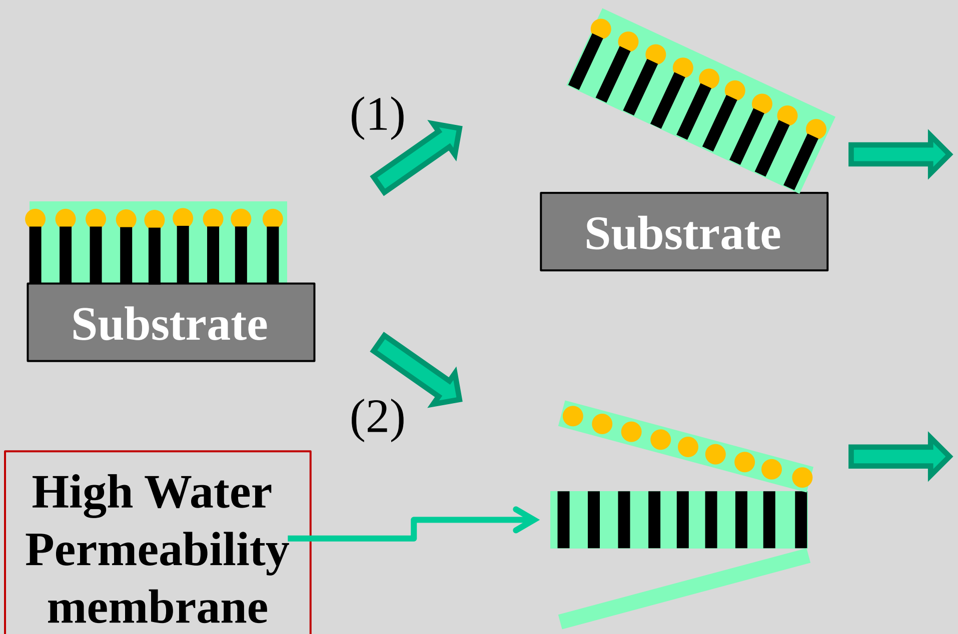
J. Nanosci. Nanotechnol. 10, 3739–3758, **2010**

Step 2. Filling the voids of nanotube with impermeable material



Example: SiNx, Epoxy, Polystyrene,…

Step 3. Reactive ion etching (RIE) and/or chemical etching



(1) To separate the composite film from the substrate

(2) To remove catalysts and excess of the matrix and to open CNT tips

High Water Permeability membrane

● Metallic NP, ▌CNT, ▬ Impermeable material

E. V. Hooijdonk et al. Beilstein J. Nanotechnol. **2013,** *4,* 129–152

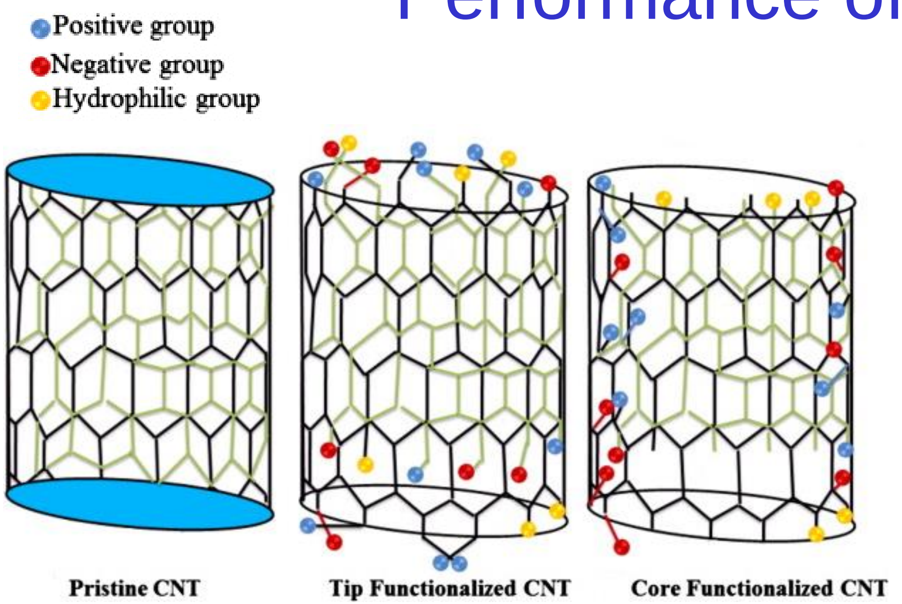
Performance of CNT membranes

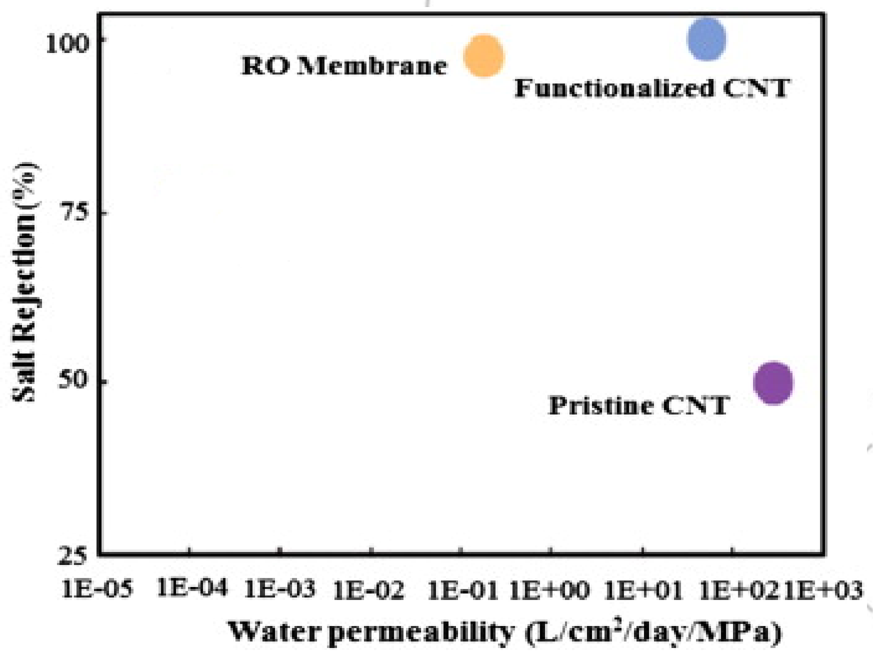
Feature	CNT membrane	Reverse Osmosis RO
Thickness (µm)	2–6	~0.1–0.2
Water permeability ($mPa^{-1} s^{-1}$)	$\sim 7 \times 10^{-7}$	$\sim 3 \times 10^{-12}$
Solute rejection ability	Good	Good
Self-cleaning capability	Capable with or without functionalization.	Only with functionalization.
Tunable selectivity	Mixed matrix only	Mixed matrix only
Membrane fouling	No	Yes
Operating pressure (barr)	Negligible	30–60

- ✓ Higher water permeability
- ✓ Self cleaning capability
- ✓ No membrane fouling
- ✓ Negligible operating pressure

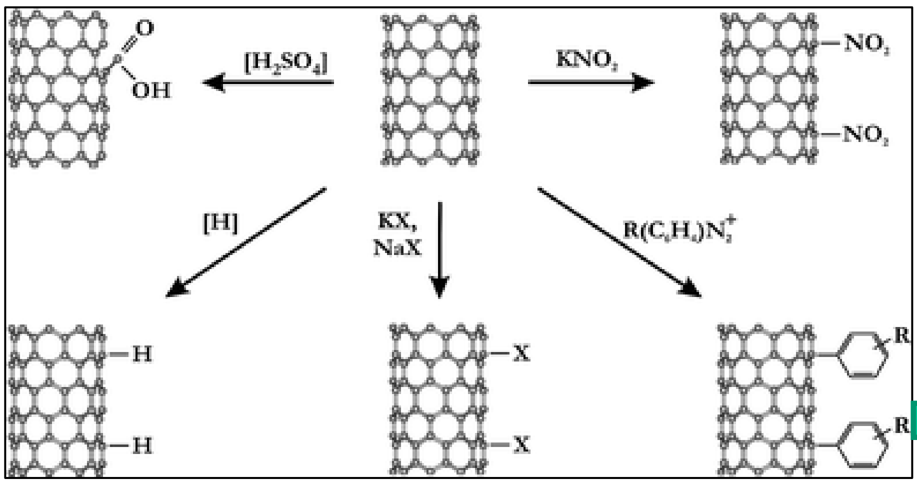
Das et al. Desalination 336 (2014) 97–109

Performance of CNT membranes





Performance of CNTs and RO membrane



Examples of methods of CNT surface Functionalization [1].

[1] K. Balasubramanian J. Mater. Chem., 2008,18, 3071-3083
M.M. Pendergast et al. Energy Environ. Sci. 4 (6) (2011), 1946-1971

Advantages of CNTs membrane-based

- ❖ Aligned CNT serve as robust pores in membranes for water desalination

- ❖ The hollow CNT structure provides frictionless transport of water molecules, allowing high fluxing separation technique

- ❖ Appropriate pore diameters provide energy barriers at the channel entries, rejecting salt ions, and permitting water passing

- ❖ Intrinsic properties of CNT: antifouling, self cleaning

R. Das et al. / Desalination 336 (2014) 97–109

Next lecture