



Nucleation and growth mechanisms of multi-walled carbon nanotubes, application in material science

Martine Mayne-L'Hermite

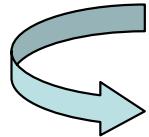
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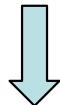
1. Context and motivation
2. Synthesis of aligned carbon nanotubes by aerosol-assisted CCVD
3. Characteristics of nanotubes
4. Growth mechanisms
5. Examples of applications : membranes and nanofluids
6. Summary

Context and motivations

Strong interest of carbon nanotubes (CNTs) in nanotechnology



CNT characteristics have to be adjusted to each application



Important to control CNT growth : quantity, quality, arrangement



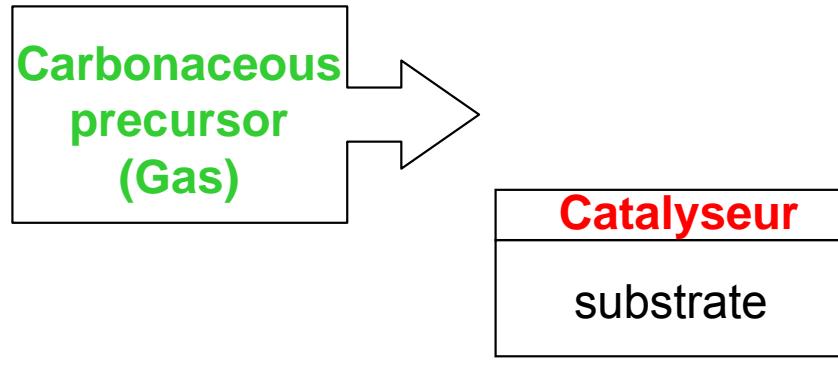
Among synthesis process :

Catalytic Chemical Vapour Deposition

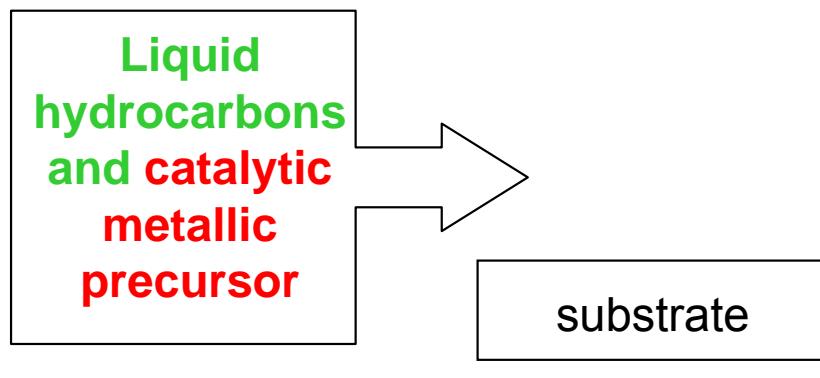
- versatile
- low cost process
- easy to scale up

CCVD methods

Principle : catalytic decomposition of gaseous or liquid hydrocarbons



- Supported catalysts
- Feeding by the hydrocarbon source only



- Continuous feeding with hydrocarbon source and catalyst precursor

*Andrews et al.. Chem. Phys. Lett. 1999,
Kamalakaran et al. Appl. Phys. Lett. 2000,
Mayne et al. Chem Phys Lett, 2001*

Different ways to feed the reactor with the solution

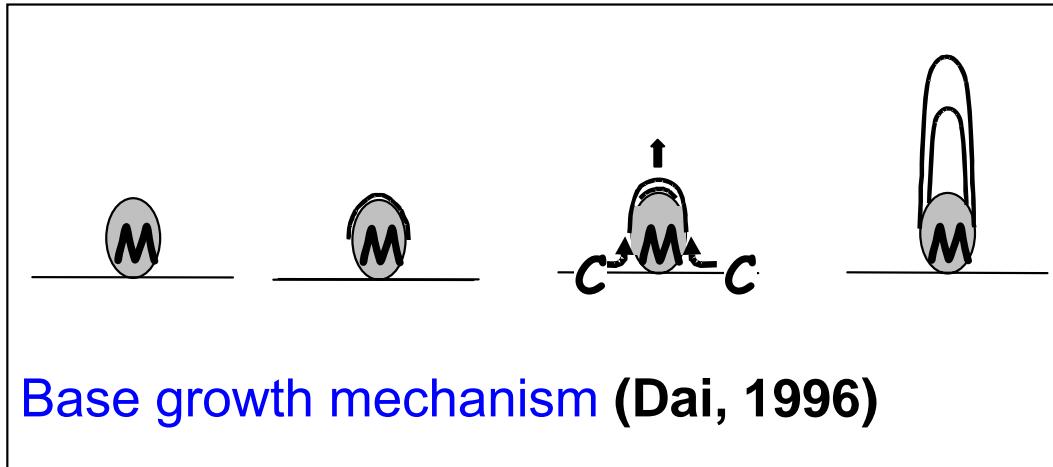
→ **Aerosol assisted-CCVD developed at Laboratoire Francis Perrin**

M. Mayne-L'Hermite et al., Proceeding Chemical Vapor Deposition-XVI and EUROCVD-14, 2003

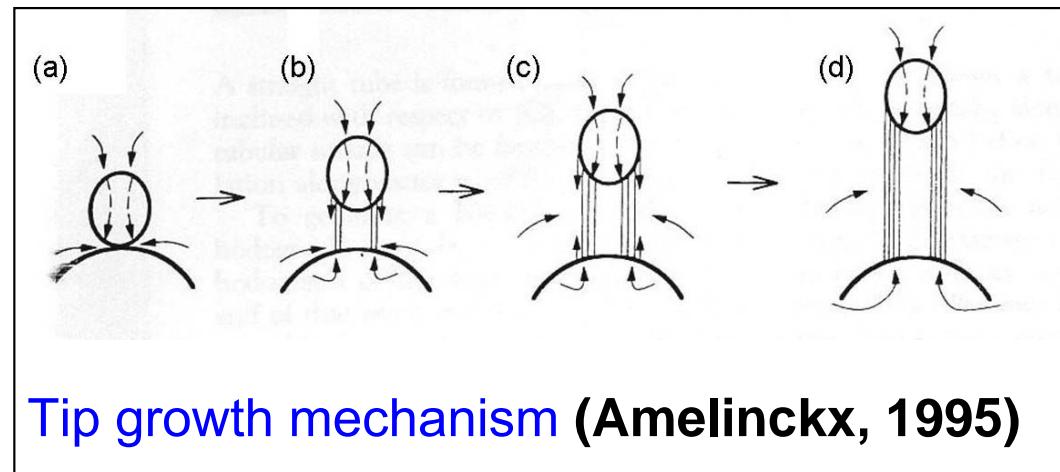
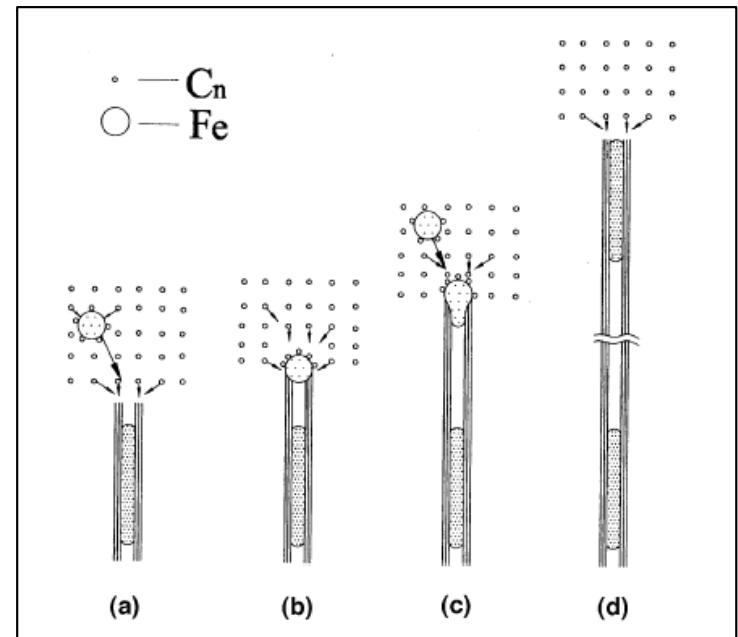
Different growth mechanisms

→ Location of the particle on the nanotube

- Supported catalyst



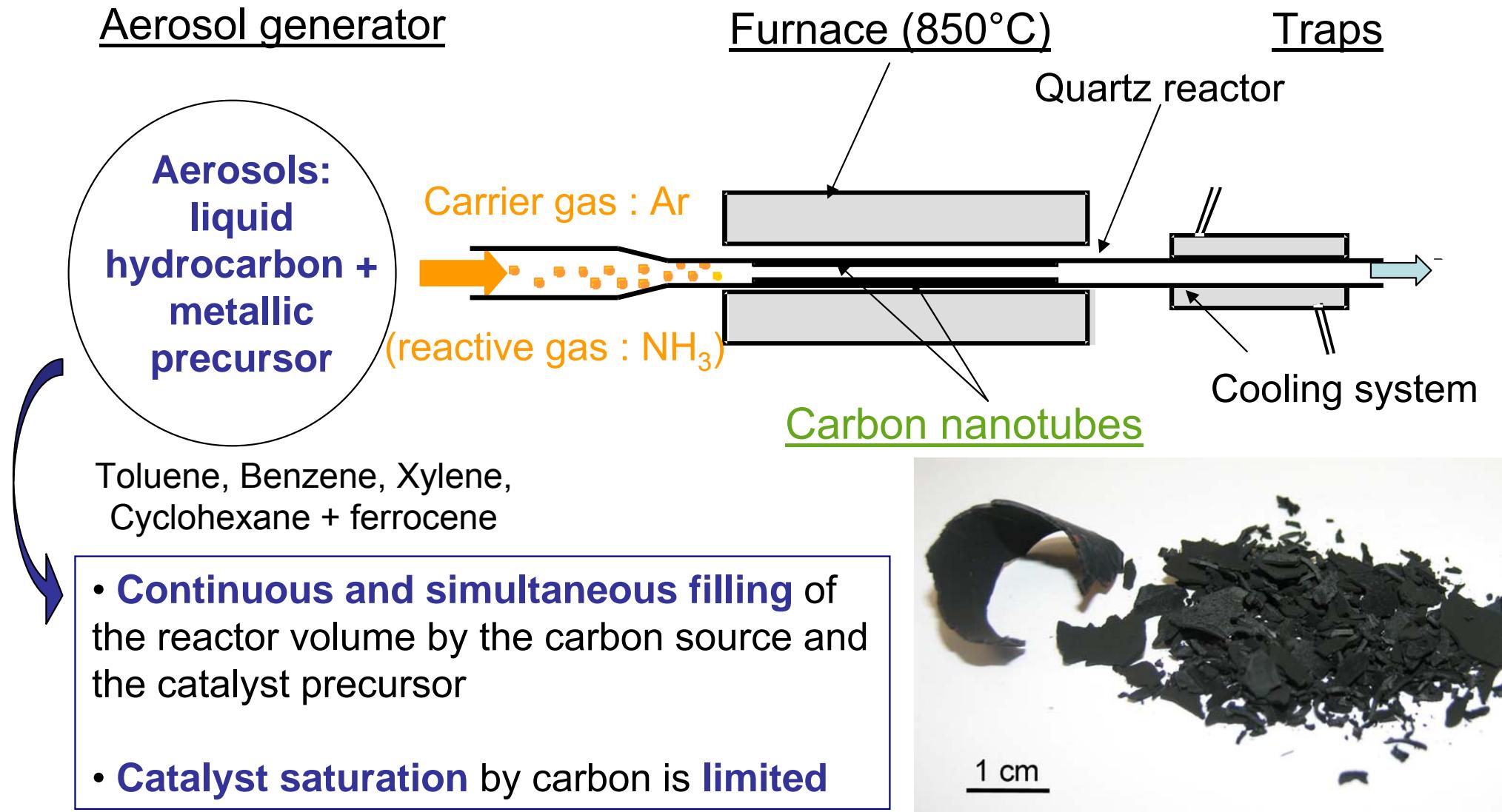
- Continuous feeding with catalyst



Proposed in the case of
catalyst continuous feeding
(Zhang, 2002)

Synthesis of aligned CNTs by aerosol-assisted CCVD

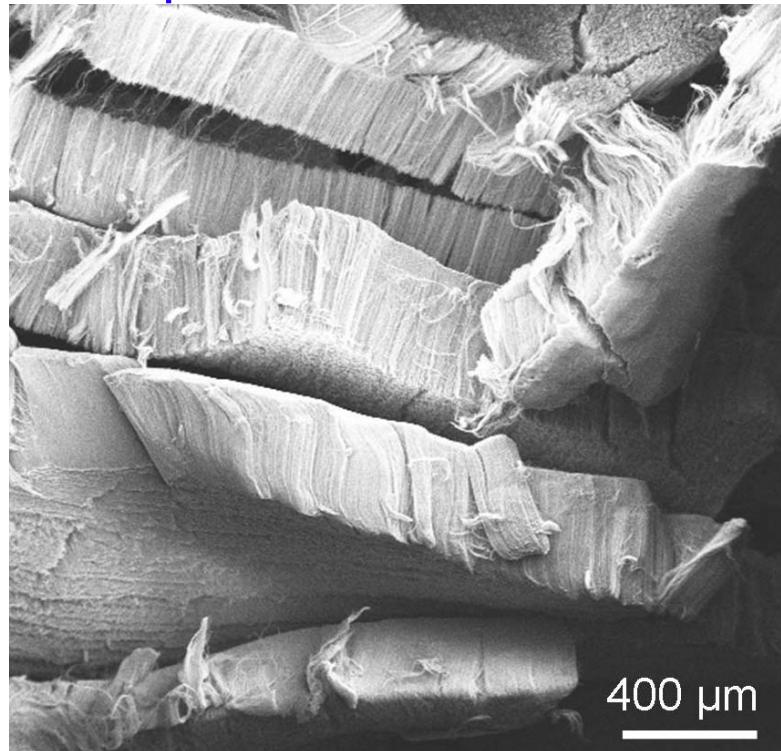
Catalytic decomposition of liquid hydrocarbon-based aerosols



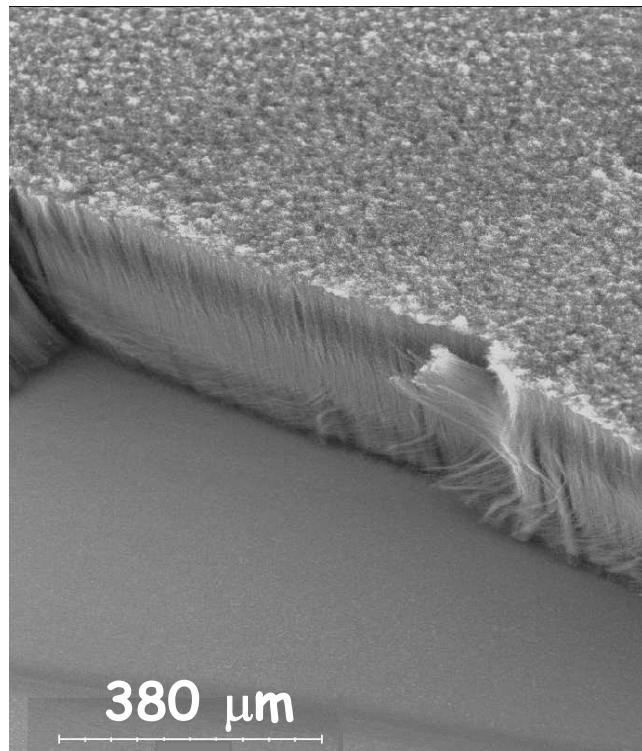
M. Mayne et al, Chem. Phys. Lett, 2001, M. Pinault et al, Diam. Rel. Mat. 2004

Morphology and length of aligned carbon nanotube carpets

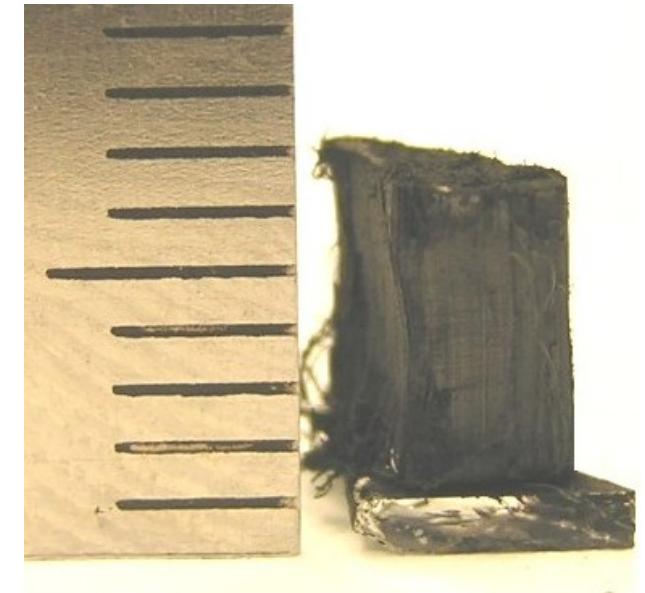
- On quartz reactor walls



- On Si substrate



- On quartz substrate



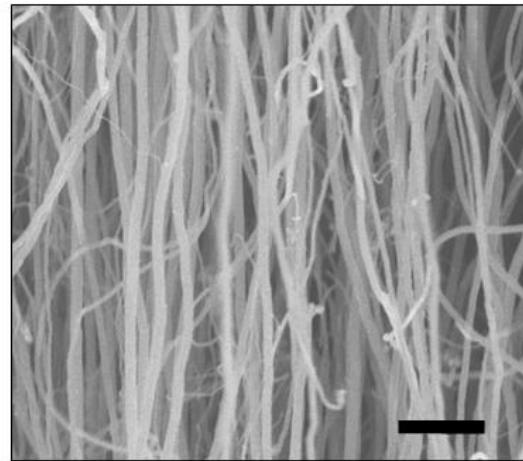
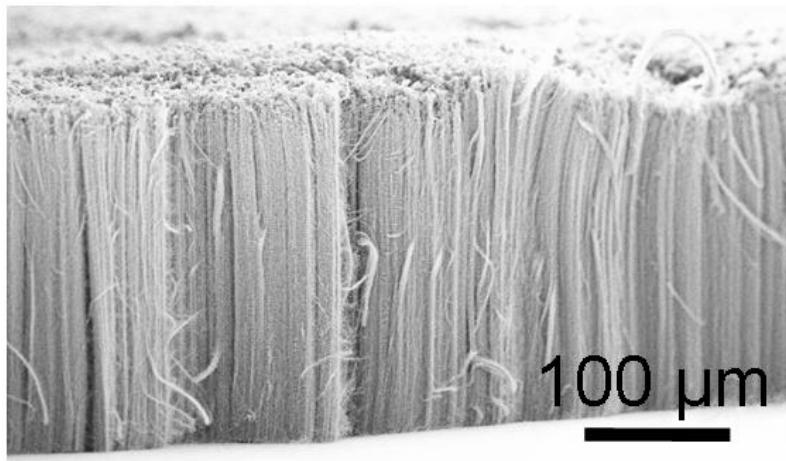
Thesis M. Pinault, 2005

- **High purity:** almost no carbonaceous by-products
- High catalytic yield, **high growth rate** (30 to 60 $\mu\text{m}/\text{min}$)
- **Very long** nanotubes : 20 μm up to 6 mm
- Very good alignment degree ($\pm 5.5^\circ$)
= main advantages of the continuous feeding

M. Pinault et al., Nano Letters, 2005 ; V. Pichot et al., Appl. Phys. Lett. 2004

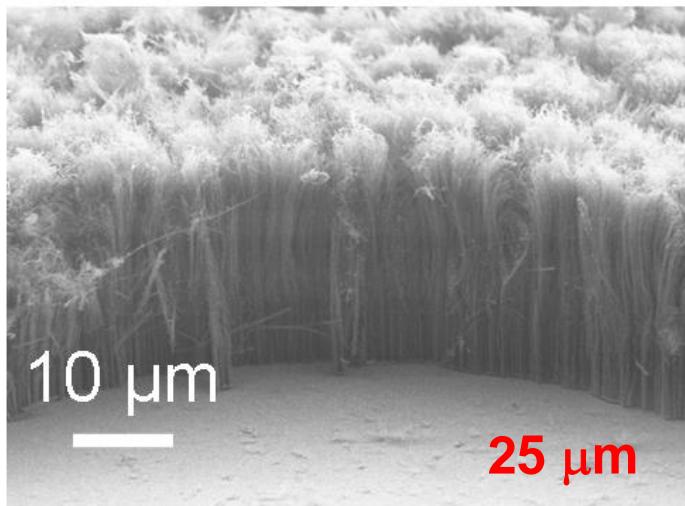
Insertion of nitrogen in aligned carbon nanotube carpets

Carbon nanotubes : 250 μm thick

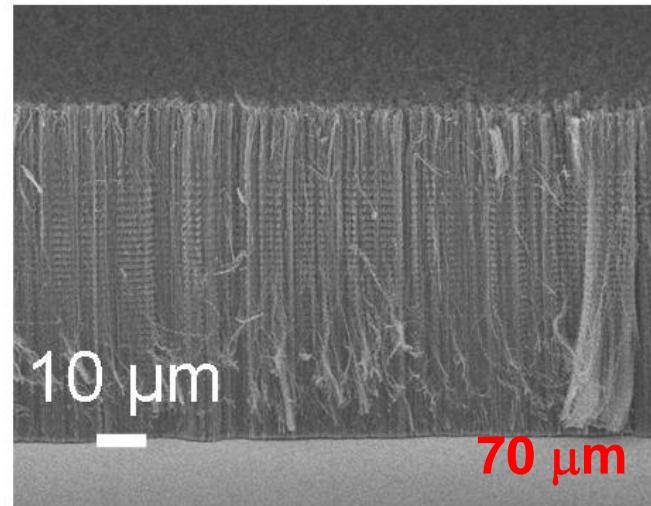


CN nanotubes

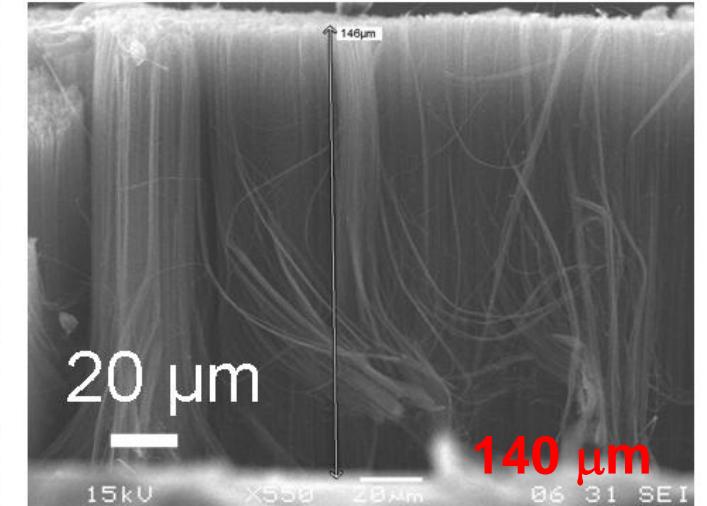
NH₃ 10%



20%

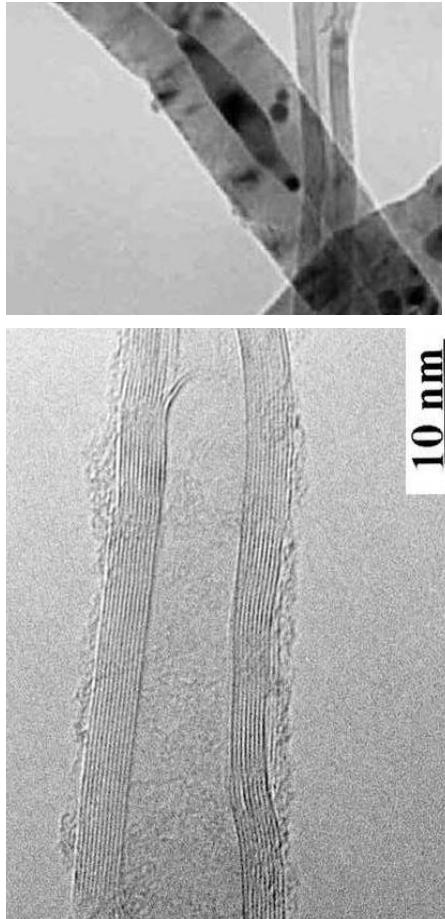
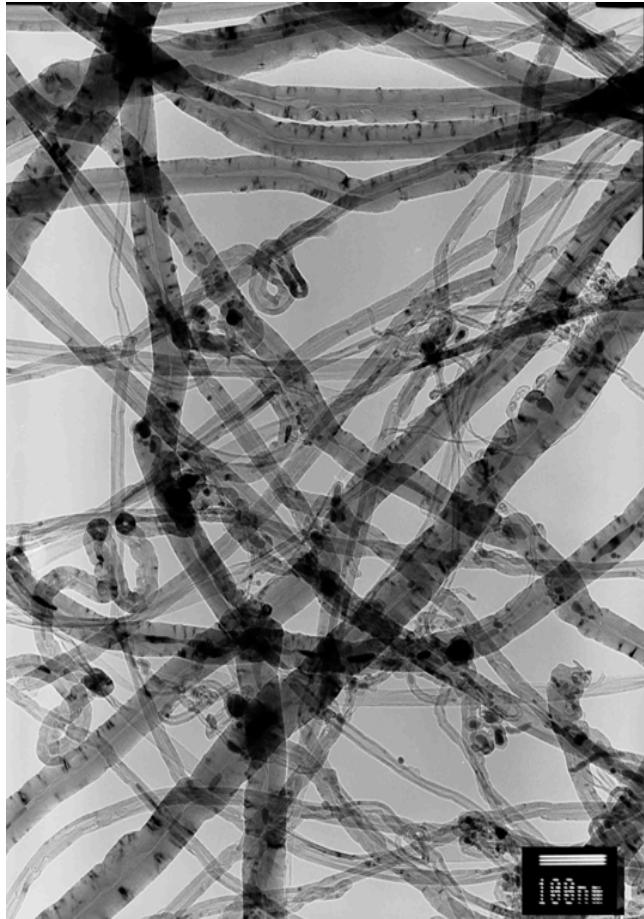


35%

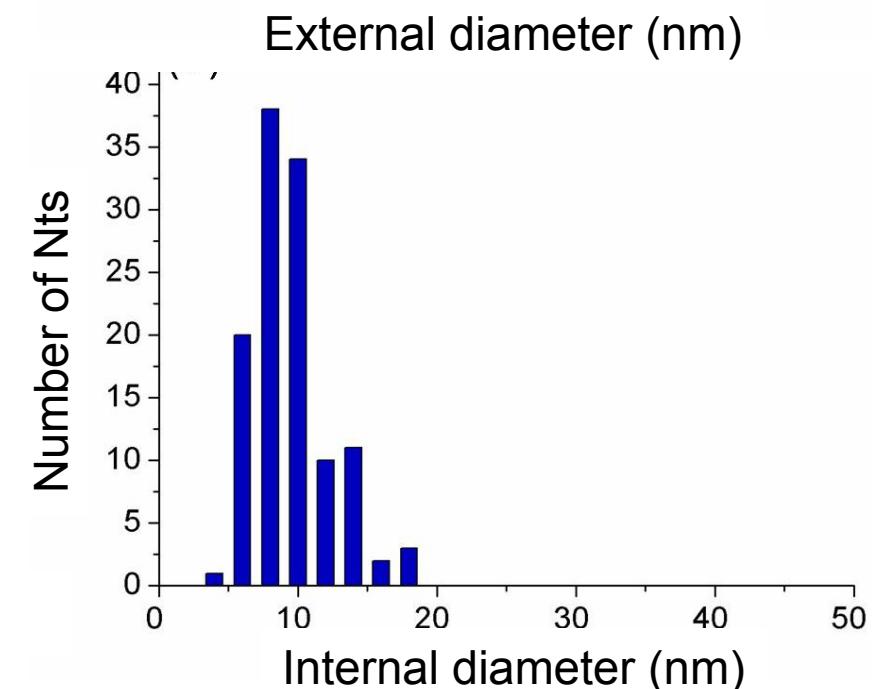
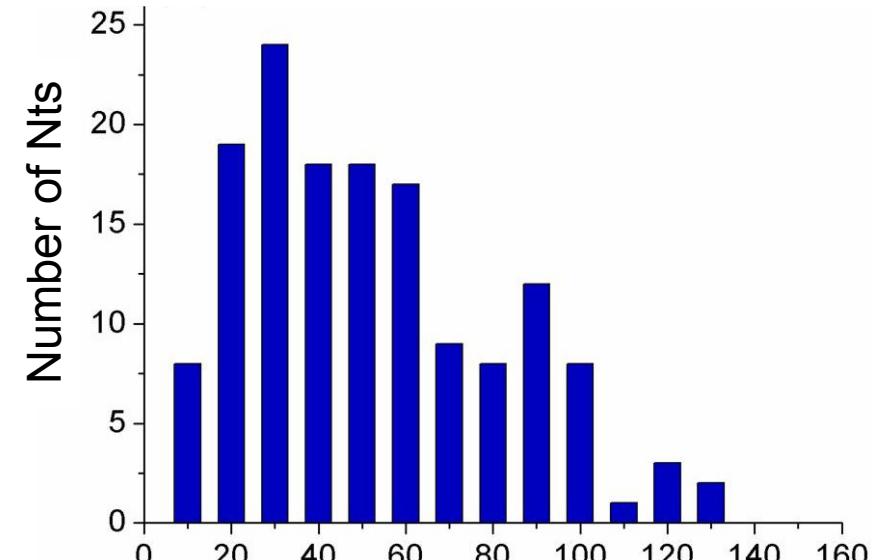


Diameters and structure of CNTs

TEM and HRTEM analysis

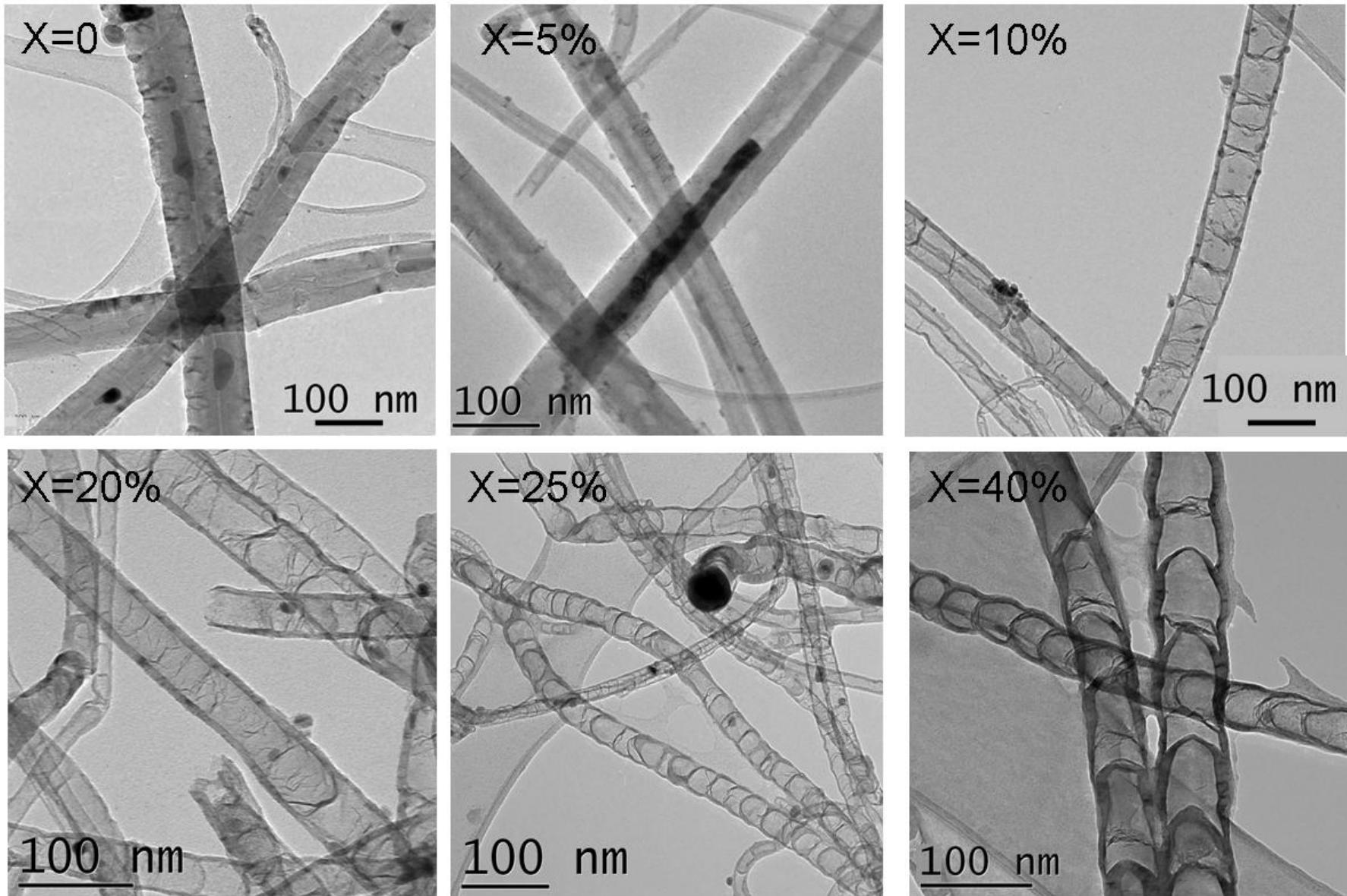


- Multi-Walled carbon nanotubes
- Large distribution of external diameters
- Short encapsulated iron-based nanowires
- Iron content about 3 wt %



Diameters and structure of CN nanotubes

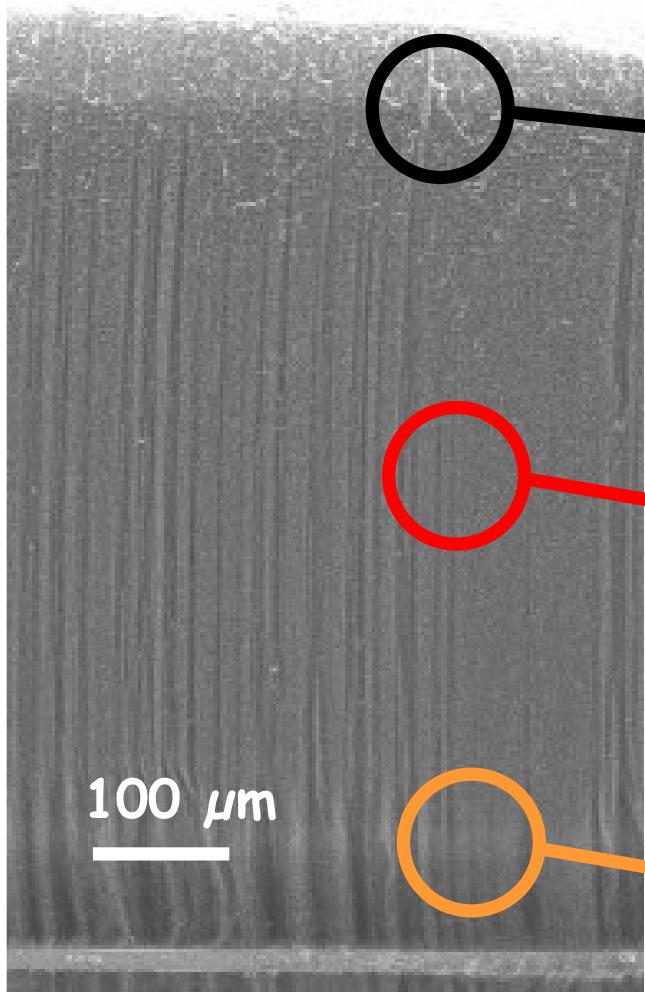
CN nanotubes (toluène/ferrocène carried by an Ar flow + NH₃ (X%))



Central core with compartments in CN nanotubes

Identification of crystalline Fe-based phases

X-Ray diffraction analysis along nanotube carpet



- $\text{Fe}\gamma$ oriented nanowires
- $\text{Fe}\alpha$ and Fe_3C

- Mainly $\text{Fe}\gamma$ nanowires oriented
- $\text{Fe}\alpha$ and Fe_3C minor phase

- Fe_3O_4 or $\gamma\text{-Fe}_2\text{O}_3$ (isostructural)

→ Different iron-based phases all along nanotube carpet

Question of growth mechanisms

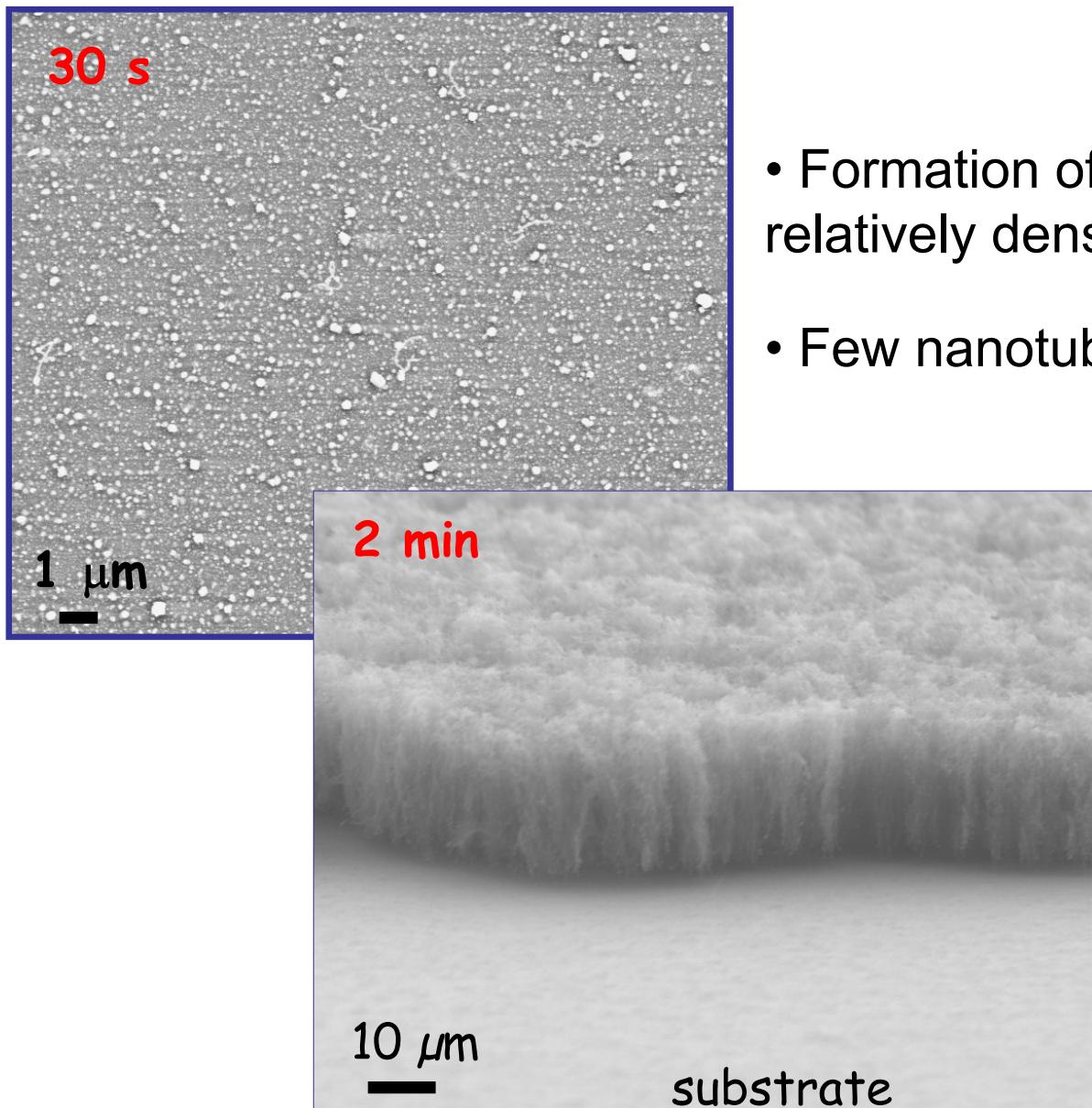
Identification of the different steps of nanotube growth

Two complementary approaches

- Study of the early stages of nanotube growth
 - 1) Development of synthesis during short time
 - 2) Analysis of products obtained
- Study of the chronology of nanotube growth
 - 1) Developement of sequential synthesis process
 - 2) Analysis of products obtained

Early stages of nanotube growth

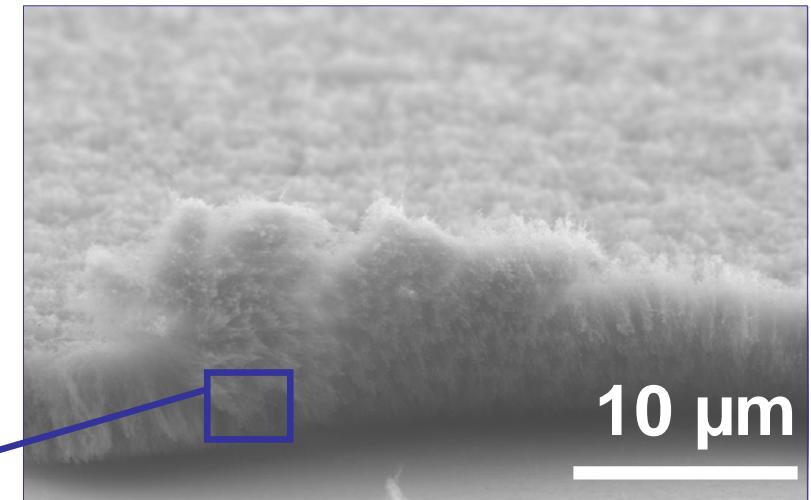
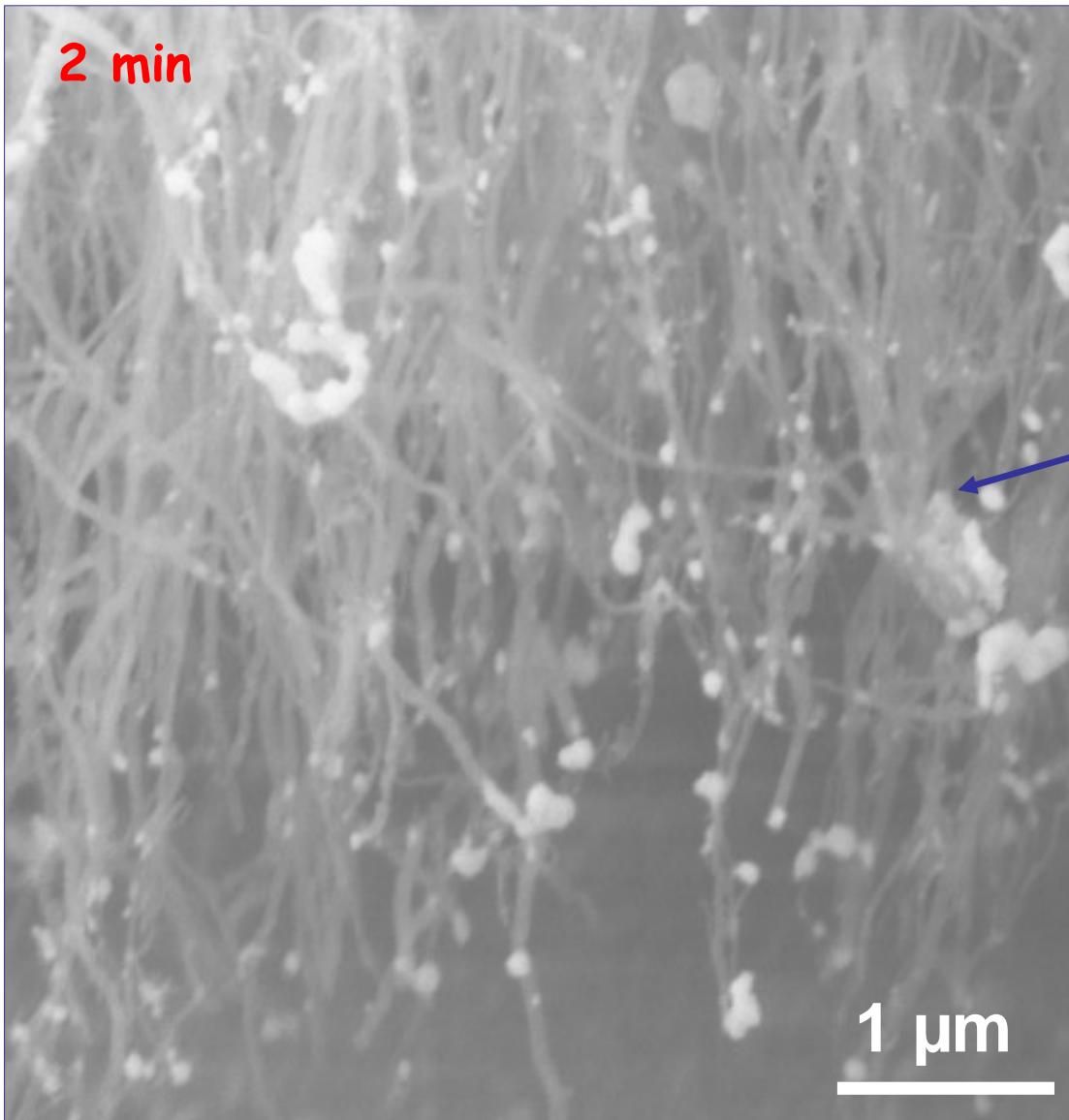
Synthesis parameters : 850°C, toluene + ferrocene 5% on Si substrates



- Formation of **a layer of catalytic particles** relatively dense ($\varnothing = 15 \text{ à } 300 \text{ nm}$)
- Few nanotubes growing
- Increase of the number of growing nanotubes
- Formation of **an assembly of aligned MWNTs (20 μm high)** through steric hindrance
- **Low alignment degree**

Location of catalytic particles

Carpet detached from the substrate



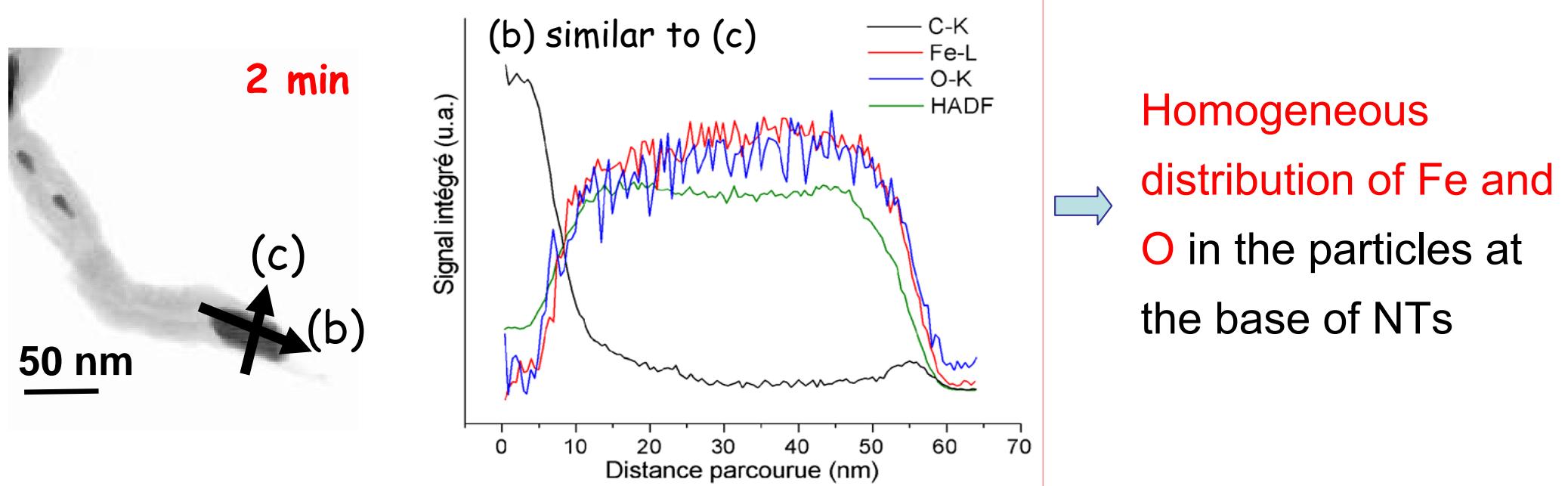
- Catalytic particles anchored at the nanotube base

→ **Base growth mechanism**

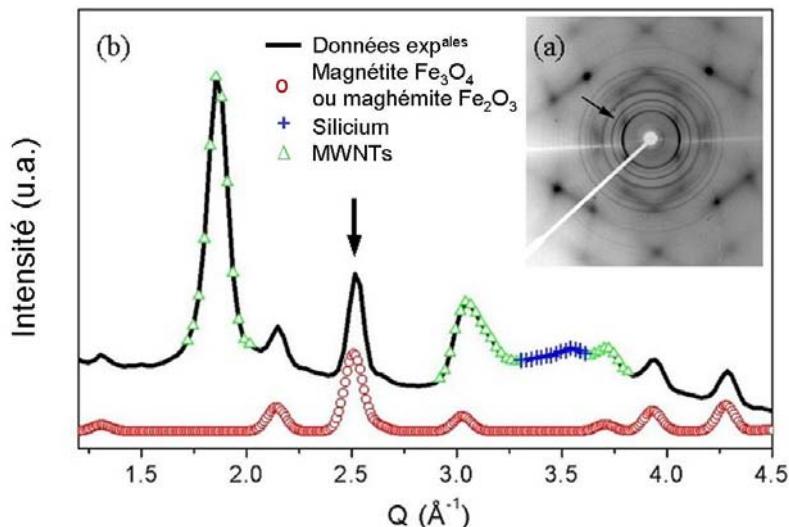
M. Pinault et al., Diamond and related materials 2004; M. Pinault et al., Carbon 2005

Chemical composition and structure of catalytic particles

Electron Energy Loss Spectroscopy (EELS)



X-Ray diffraction analysis

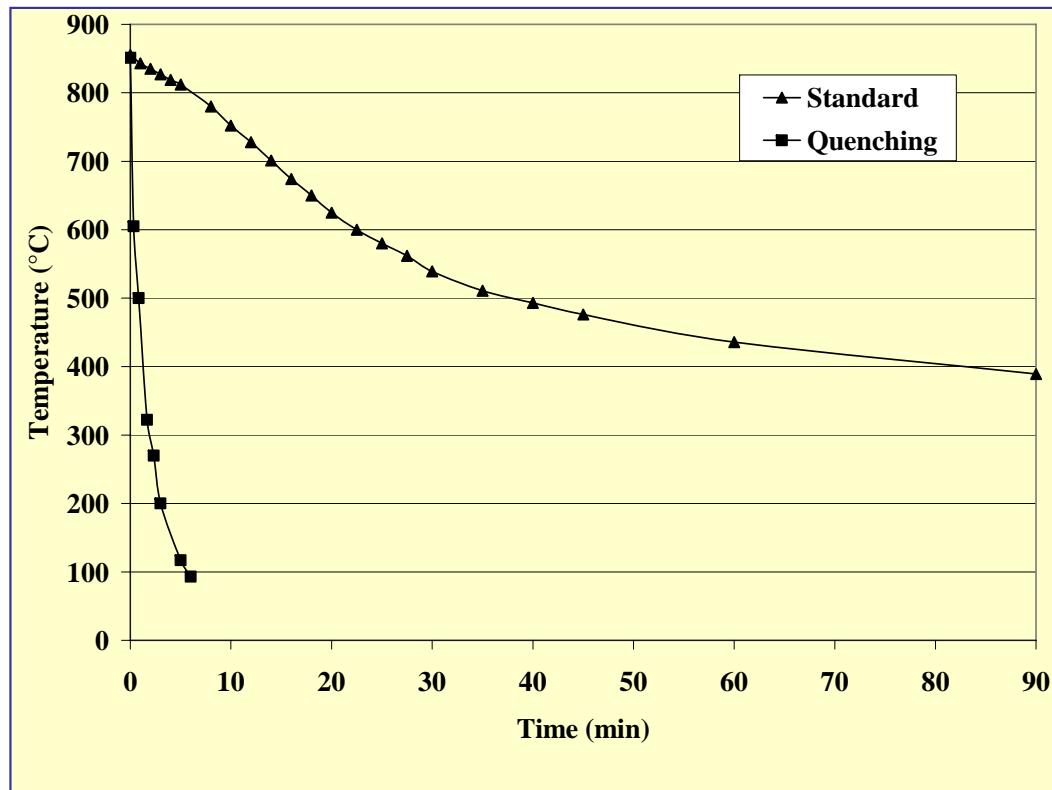


→ Occurrence of Fe₂O₃ or Fe₃O₄ (same cubic structure)

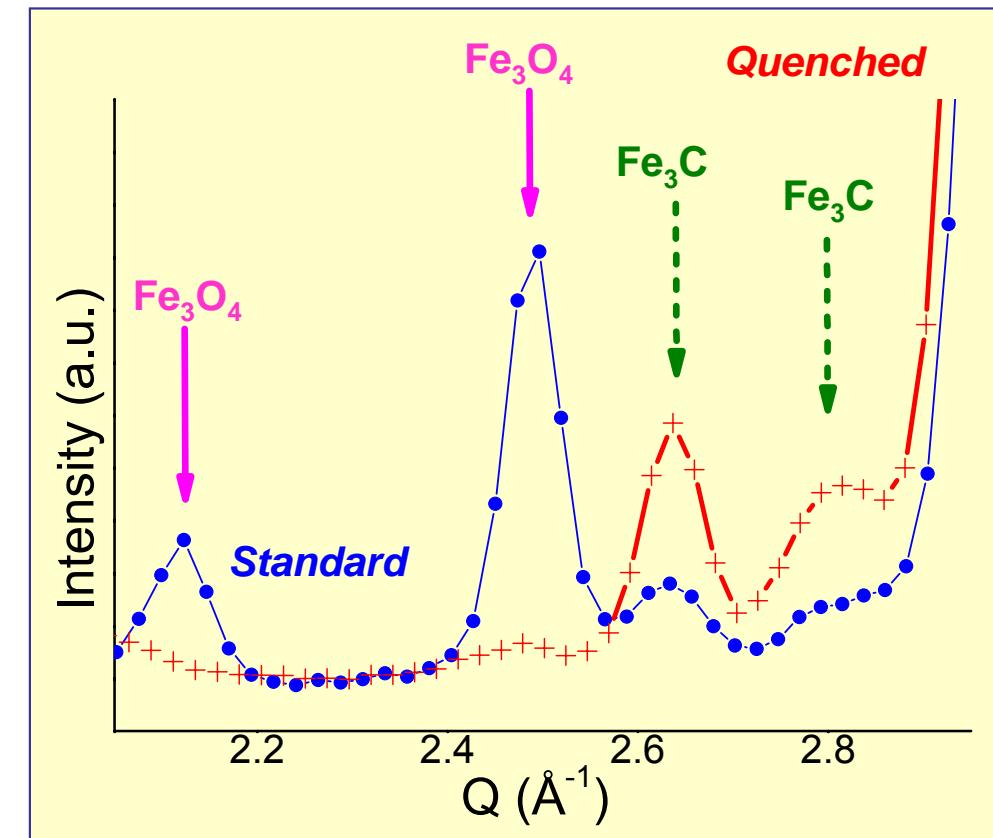
M. Pinault et al., Carbon 2005

Effect of cooling step on structure of catalytic particles

Slow cooling or quenching



X-ray diffraction on the 2 samples



Iron oxide phase disappears in quenched samples
⇒ iron oxide should form during standard cooling

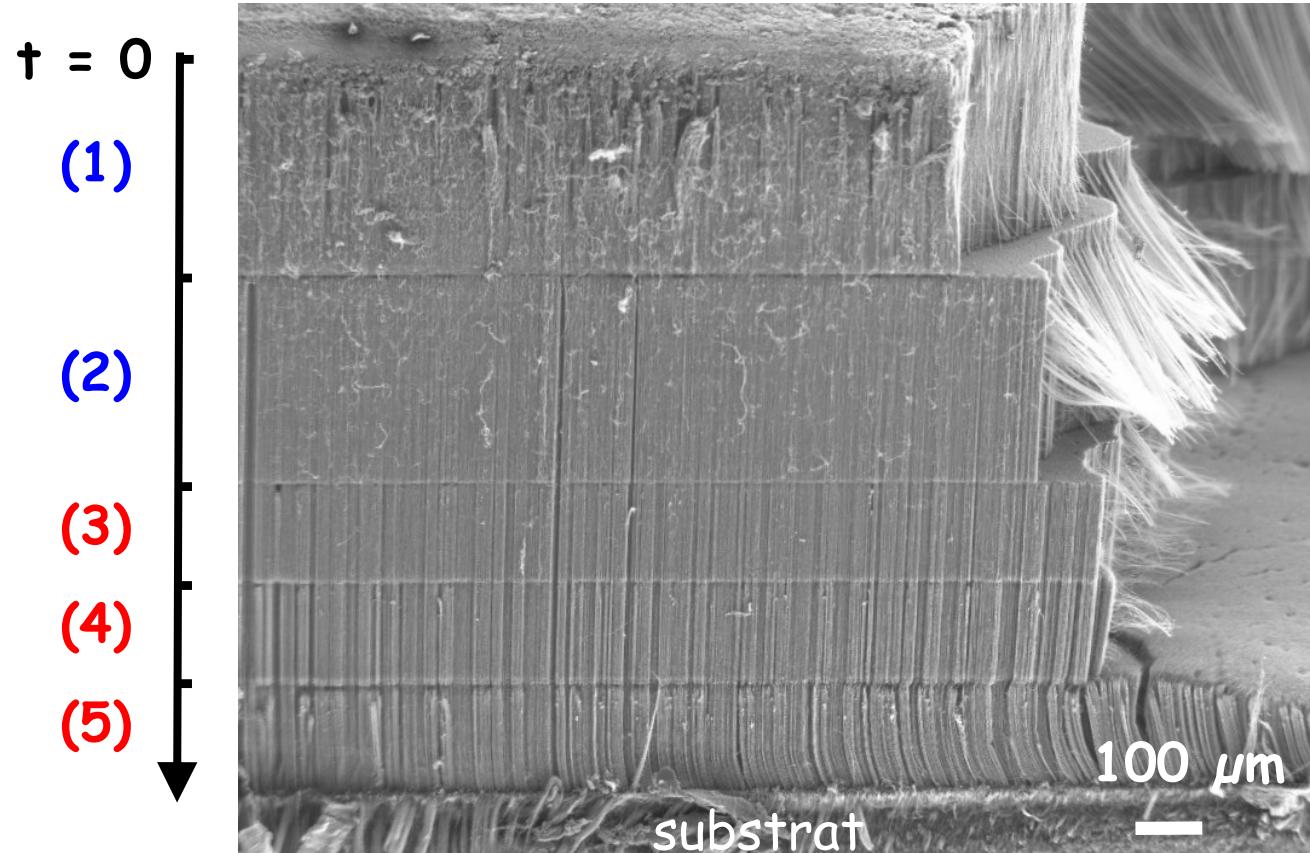
V. Heresanu et al., J. Phys. Chem. C, 2008

Question still open : how is it really during NT growth?
Studies in progress in the framework of a national program

Chronology of nanotube growth : sequential synthesis

| (1) | (2) | (3) | (4) | (5) |
|--------|--------|-------|-------|-------|
| 10 min | 10 min | 5 min | 5 min | 5 min |

Solution : toluene + 5 wt% $FeCp_2$
Temperature : 850°C



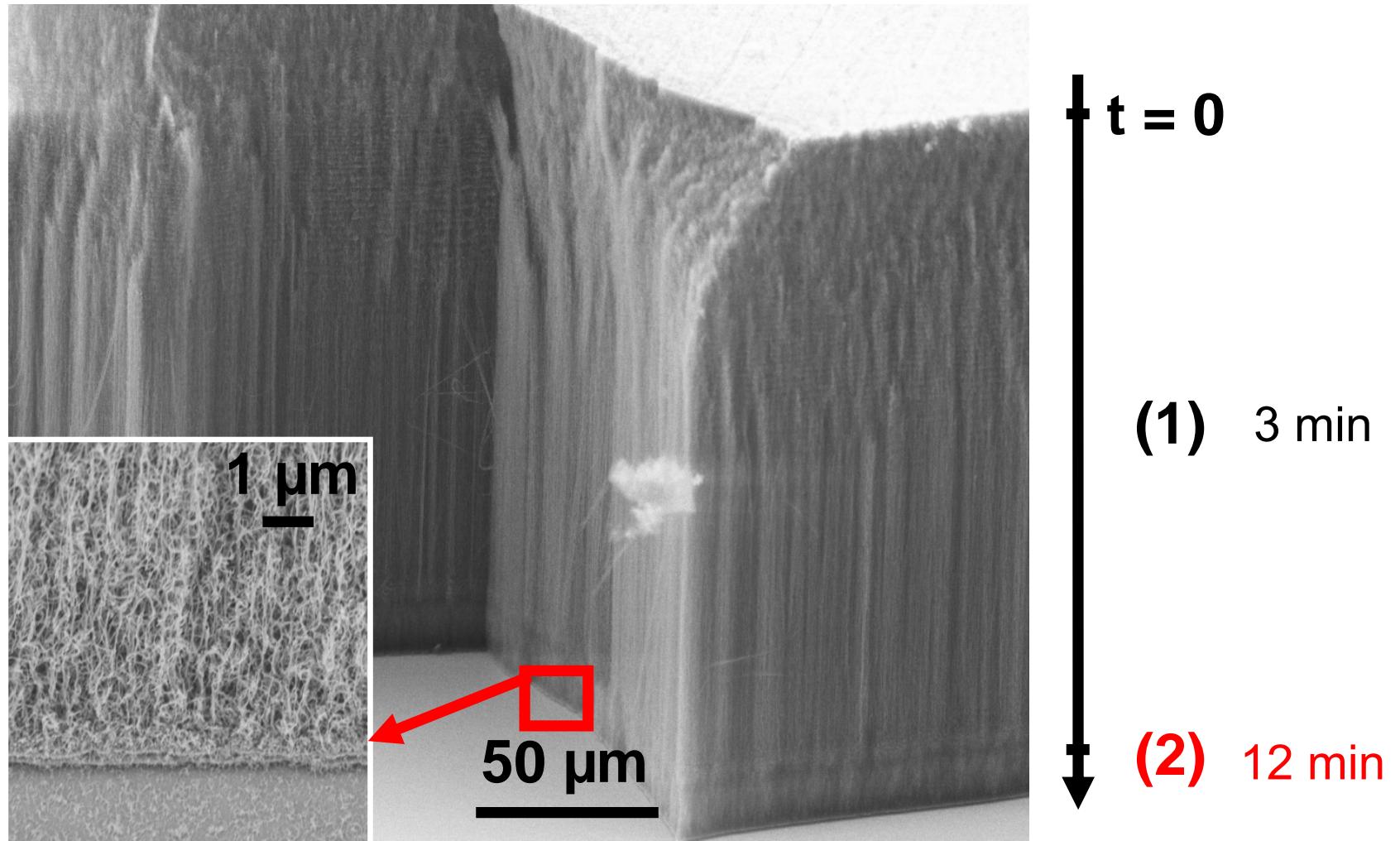
- Growth rate : cte
- Number of layers
= Number injection

- Multi-layered carpet is obtained
- Growth of each new layer on the substrate surface by lifting up the pre-existing layers
→ **base growth mechanism is maintained**

Mathieu Pinault et al., Nano Letters, 2005

Effect of continuous feeding of catalyst precursor

(1) *T+ F 3 min + (2) Toluene only 12 min*

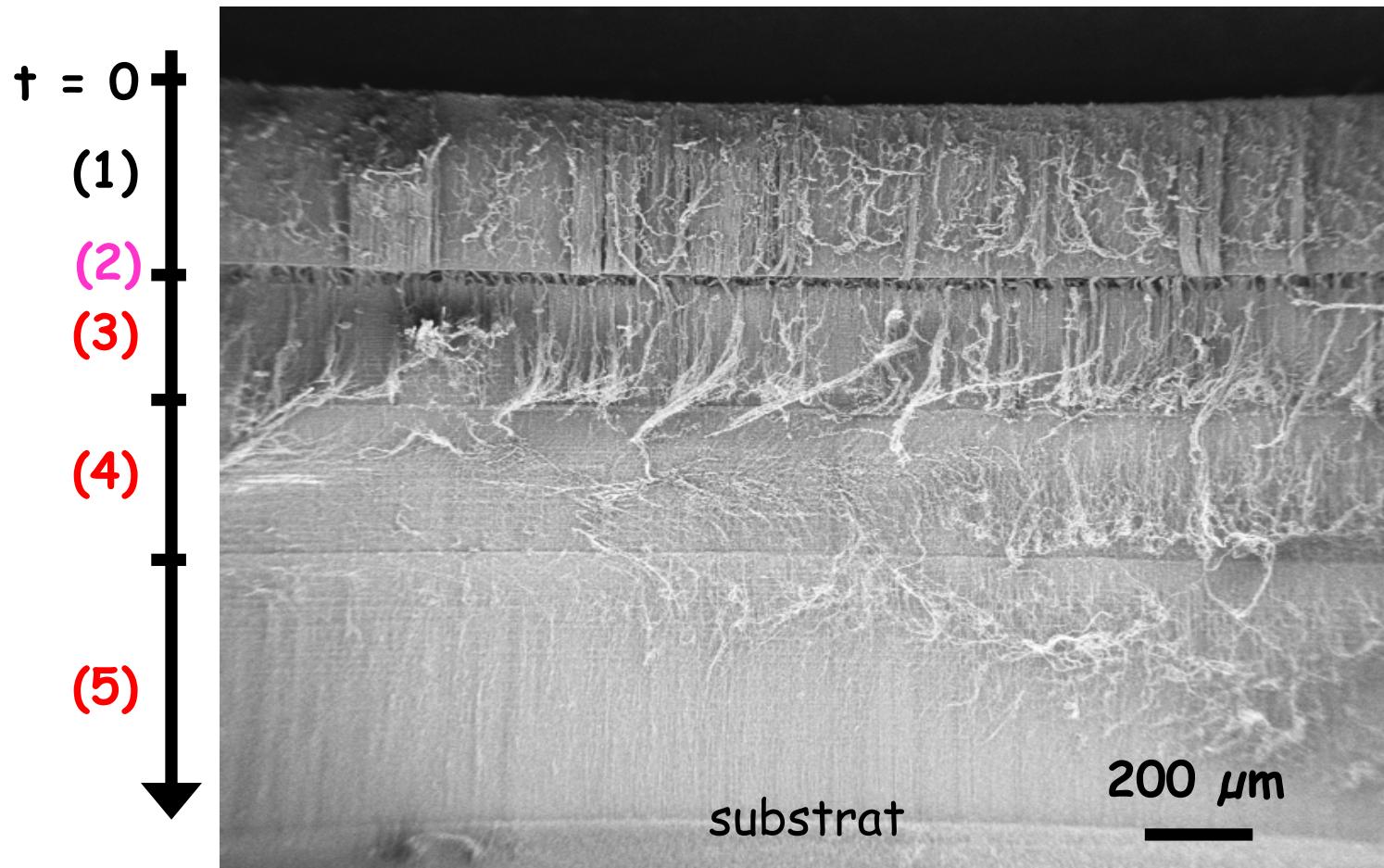


Without catalyst : no nanotube growth

→ Continuous feeding of catalyst is ensuring nanotube growth

Does nanotube growth re-start?

(1) $T+F$ pdt 5 min, (2) T seul + Re-injection $T+F$ pdt (3) 5 min + (4) 5 min + (5) 10 min

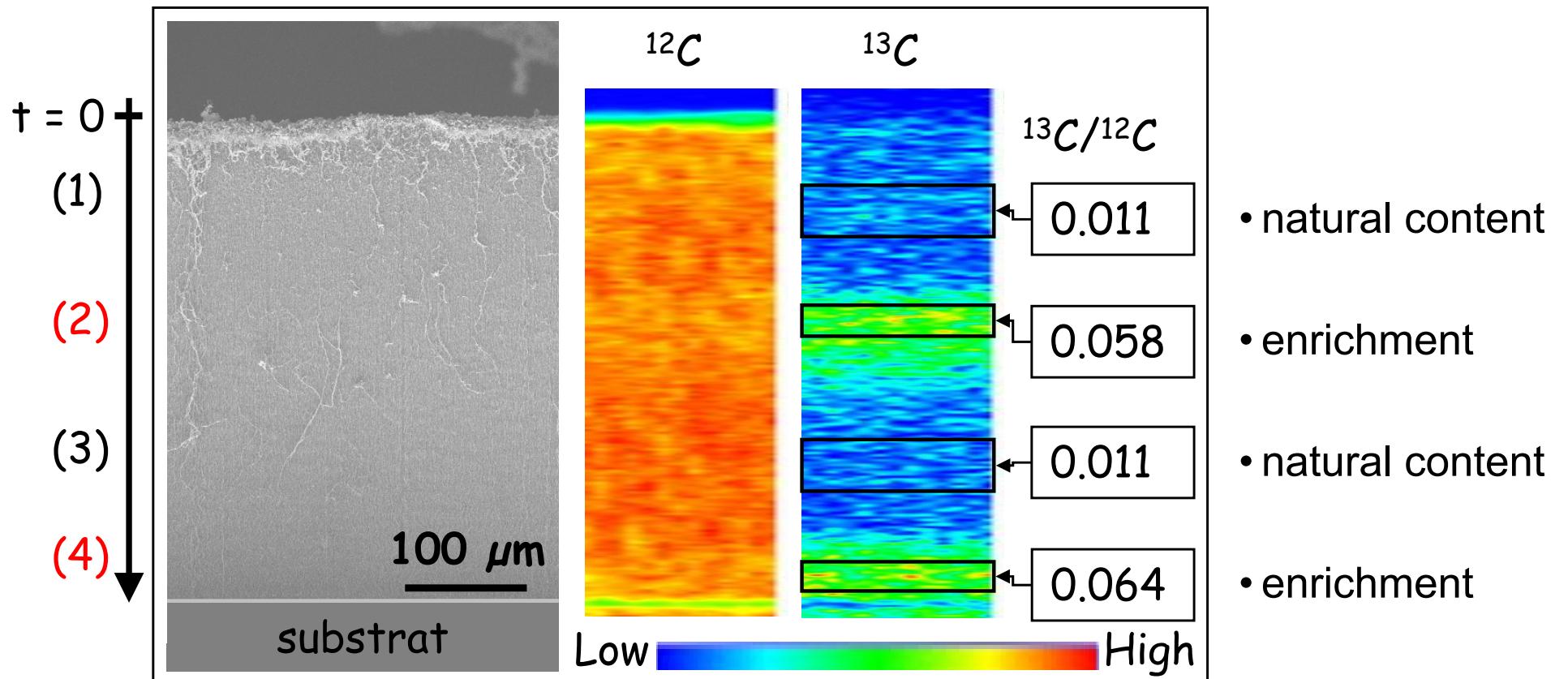


- NT growth start or re-start on substrate surface as soon as catalyst is fed in the reactor
 - Continuous feeding of the substrate surface by catalyst is necessary
 - Catalyst is only active at carpet base

Mathieu Pinault et al., Nano Letters, 2005

Carbon progress through ^{13}C

| (1) | (2) | (3) | (4) |
|--|--|--|--|
| Benzene $\approx 7 \text{ min } 30$ | Benzene (^{13}C) $\approx 1 \text{ min } 30$ | Benzene $\approx 7 \text{ min } 30$ | Benzene (^{13}C) $\approx 2 \text{ min } 30$ |



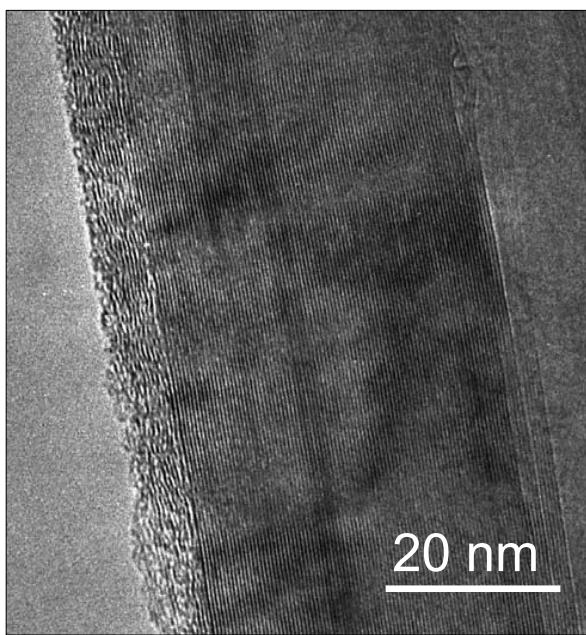
C diffuses through all pre-existing carpets and reacts on catalytic particles located on substrate surface

Mathieu Pinault et al., Nano Letters, 2005

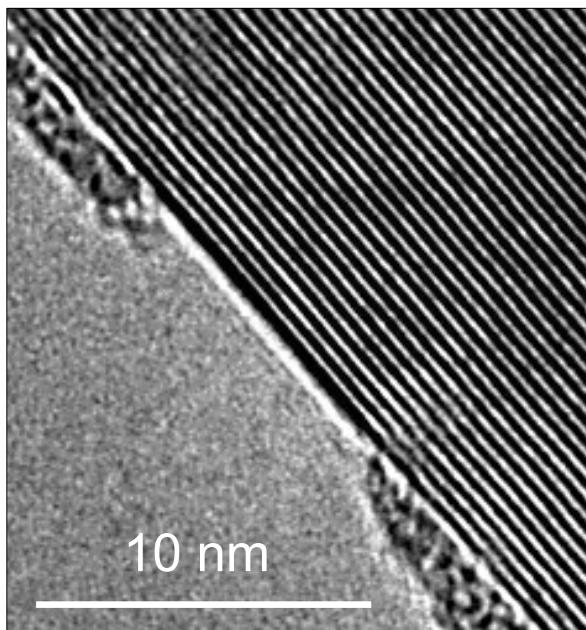
Towards applications : annealing at high temperature

HRMET observations

Raw MWNTs



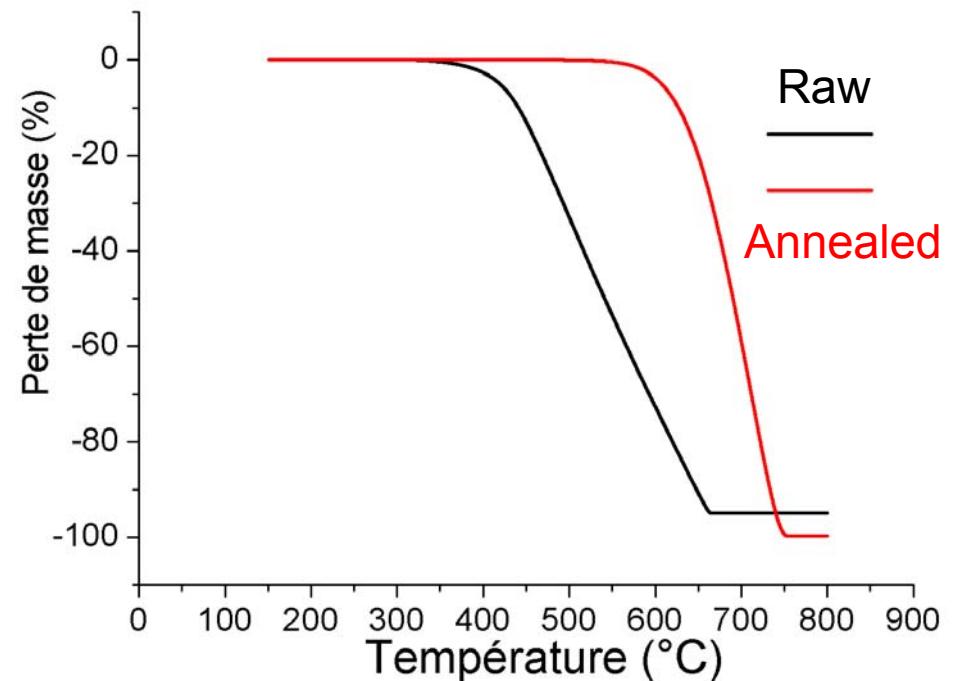
MWNT annealed at 2000°C



- Removal of encapsulated Fe
- Nt ends are opened
- Decrease of the number of structural defects

Temperature > 1700°C, Ar atmosphere

Thermal behaviour under air



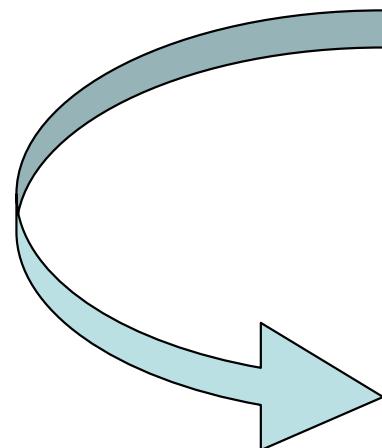
Annealed MWNTs are stable under air at higher temperature

M. Pinault et al., Diamond and related materials 2004

Motivations

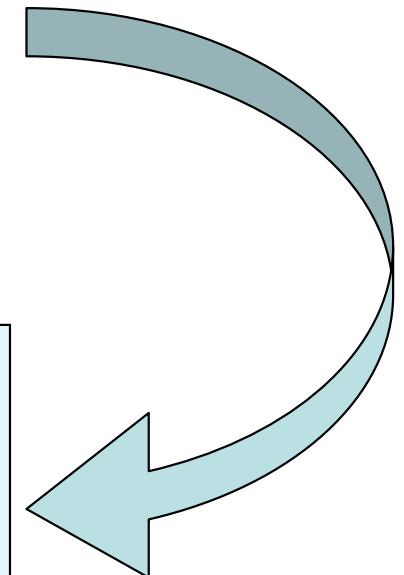
Take benefit of :

- alignment of nanotubes
- length of nanotubes



*to prepare
materials or
devices*

Composites
Membranes
Nanofluids
Sensors



Electrical and mechanical properties
Permeability
Thermal properties

1D composites and membranes

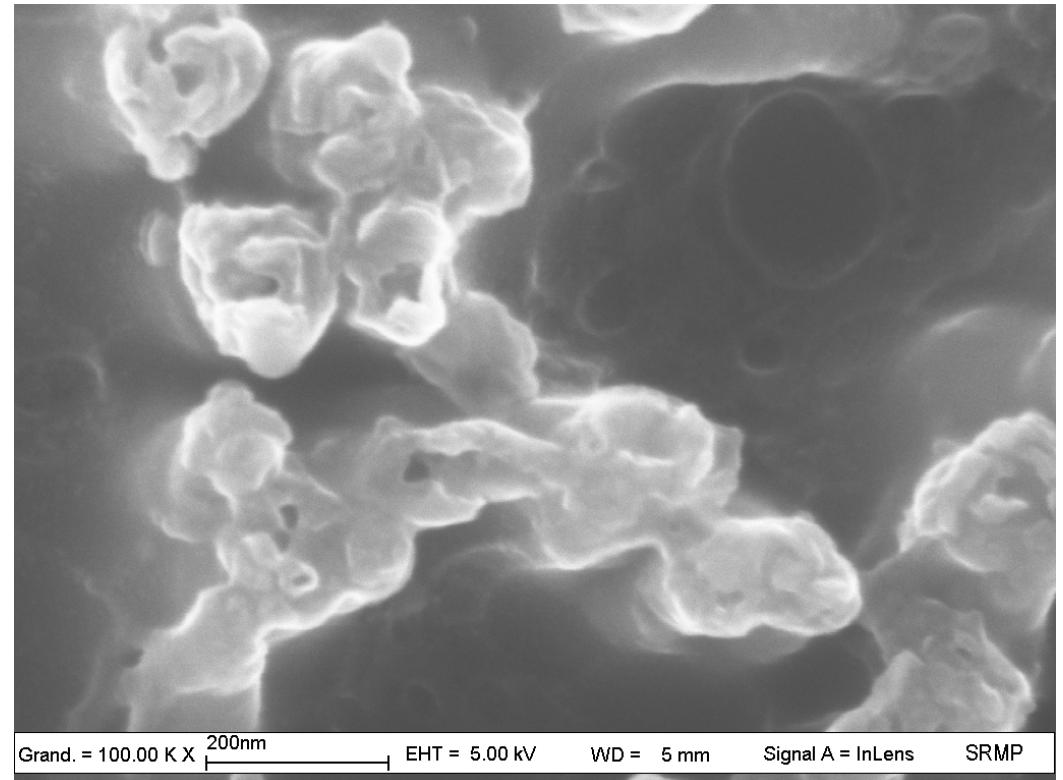
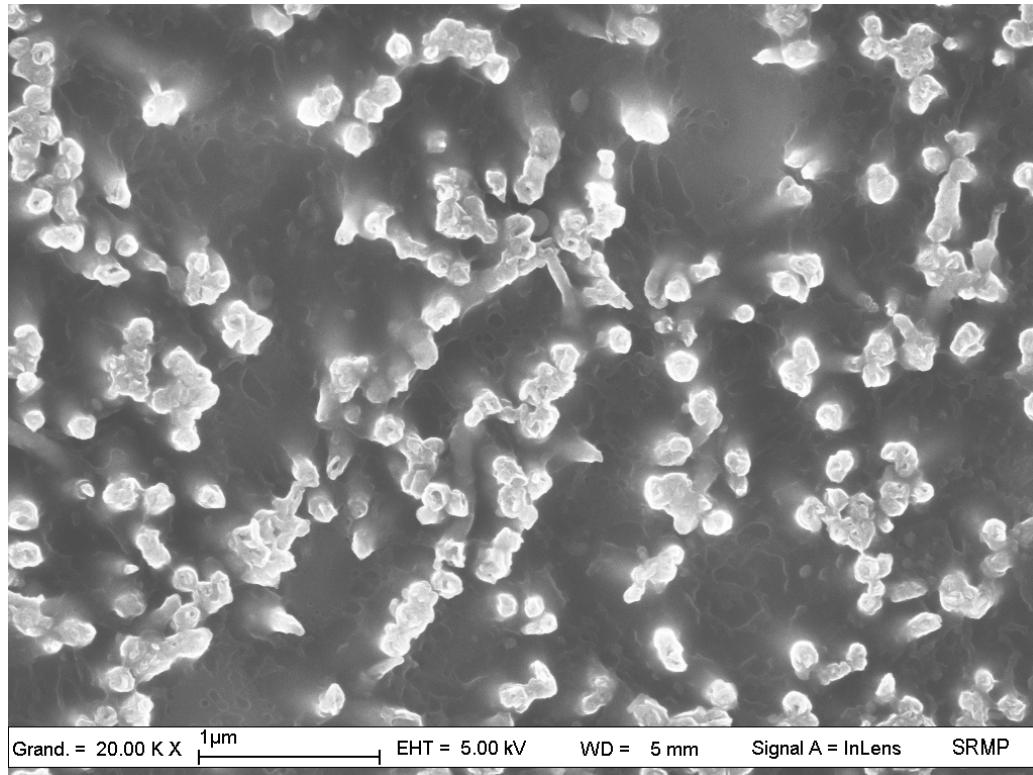
Elaboration



- Aligned carbon nanotube **carpets** used : 1 to 2 mm thick
- 1D Composites: ~ 1 mm thick
- Membranes: ~ 100 to 200 μm thick

Characteristics of composites and membranes

SEM observations of the surface



Nanotube end protruding from both composite or membrane surface

Nanotube ends are opened

Nanotube density around 1×10^9 tubes/ cm²

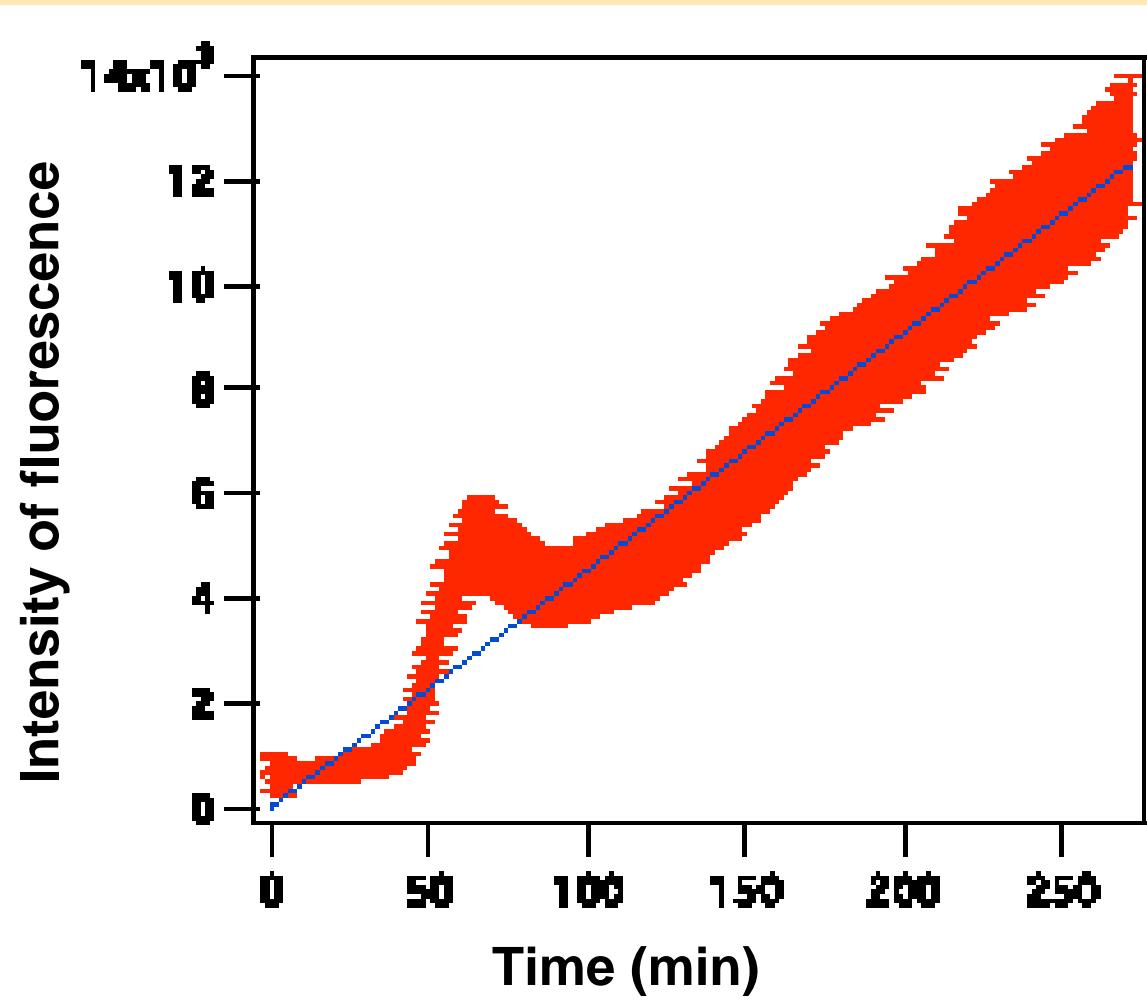
Permeability of membranes

Nanotube membrane separates two compartment cells : one containing fluorescein solution in water and the other one containing only water

Measurement of **fluorescence intensity** in the second compartment cell



Increase of fluorescence intensity in the second compartment cell



Membranes are permeable in aqueous media

Water-based nanofluids

Elaboration : dispersion of nanotubes in water

From pure and aligned multi-walled nanotubes

Average diameter (TEM) : 40 nm

Length (before ultrasound treatment) : 300 µm

By **sonication** with a high intensity ultrasonic (US) probe (750 W max)
with duration varying from a few minutes to several hours.

Stabilisation of the suspensions by **surfactant**: gum Arabic (GA) : 1 or 2wt%

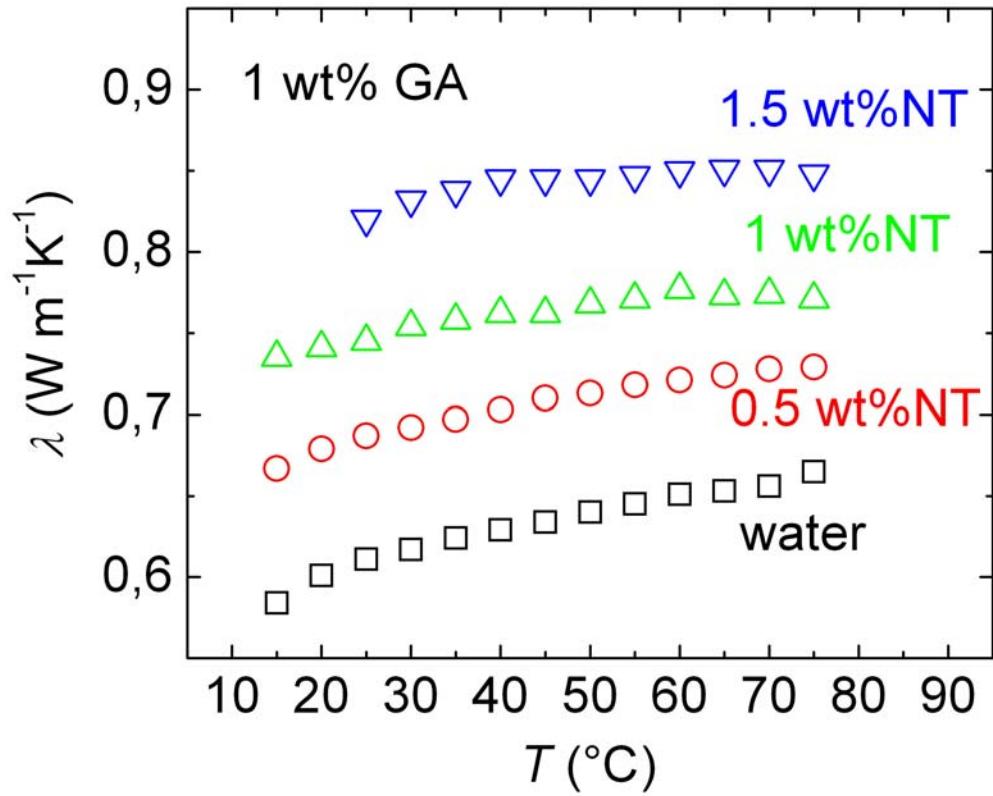
Suspensions are stable at least a week
and much more after removing the first
decantation products

J. Glory et al, J. Nanosci. Nanotechnol., 2007



Thermal conductivity as a function of temperature

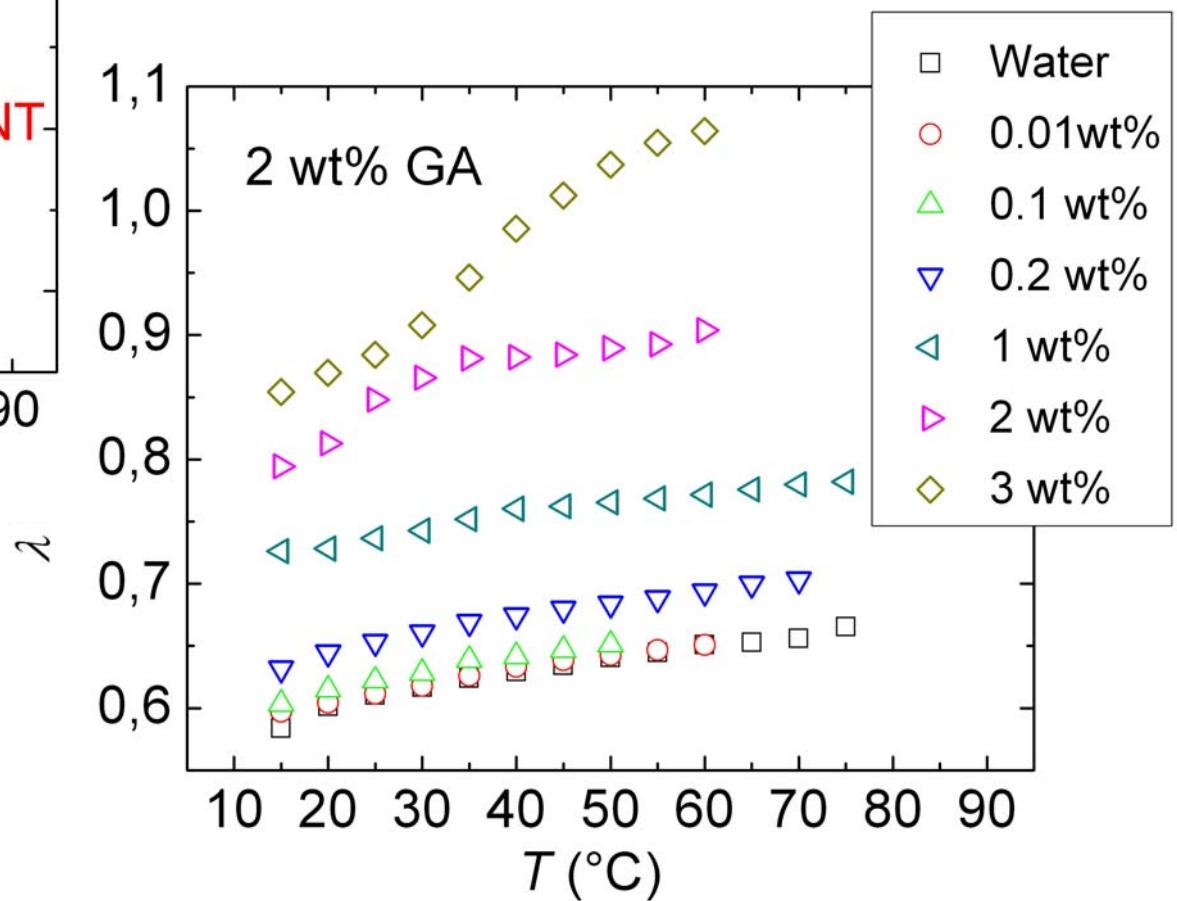
Steady-state method using a home-made cell with coaxial-cylinders



No temperature effect for NT concentration <2wt%

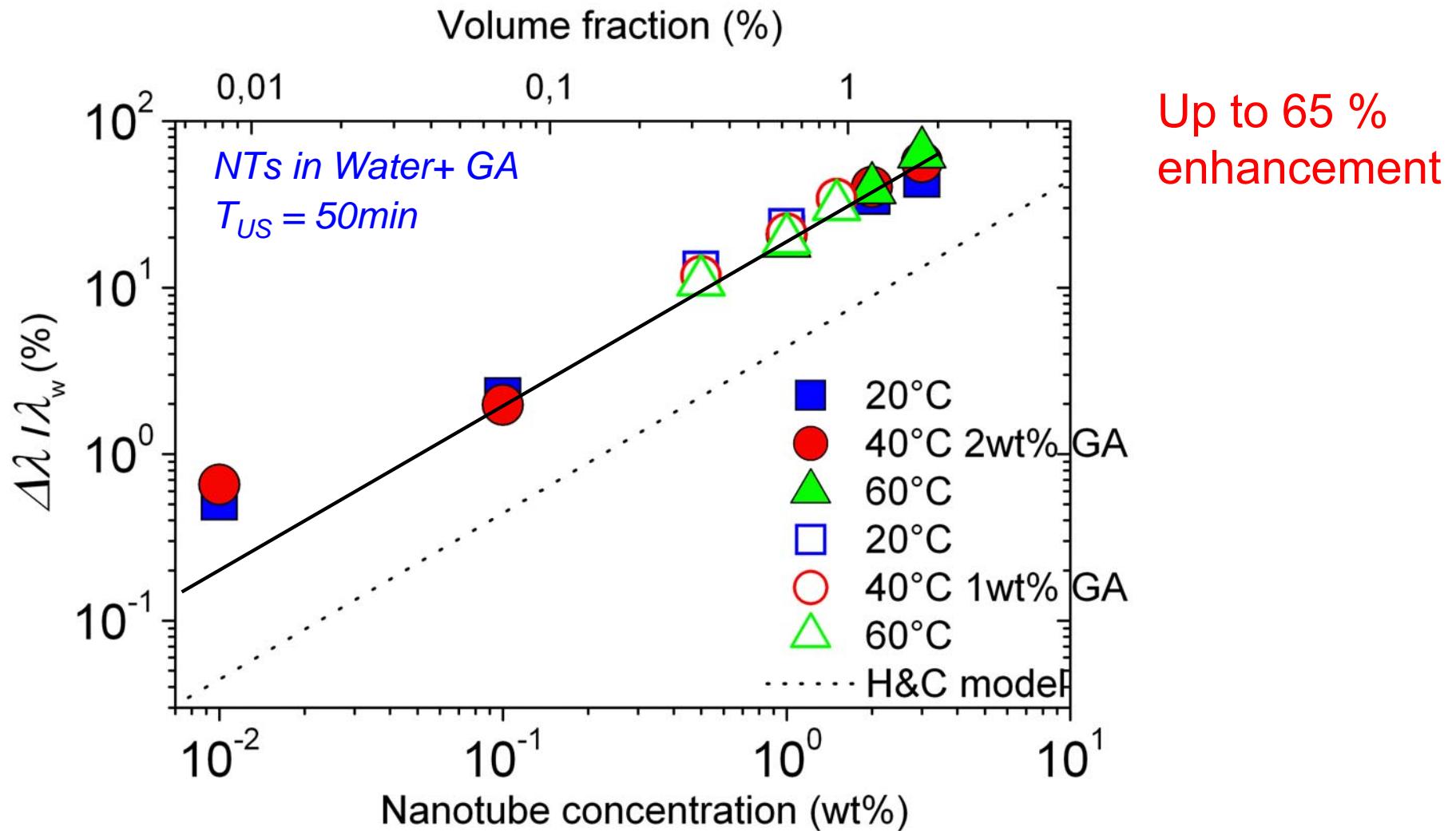
J. Glory et al., J. Appl. Phys. 2008

Suspensions of nanotubes after 50 min sonication ($\langle L \rangle = 1.7 \mu\text{m}$; $\langle d \rangle = 40 \text{ nm}$)



Effect of nanotube content

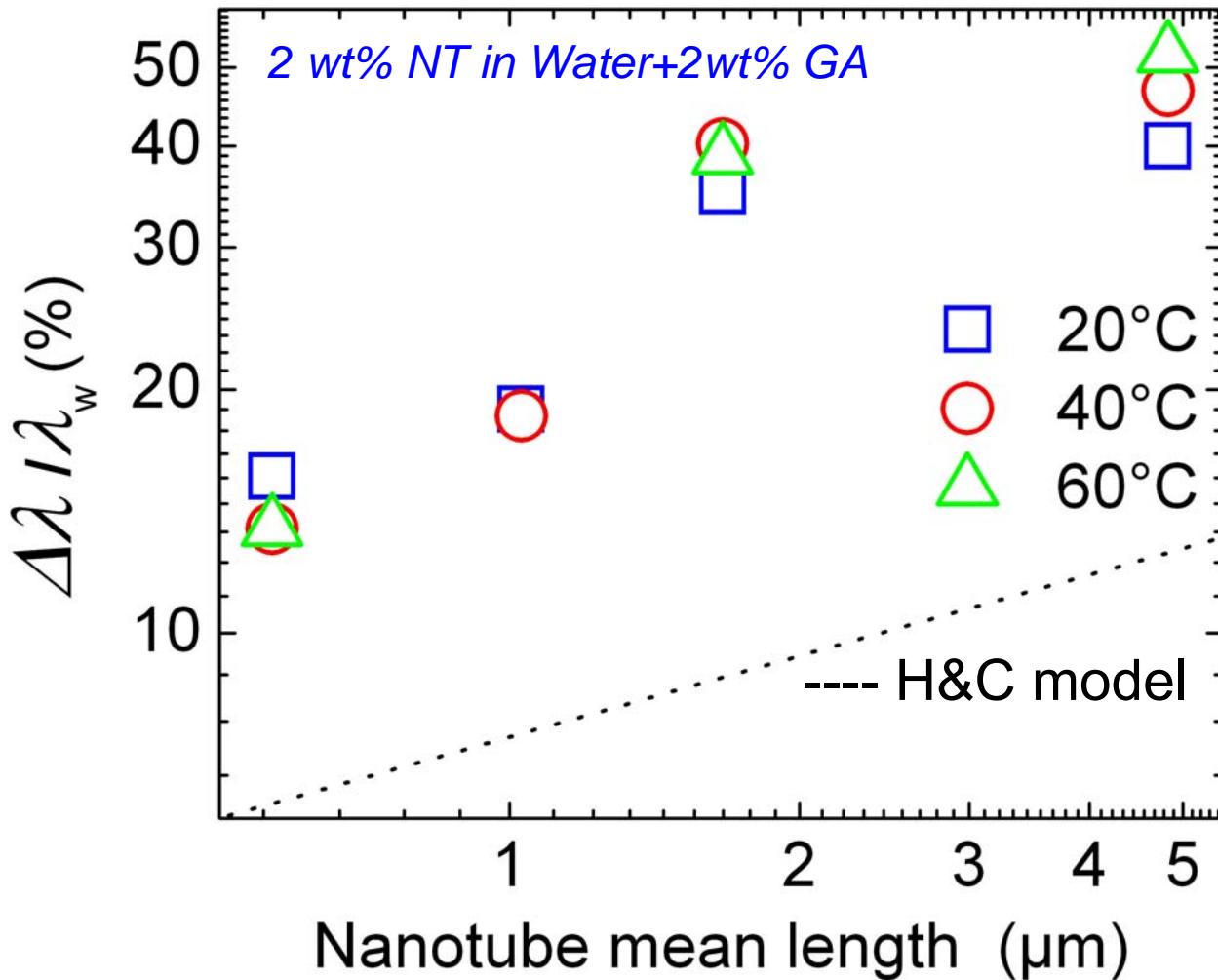
Large range of nanotube content : [0,01 – 3] wt%



Thermal conductivity enhancement increases nearly linearly with the NT content on an extended range of NT content : $\Delta\lambda/\lambda$ (%) = 35 α (%)

Effect of the aspect ratio

Measurements for different sonication durations : different nanotube length



From 0.5 to 5 μm ,
the enhancement is
increased by a factor of 3

Increase of λ much higher than predicted by Hamilton & Crosser model

J. Glory et al., J. Appl. Phys. 2008

Nanotube growth

- *Aerosol-assisted CCVD* : macroscopic samples of aligned carbon nanotubes
clean, high length, well aligned
- *Growth mechanisms* :
 - Base growth all along carbon nanotube growth
 - C diffuses all along carpet height
 - Nature and structure of the catalytic particle depends on the cooling procedure

Applications : from long and aligned carbon nanotube macroscopic samples

- Possible to prepare polymer-based composites, membranes, nanofluids and sensors
- Possible to measure macroscopically the properties of materials or devices

Possible to get a significant enhancement of the properties
Nanofluid thermal conductivity strongly affected by NT length

Collaborations :

- P. Launois, J Cambedouzou, V. Pichot V. Heresanu, LPS (Orsay) : XRD
- S. Poissonnet et P. Bonnaillie, DEN/DMN/SRMP, CEA-Saclay : SEM
- J-M Verbavatz, DSV CEA-Saclay ; JN Rouzaud, ENS Géologie (Paris) : TEM/EDX.
- M. Kociak et O. Stephan, LPS (Orsay) : EELS
- H. Khodja, LPS, CEA-Saclay : nuclear microprobe
- D. Lairez, LLB, CEA-Saclay : permeation measurements
- M. Bonetti, SPEC, CEA-Saclay : thermal measurements