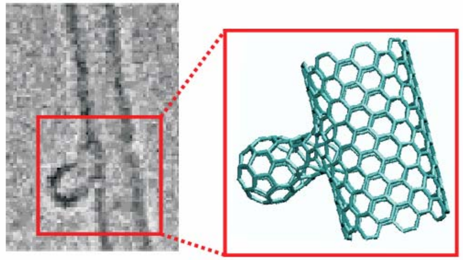
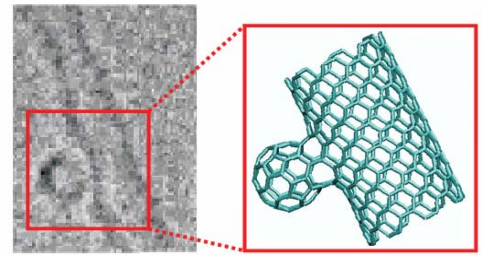




NanoMaterials Group

CARBON NANOTUBE SYNTHESIS

TUTORIAL at NT06

Nagano, Japan, June 18, 2006

Prof. Dr. Esko I. Kauppinen

NanoMaterials Group
Center for New Materials and Laboratory of Physics
Helsinki University of Technology
Espoo, Finland

Collaboration

Dr. Albert G. Nasibulin (aerosol synthesis of CNTs)
Dr. Hua Jiang (HR-TEM, ED/TEM)
Dr. David P. Brown (combined aerosol-CFD modelling)
Dr. David Gonzalez (charging of CNT's)
Dr. Paula Queipo (cluster-catalyzed surface CVD synthesis of CNTs)
Prof. Sergei D. Shandakov (Marie Curie Fellow 2006-07, high yield synthesis)
Andrei Ollikainen, Anton Anissimov (growth and applications in electronics)

Prof. Daniel E. Resasco, Oklahoma U., USA (CVD growth & chirality)
Prof. David Tomanek, Michigan State U., USA (atomic modelling)
Dr. Peter V. Pikhitsa, Odessa Nat. Univ., Ukraine (SWCNT Nucleation)
Prof. Risto Nieminen, Dr. Arkady Kraseninnikov, COMP/HUT Finland (atomic modelling)
Dr. Bernd Freitag, FEI, Netherlands (C_s-TEM imaging)

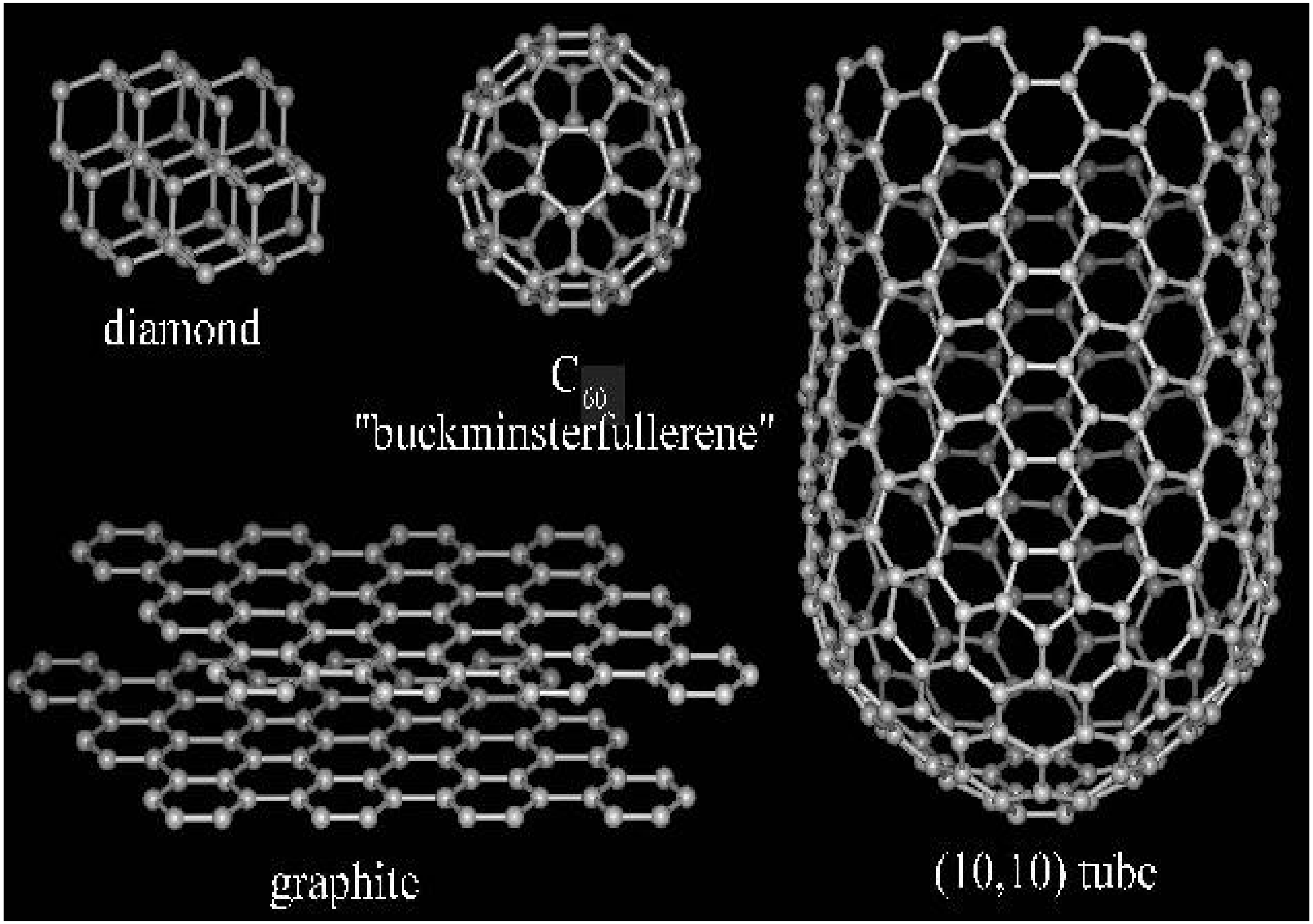
Funding
- **Academy of Finland via TULE program/ELENA Consortium**
- **EU FP5 RTN NanoCluster**
- **EU FP6 Marie Curie Fellow**
- **TEKES FinNano & MASI Programs**

Tutorial Material
Dr. A. Loiseau, Prof. S. Maruyama, Prof. M. Endo, Prof. S. Iijima, Prof. K. Bolton, Prof. S. Farhat, Dr. C.D. Scott, Dr. Chris Kingston

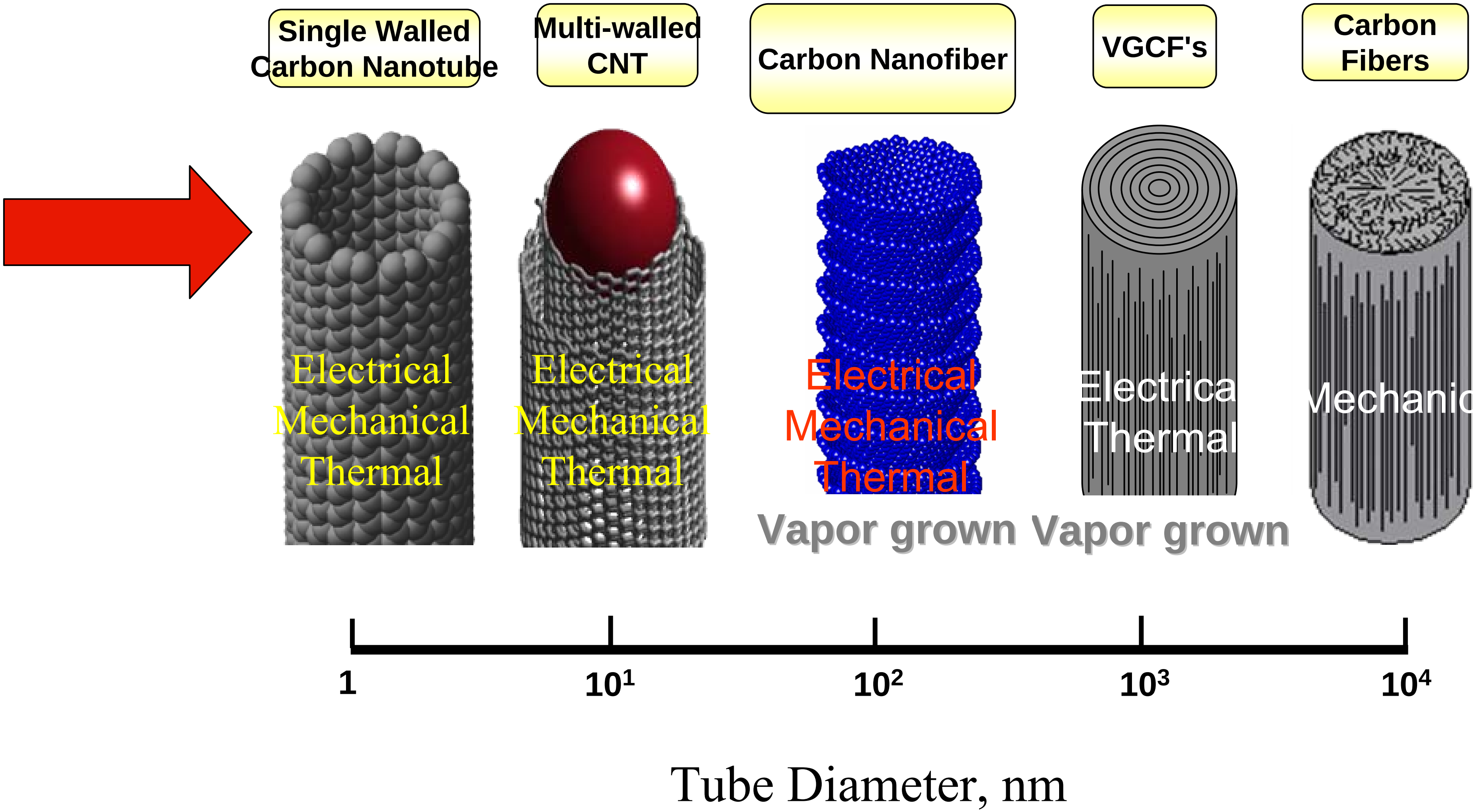
Contents

- Properties to be controlled – focus on SWNT
- Physical methods (brief)
  - Arc discharge
  - Laser methods
- CVD methods
  - Floating catalyst (detailed)
    - HiPCO
    - Hot Wire Method
    - DIPS
    - NT nucleation mechanisms based on MD simulations
    - Catalyst particle growth modelling
  - Substrate CVD methods (brief)
    - CoMoCat
    - ACCVD
    - Chirality
- Individual NTs – controlling bundling via gas-phase charging (new)
- Simultaneous Floating Catalyst CVD synthesis of fullerenes and NTs – in-situ functionalization of tubes with fullerenes – new material ***”Carbon Nanobud*”** (new)

Three allotropic modifications of carbon: diamond, graphite, and fullerene structures (fullerenes and CNTs).



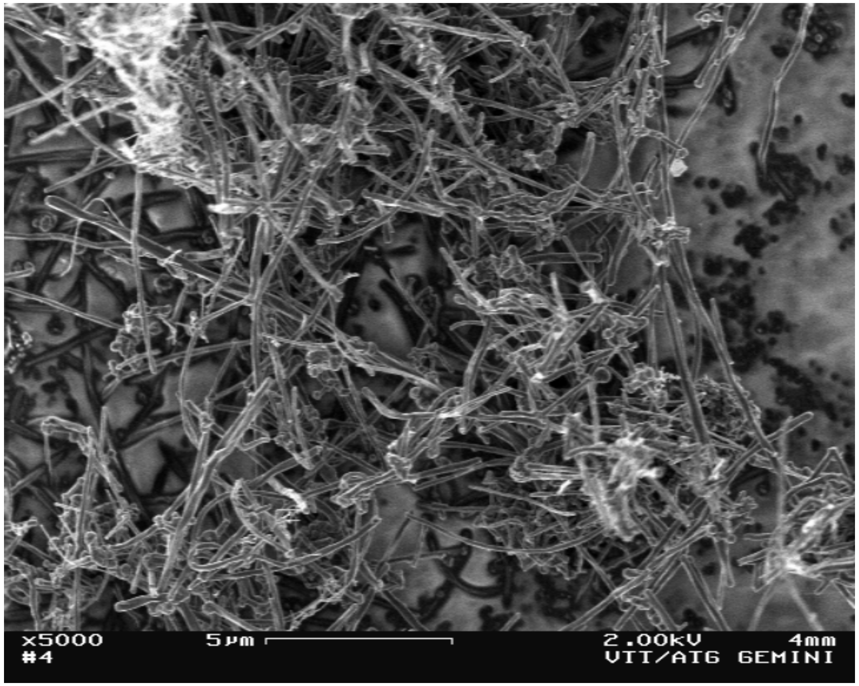
Carbon Fiber/Nanotube Products

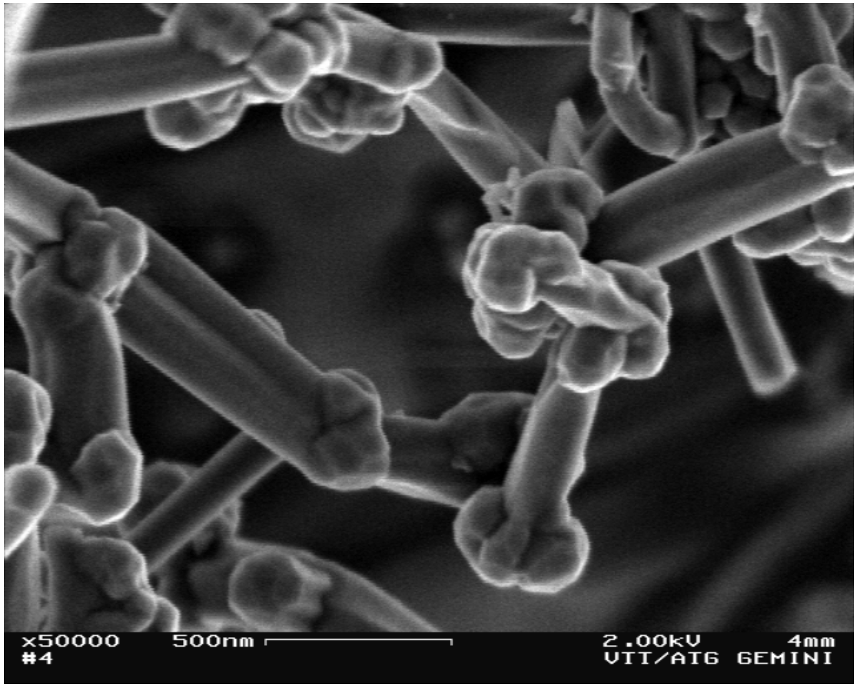


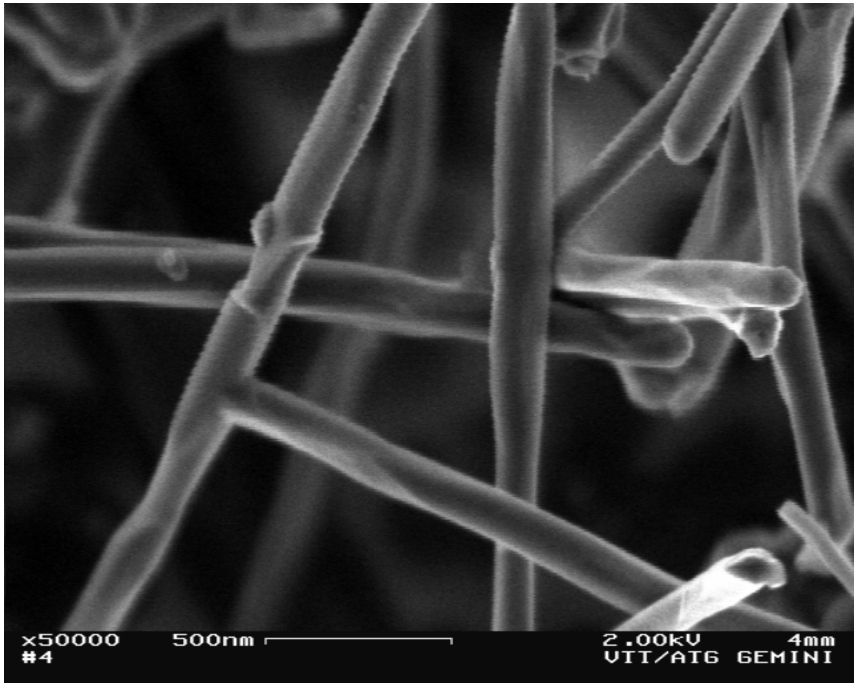
Prof. Endo VGCNF

SEM images of vapor grown carbon nanofibres produced by Showa Denko, Fine Carbon Department, Nagano, Japan, by ***floating catalyst CVD method***

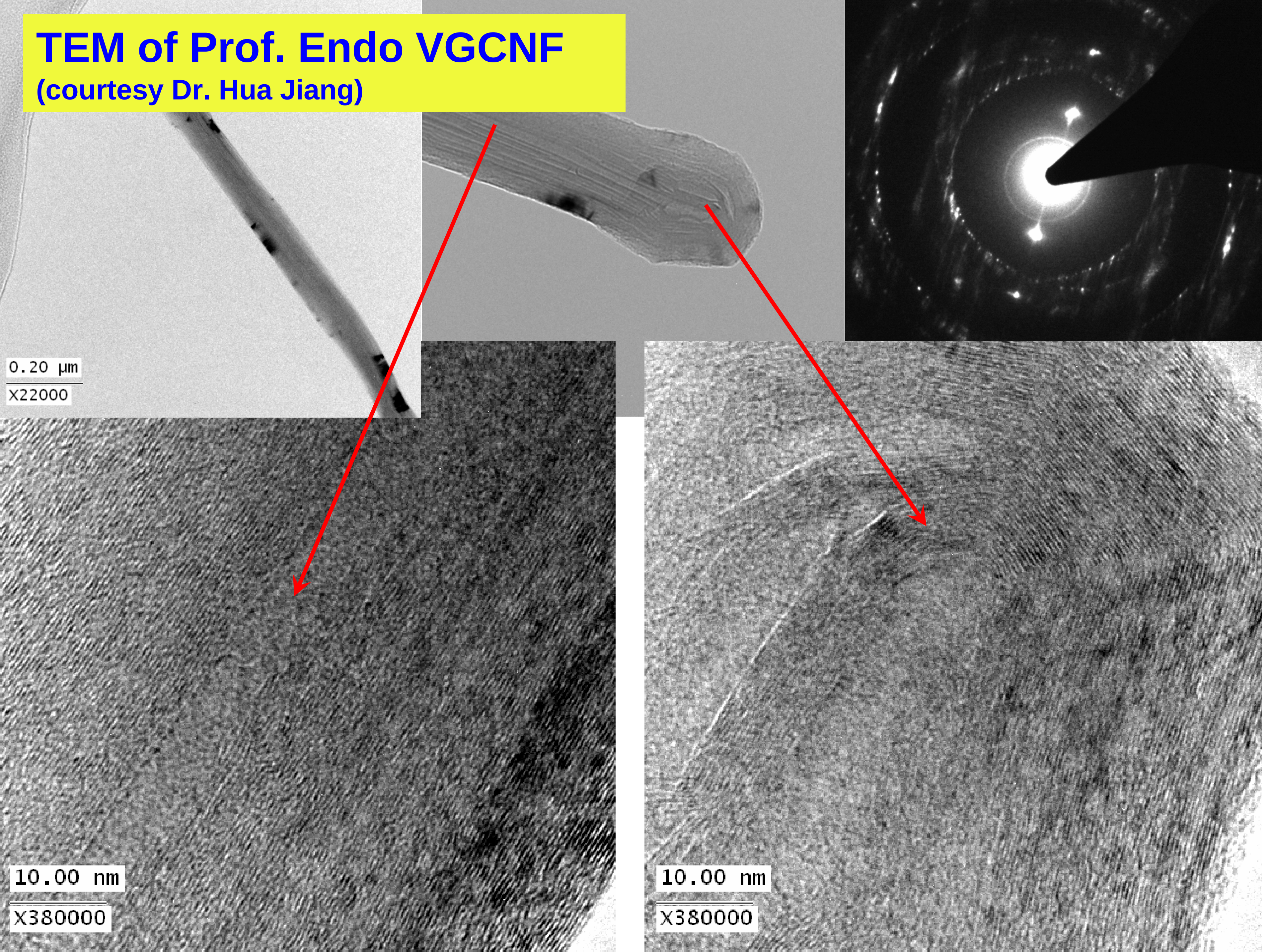
(courtesy Dr. Hua Jiang)







TEM of Prof. Endo VGCNF
(courtesy Dr. Hua Jiang)

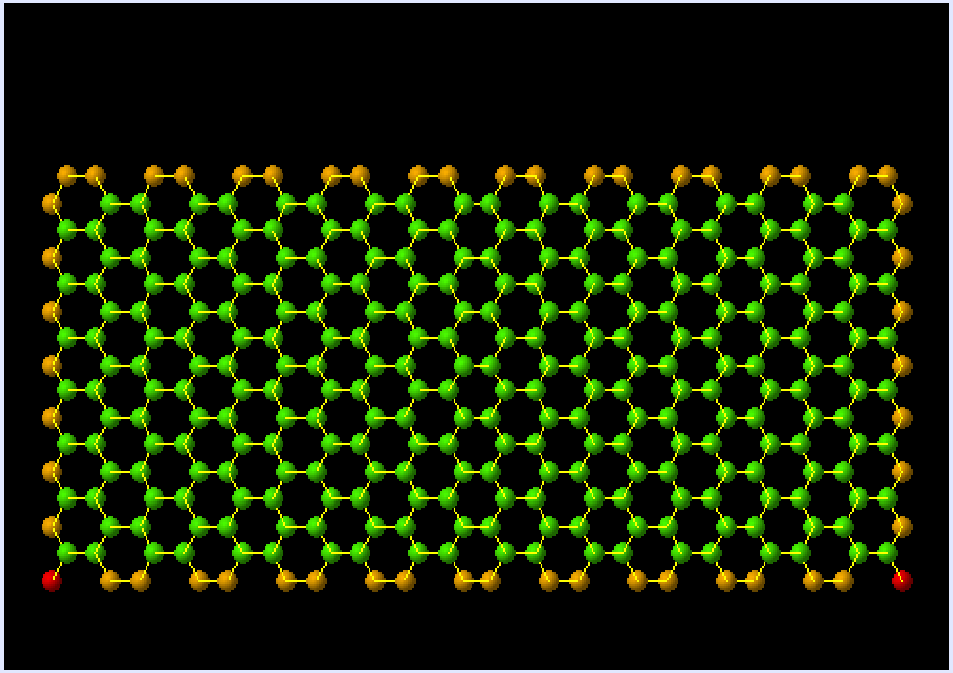


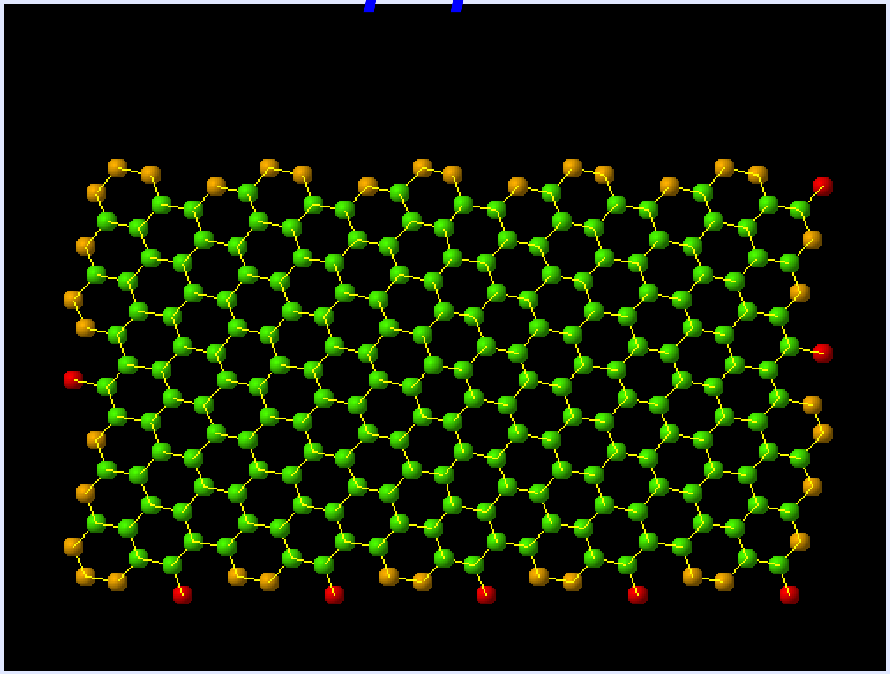
Known forms of Carbon Nanomaterials

Carbon Nanotube (SWCNT):

Roll of carbon sheet one atomic layer thick

1 000 000 times thinner than paper





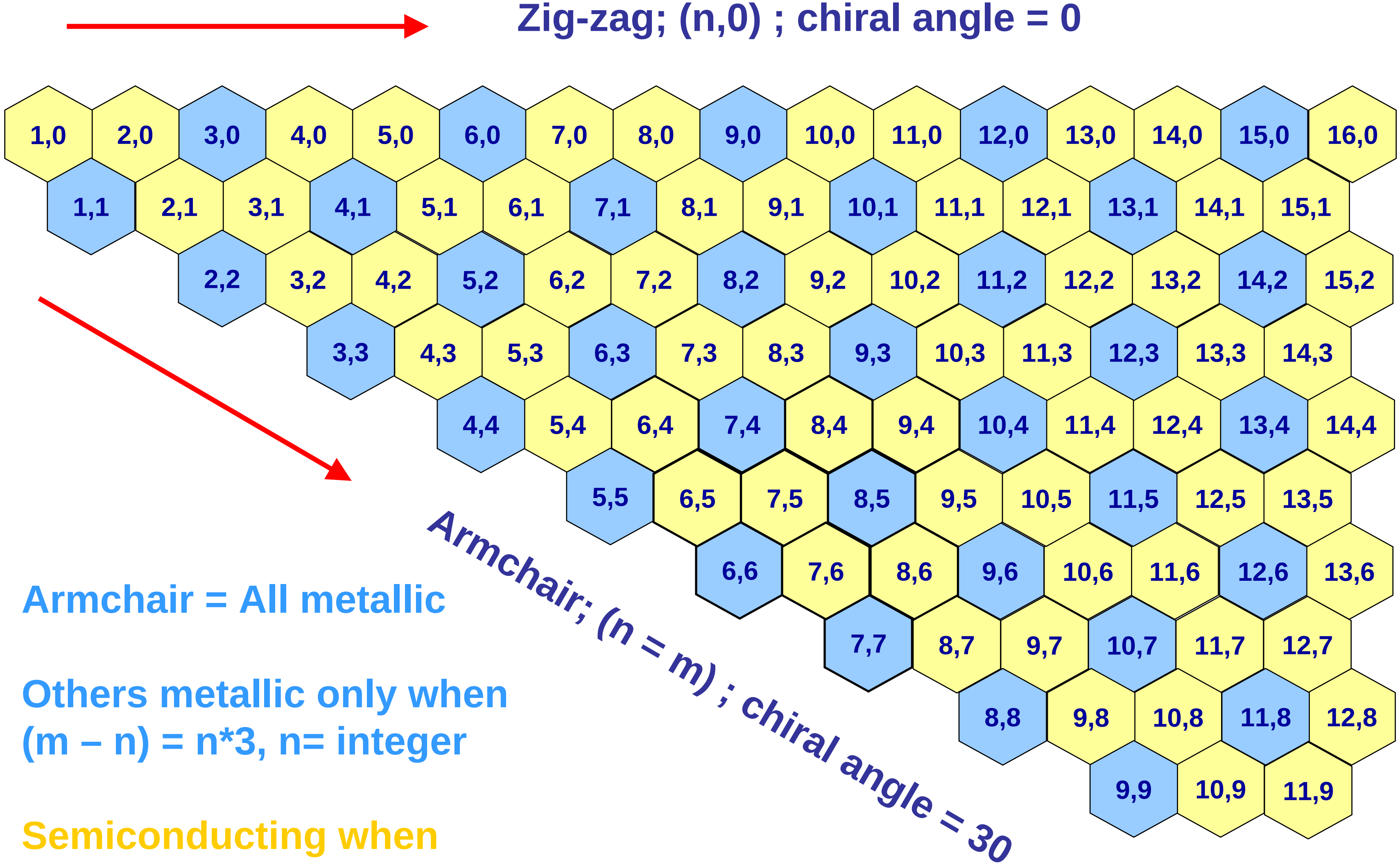
Rolling in different directions makes different kinds of tubes

(10,10) armchair tube
METALLIC

(10,5) helical (chiral) tube
SEMICONDUCTING

Courtesy Prof. S. Maruyama

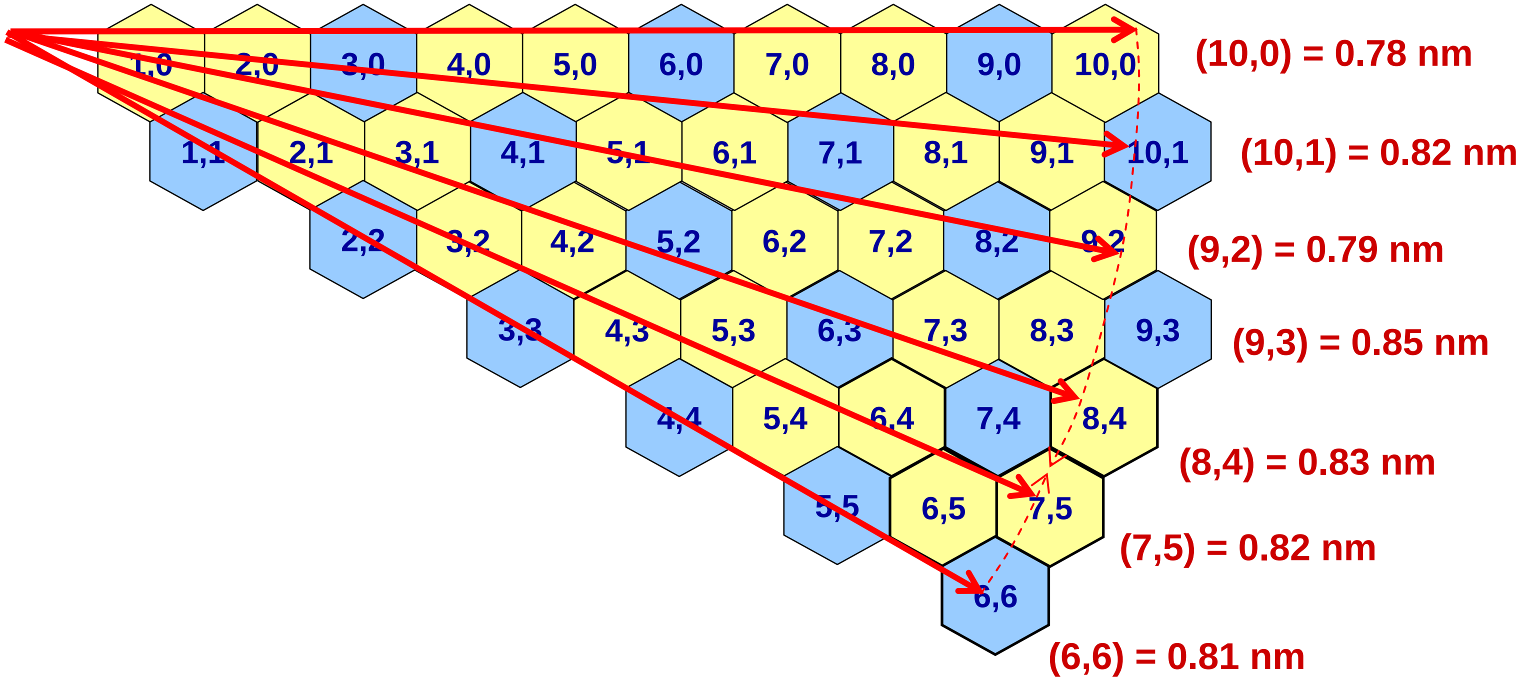
Chirality Map



- Armchair = All metallic
- Others metallic only when (m – n) = n*3, n= integer

Semiconducting when (m - n) # n *3

Chirality Map



Distance from origin is proportional to nanotube diameter

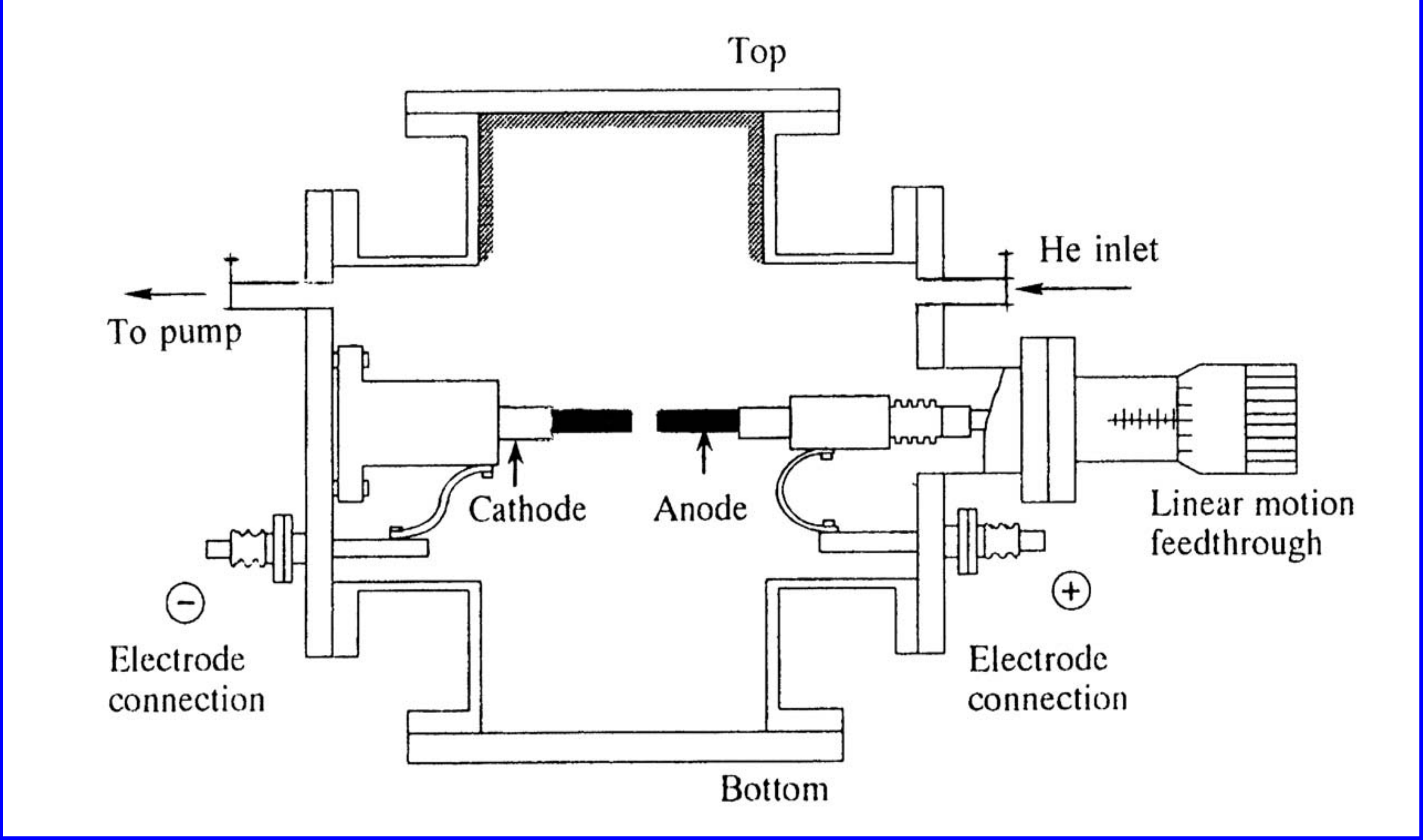
Properties to be controlled during synthesis

- Number of walls (SW, DW, MW)
- Diameter
- Length, orietation
- Purity (catalyst and non-tubular carbon)
- Bundling
- Chirality
- Functionalization

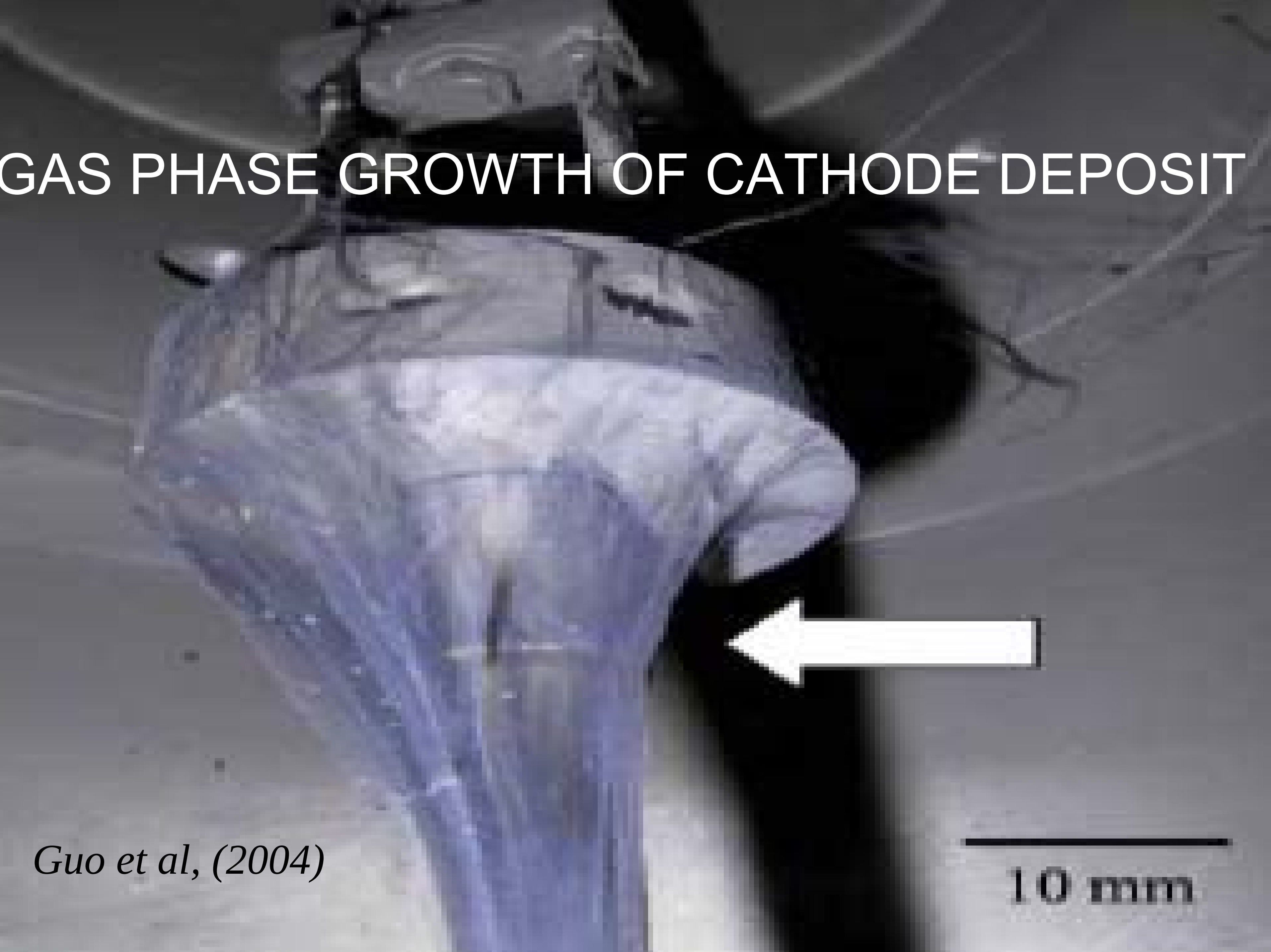
Physical methods

- **Arc discharge**

High electrical current is applied between two carbon electrodes. Carbon plasma is generated from anode (positive), forms nanotubes and deposits on cathode (negative).



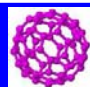
GAS PHASE GROWTH OF CATHODE DEPOSIT



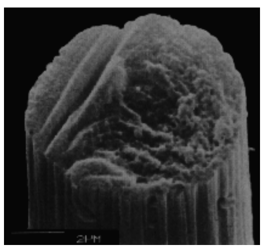
Guo et al, (2004)

ELECTRIC-ARC DISCHARGE

History



WISKERS
1960

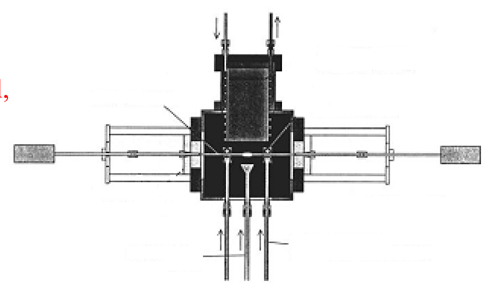


Bacon., J. Appl. Phys. 31, 283 **(1960)**

FULLERENE
1985

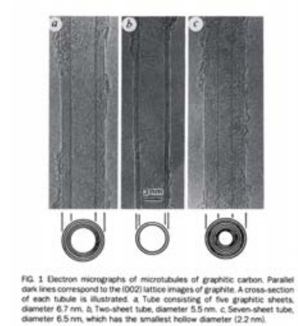
Kroto, Heath, O'Brien, Curl, and Smalley, *Nature 318*, 162(**1985)**

FULLERENES
1990



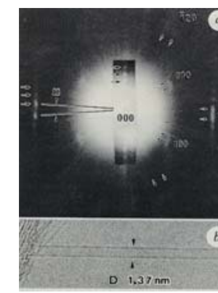
*Krätschmer, Lamb, Fostiropoulos and Huffman, Nature **347**, 354 **(1990).***

MWCNT
1991



*Iijima, S., Nature 354, 56, **(1991)***

SWCNT
1993

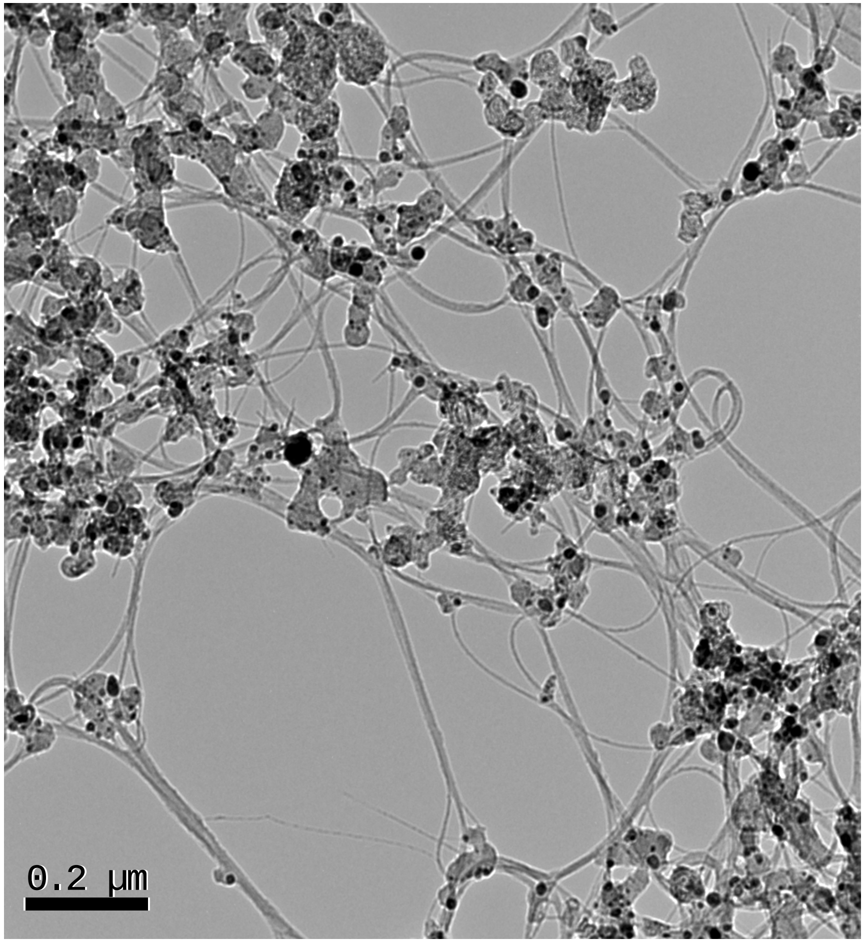


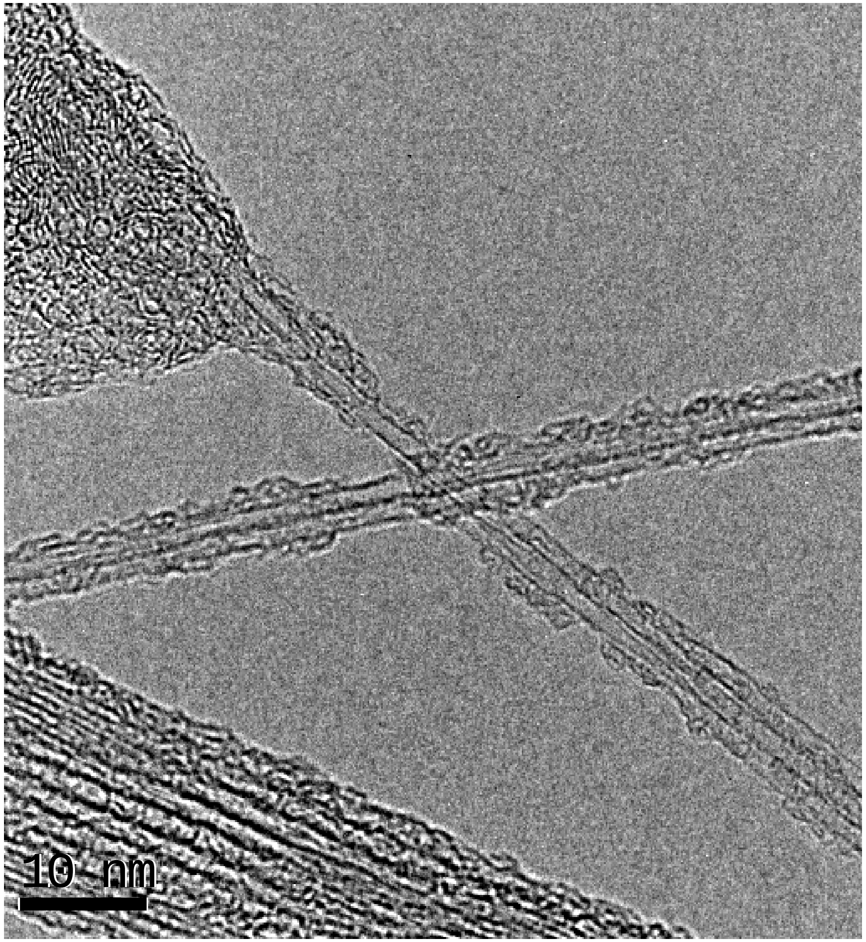
*S. Iijima & T. Ichihashi Nature 363, 603 **(1993)***

Courtesy Prof. S. Farhat

TEM images of commercial SWCNTs produced (2002) by arc-discharge – no purification

(courtesy Dr. Hua Jiang)





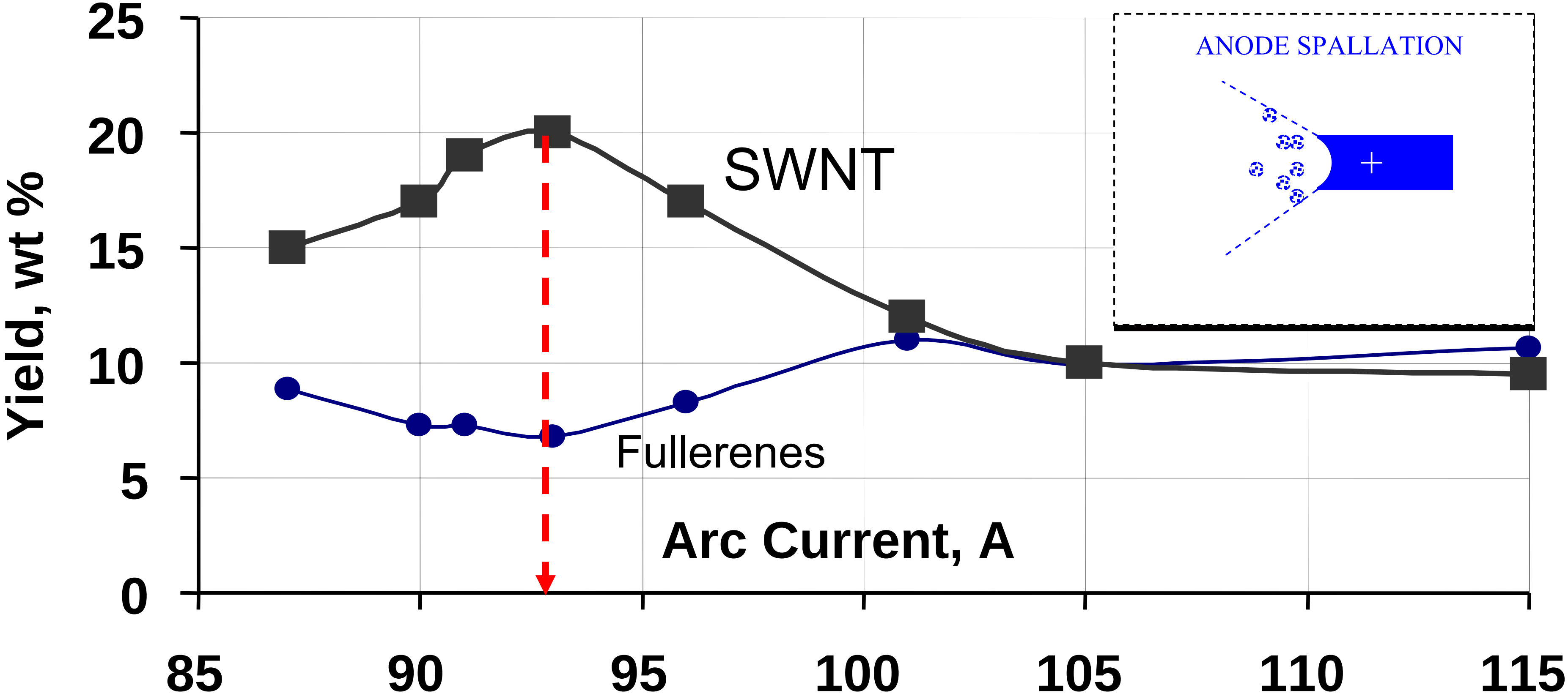
SWCNT PARAMETERS

C. Journet, et al., Nature 388 (1997)756.

➢ Gas type	Helium
➢ Pressure	P= 660 mbar
➢ Voltage	V= 40 V
➢ Current	I= 100 A
➢ CATALYSTS	C:Ni:Y 94.8:4.2:1 atom %
➢ ACD	d= 1 mm

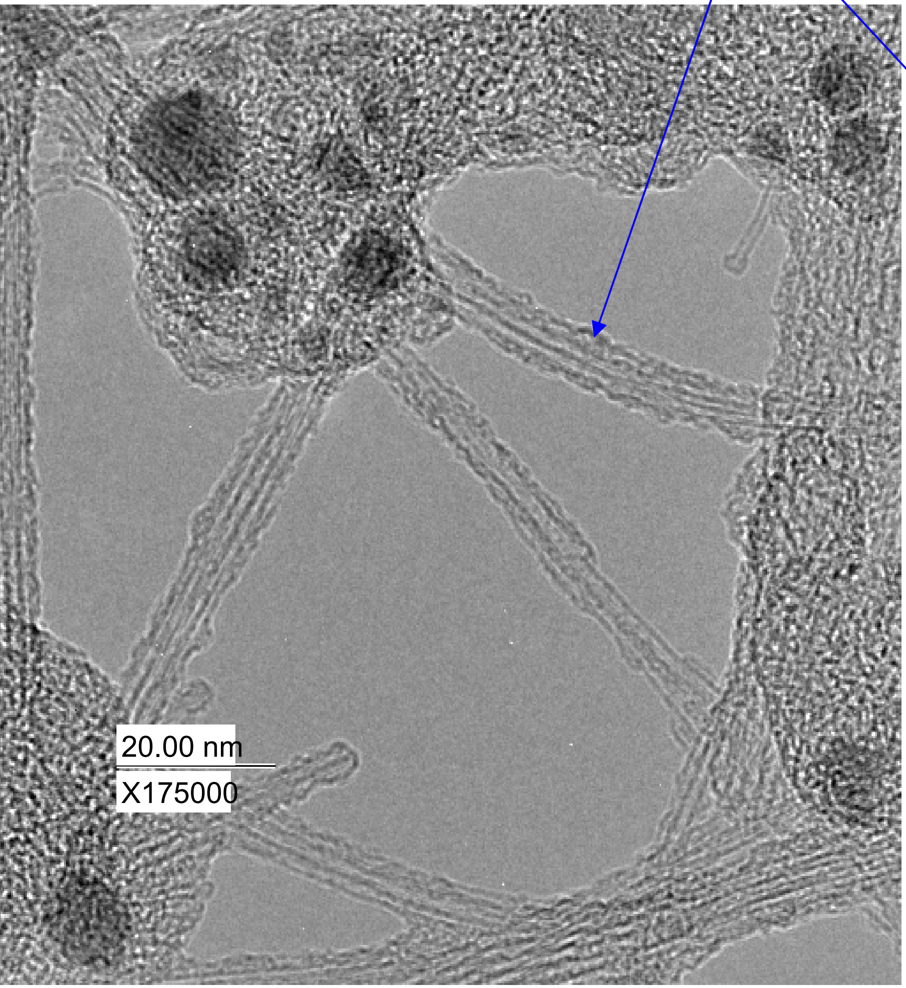
➢ Erosion rate	V_{soot}=5-20 mg/s
➢ CNT contents	10-40 Weight % (70 % for Journet et al.)

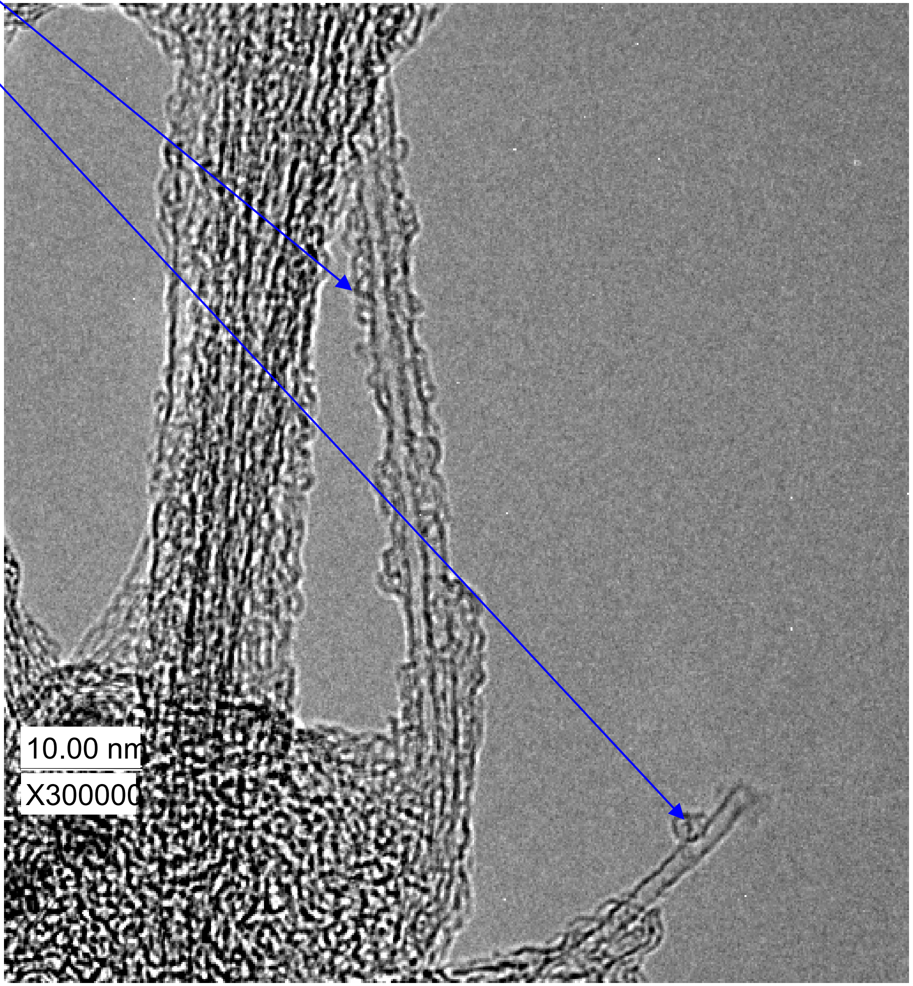
SWCNT YIELD vs ARC CURRENT



A.V.Krestinin, A.P.Moravsky, Chem. Phys. Lett., 286 (1998) 479

TEM images of commercial SWCNTs produced by arc-discharge – no purification. Fullerenes on tubes

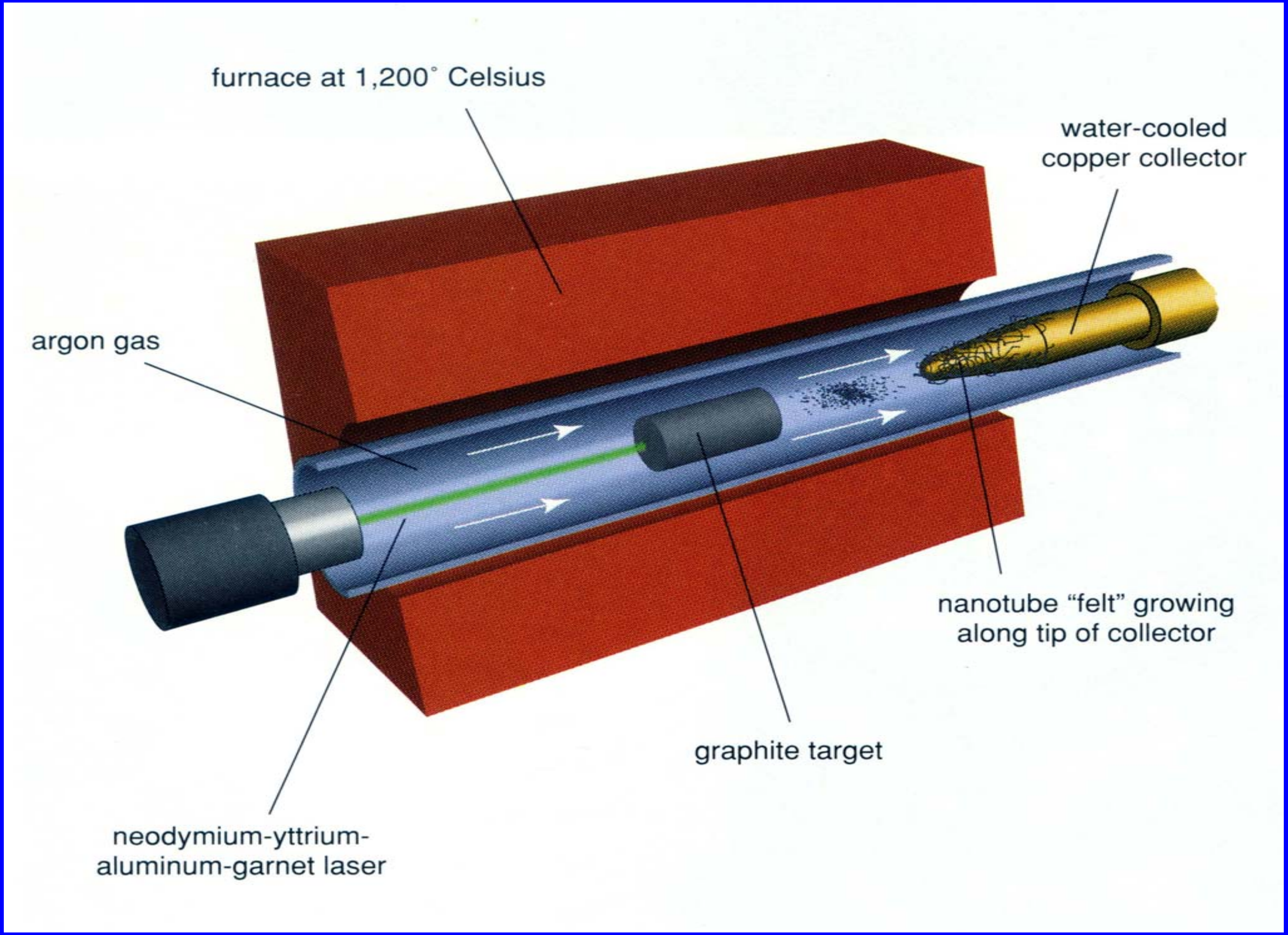




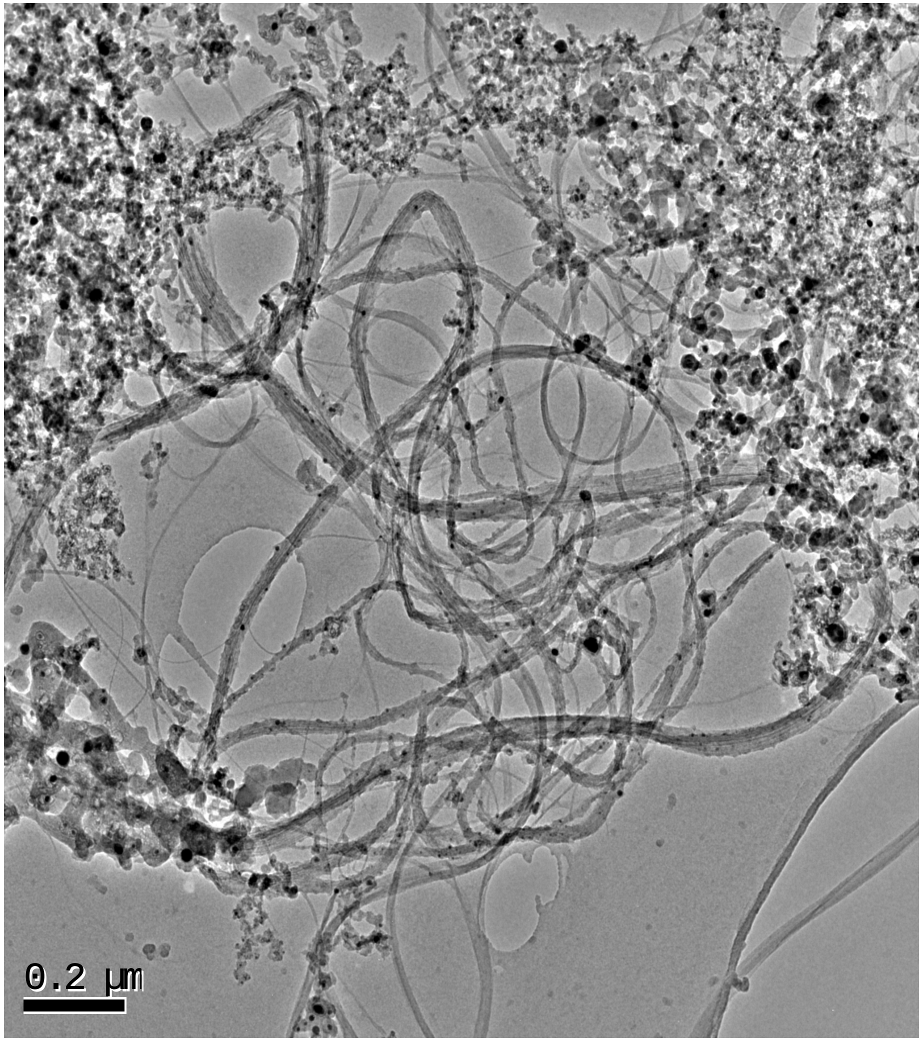
courtesy Dr. Hua Jiang

Laser vaporization

Graphite target is shot by laser, as a result carbon is vaporized and forms carbon nanotubes.



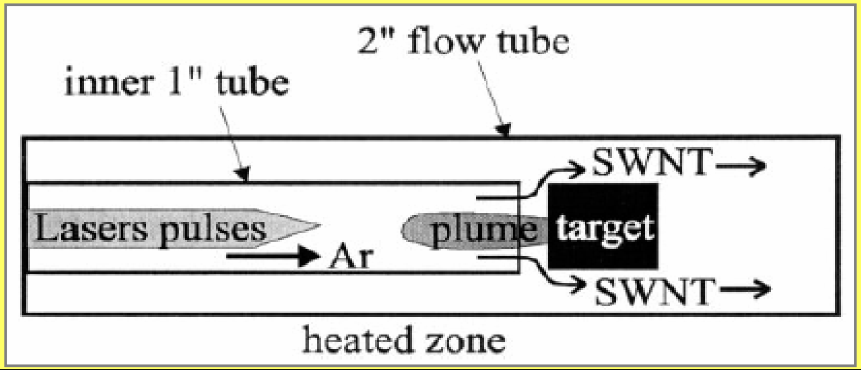
TEM images of commercial (2002) laser oven produced SWCNTs- no purification



courtesy Dr. Hua Jiang

"Double-Pulse" YAG Method

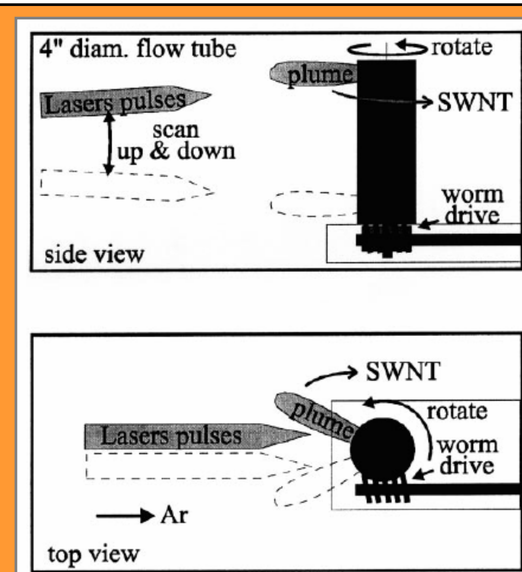
~1 g/day @ 60-90%



- 1200°C
- Ar: 100 sccm, 500 torr
- 523 nm (490 mJ) and 1064 nm (550 mJ)
- 42 ns delay
- 2" and 1" quartz tubes

- 1100°C
- Ar: 750 sccm, 500 torr
- 2 x 1064 nm lasers (930 mJ)
- 40 ns delay
- 4" quartz tube only

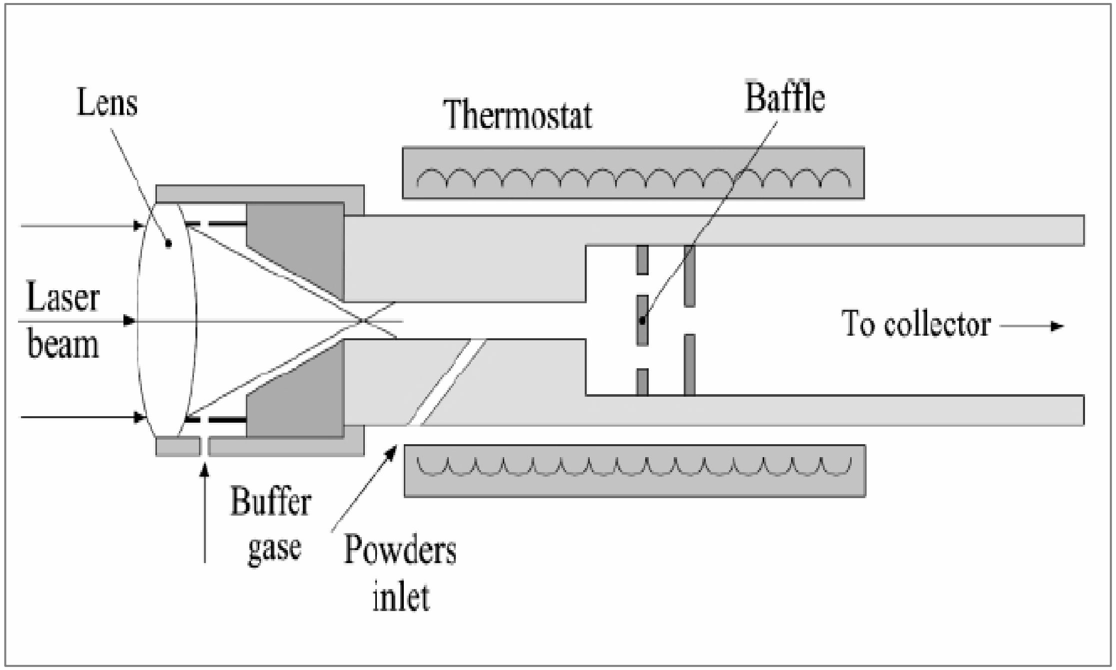
~10 g/day @ 40-50%



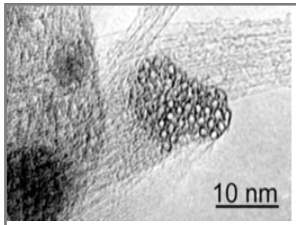
Rinzler et al., *Appl. Phys. A* **67**, 29 (1998).

Courtesy Chris Kingston NRC Canada

CO_2-Powder Method



- cw CO_2 2.1 kW
- 2 l/min Ar/N_2
- 3 g/hr powder
- CoNi (2.5 at-% each)
- 1100°C

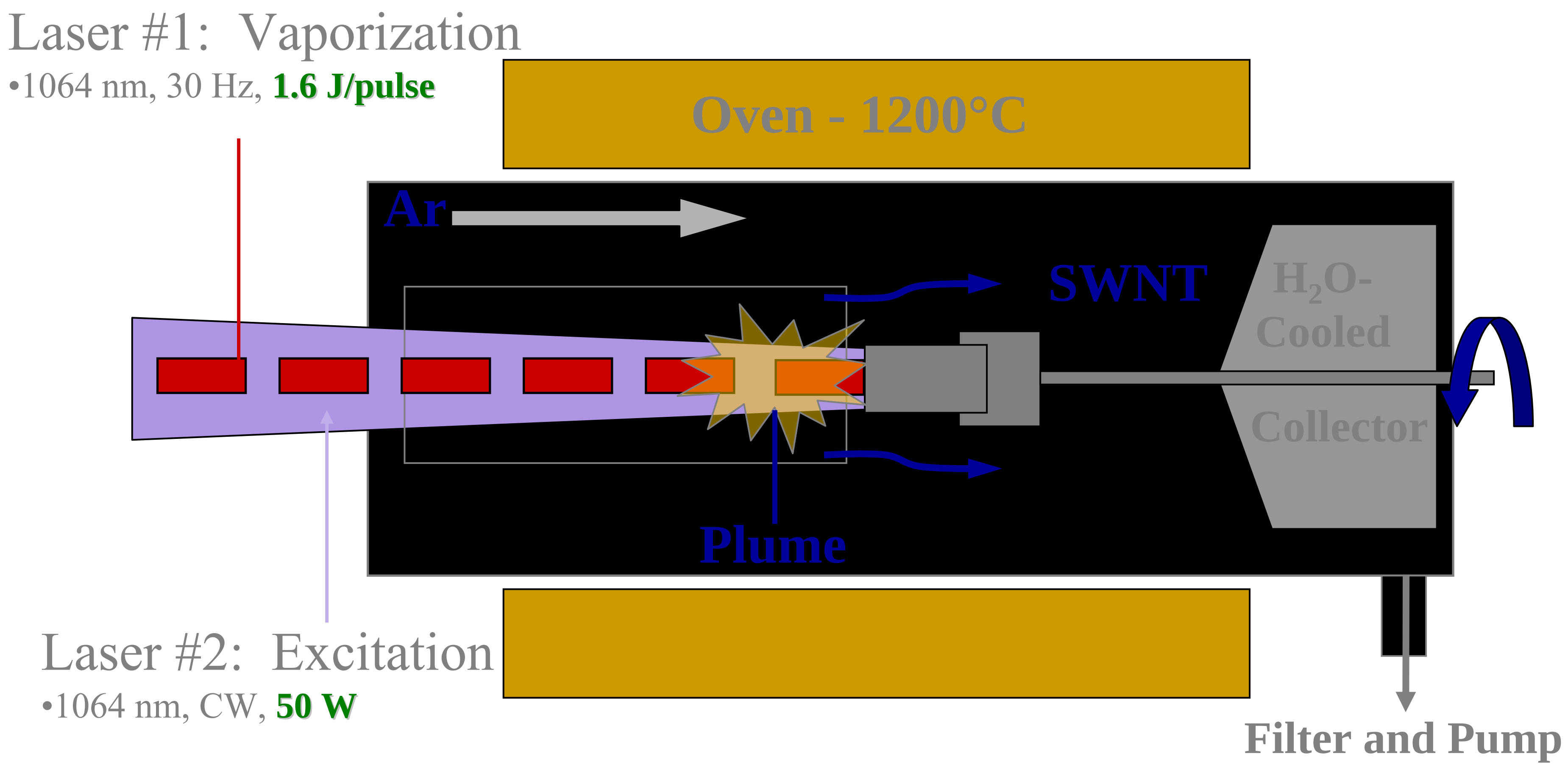


500 mg in 10 minutes at ~20-40 %

Bolshakov et al., *Diam. Rel. Mater.* 11, 927 (2002).

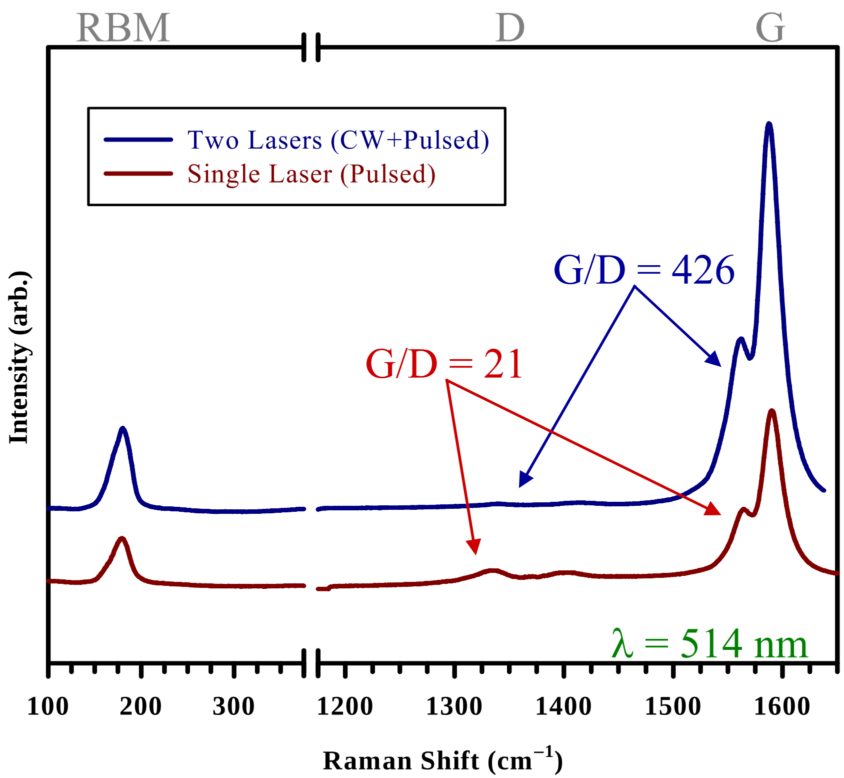
Courtesy Chris Kingston NRC Canada

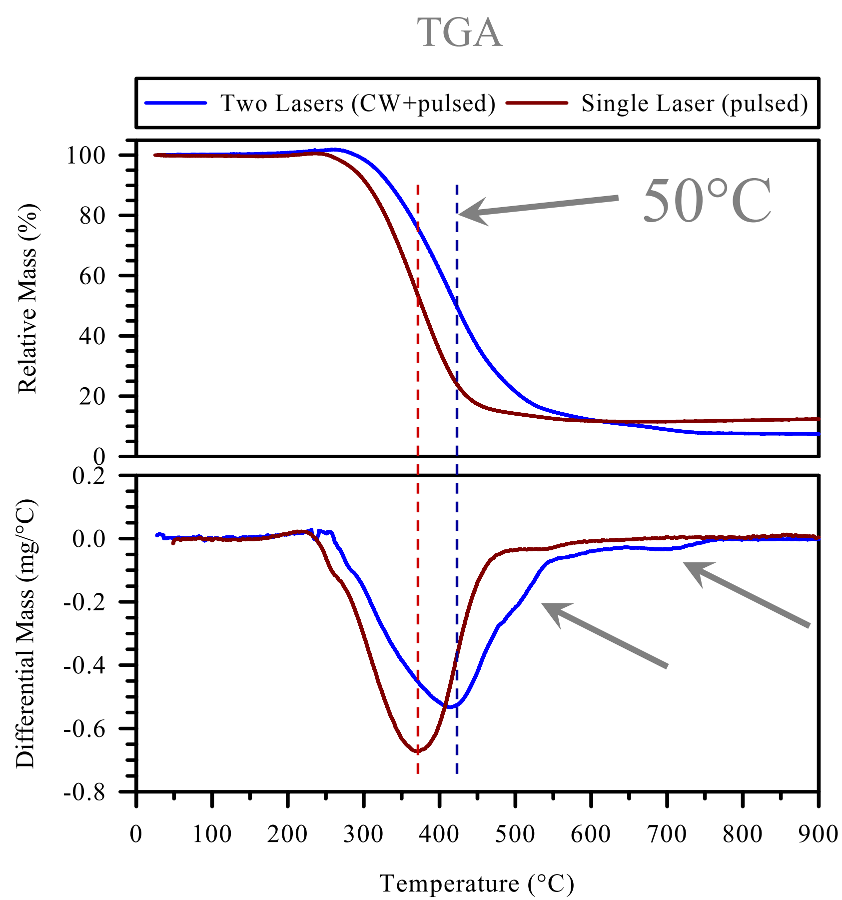
Pulsed + CW Method



Kingston et al., *Carbon* **42**, 1657 (2004).

Courtesy Chris Kingston NRC Canada





>400 mg/hr

~70 % SWNT

- CW Laser provides more efficient vaporization and modifies thermal gradients

Courtesy Chris Kingston NRC Canada

PHYSICAL REVIEW B, VOLUME 65, 245425

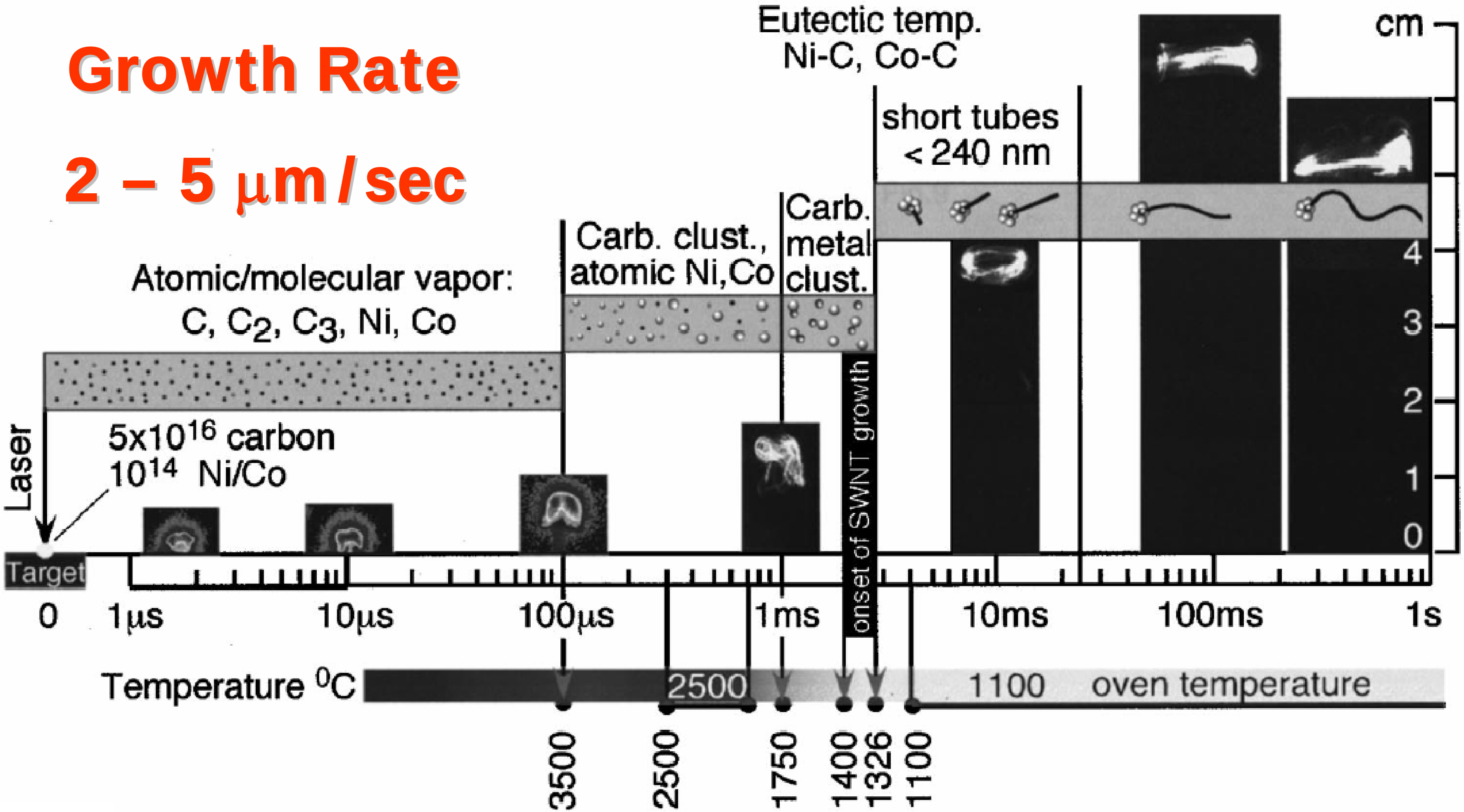
Investigations of single-wall carbon nanotube growth by time-restricted laser vaporization

(2002)

Alex A. Puretzky,[1,2] Henrik Schittenhelm,[1] Xudong Fan,[1*] Michael J. Lance,[1] Larry F. Allard Jr.,[1] and David B. Geohegan[1]

Growth Rate

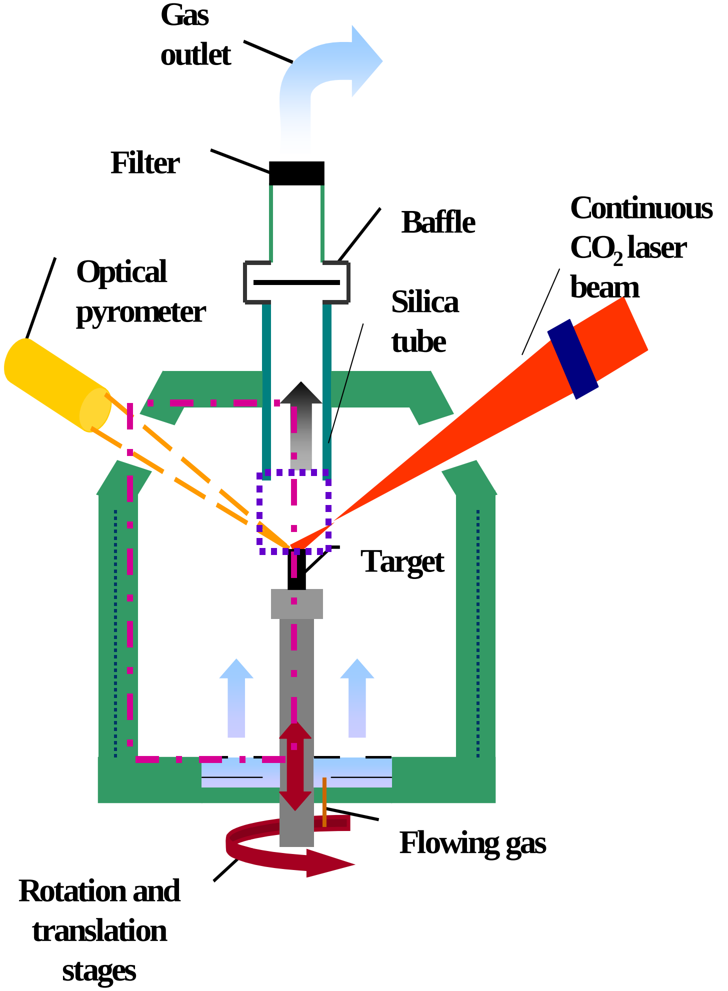
2 – 5 μm / sec



Summary of the results from the *in situ* imaging and spectroscopic diagnostic investigations of SWNT's growth inside a hot oven. Actual images of the laser plasma ($t < 200$ μs) and Rayleigh-scattering images of the plume ($t > 200$ μs) are shown vs time (scale in cm at right). During the first 100 μs after ablation, the laser plasma is very hot, and emission from excited atoms and molecules dominate LIF from ground-state species. Ground-state populations then peak and subsequently disappear due to condensation.

Continuous CNT synthesis laser reactor (Loiseau et al.)

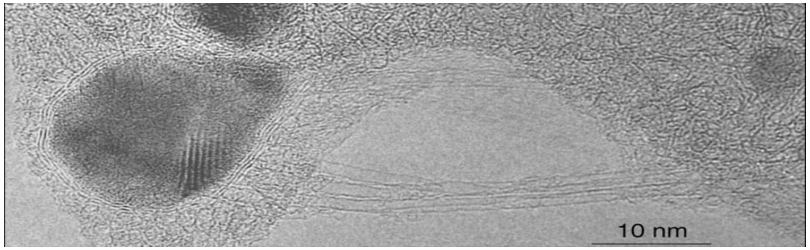
CW CO_2 laser vaporization



Conditions:

- \- target C:Co:Ni (98:2:2 at. %);
- \- helium 50 ml/s, 300 hPa;
- \- constant target surface
- temperature Ts: (3200-3500 K)
- ⇓
- SWNTs

ONERA-Palaiseau reactor



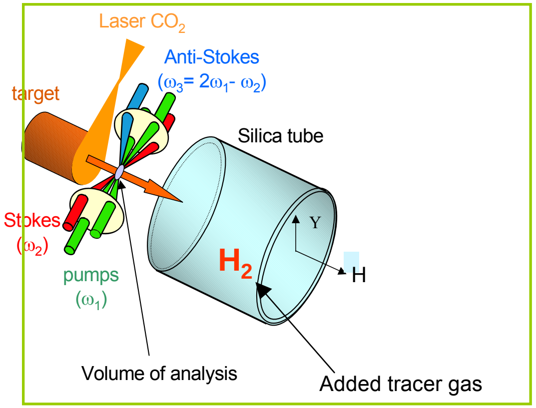
•Gavillet et al. in JNN 2004, 4, 346.

Courtesy A. Loiseau

ONERA

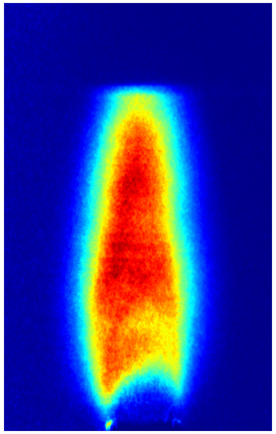
Laser-based techniques

CARS Thermometry



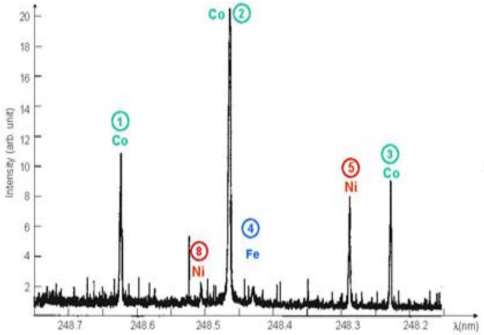
- **Coherent Anti Stokes Raman Scattering (CARS)**
- **local thermometry,** T

LII Image



- **Laser Induced Incandescence (LII)**
- **imaging carbonaceous aggregates and soot and volume fraction measurement (number density, sizes)**

LIF spectrum



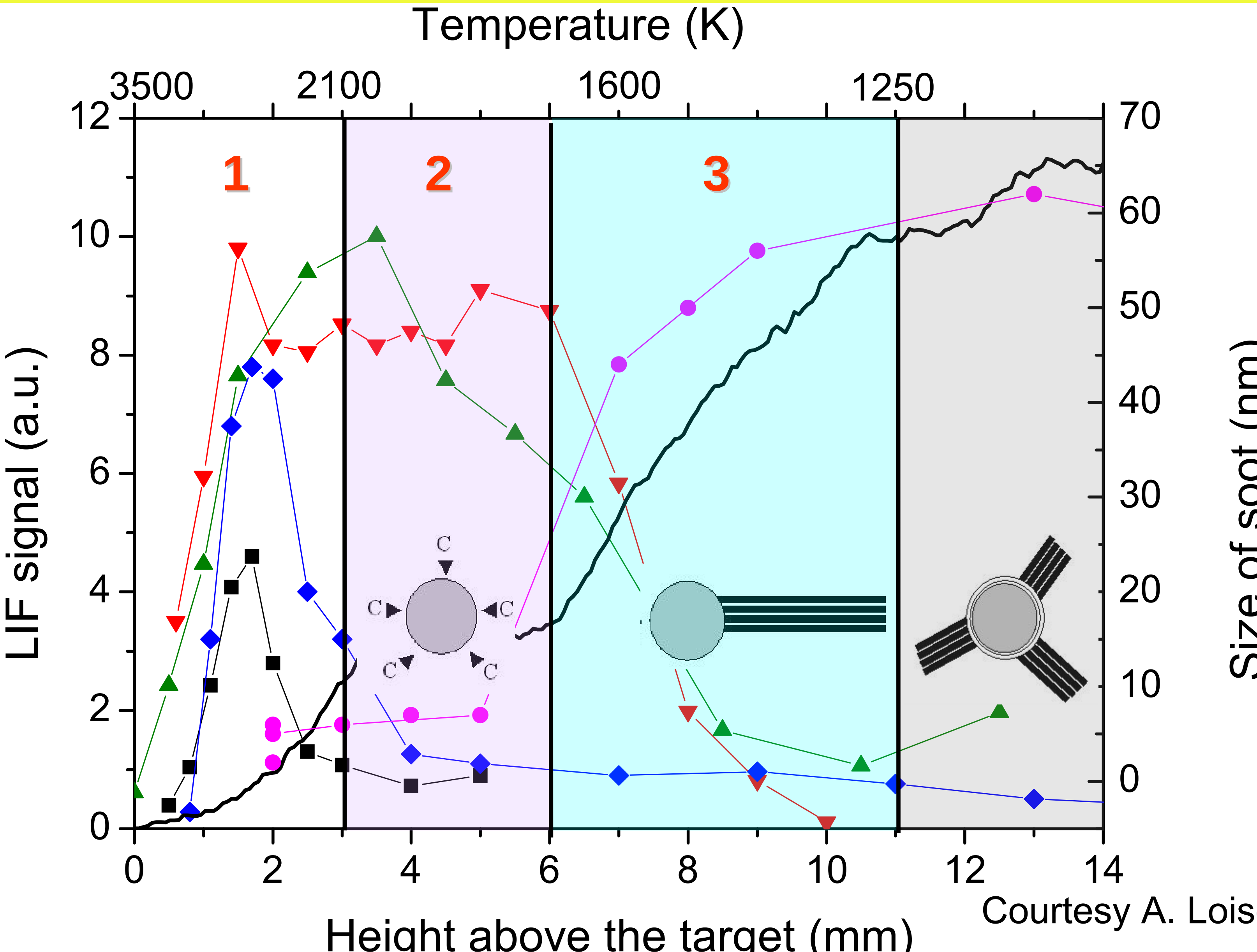
- **Laser Induced Fluorescence (LIF)**
  Diagnostic of atoms and small molecules
- Ni, Co, Fe, C_2, C_3

Preliminary results: *Dorval et al. in JNN 2004, 4, 450.*

Courtesy A. Loiseau

ONERA

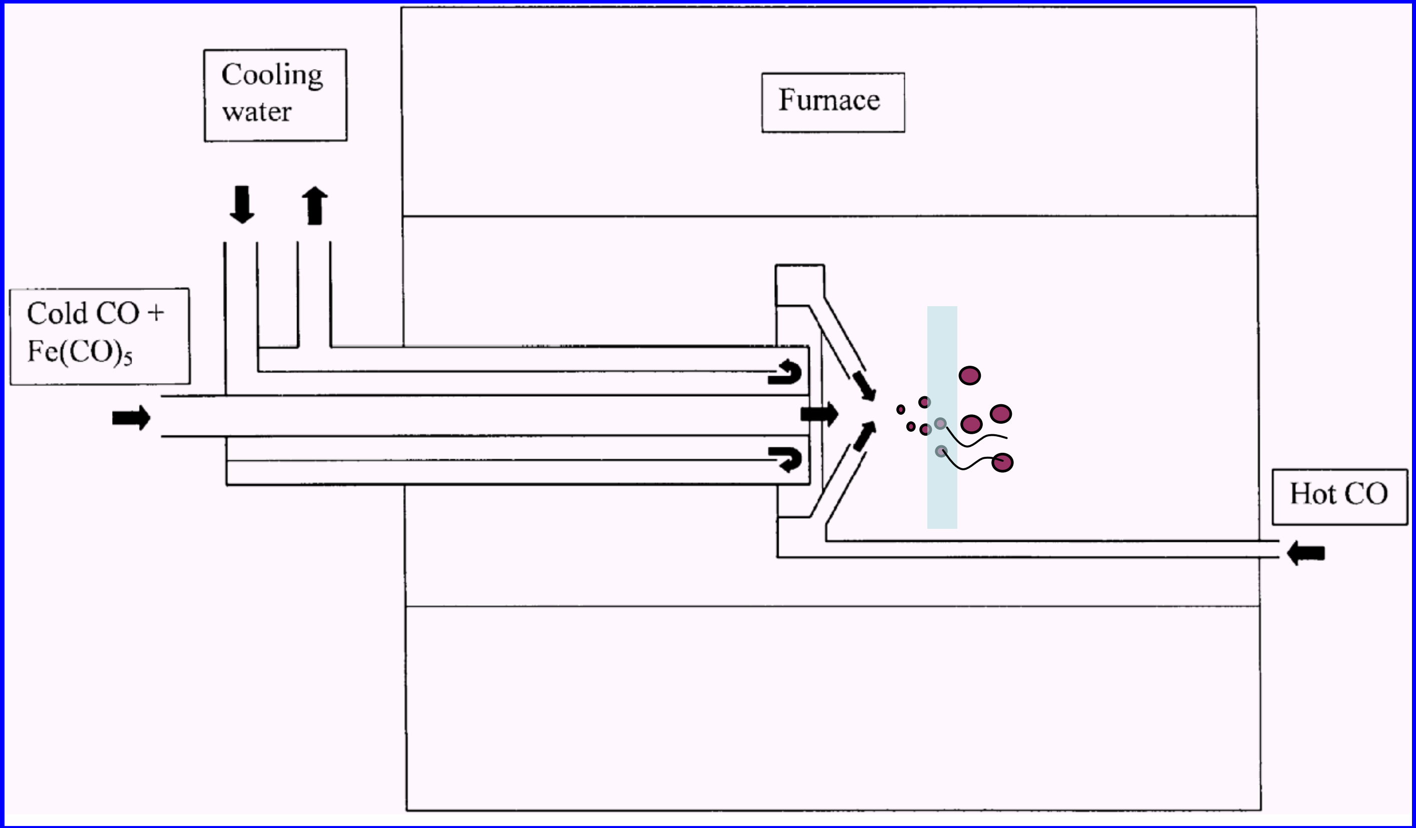
VLS model and measurements



Courtesy A. Loiseau

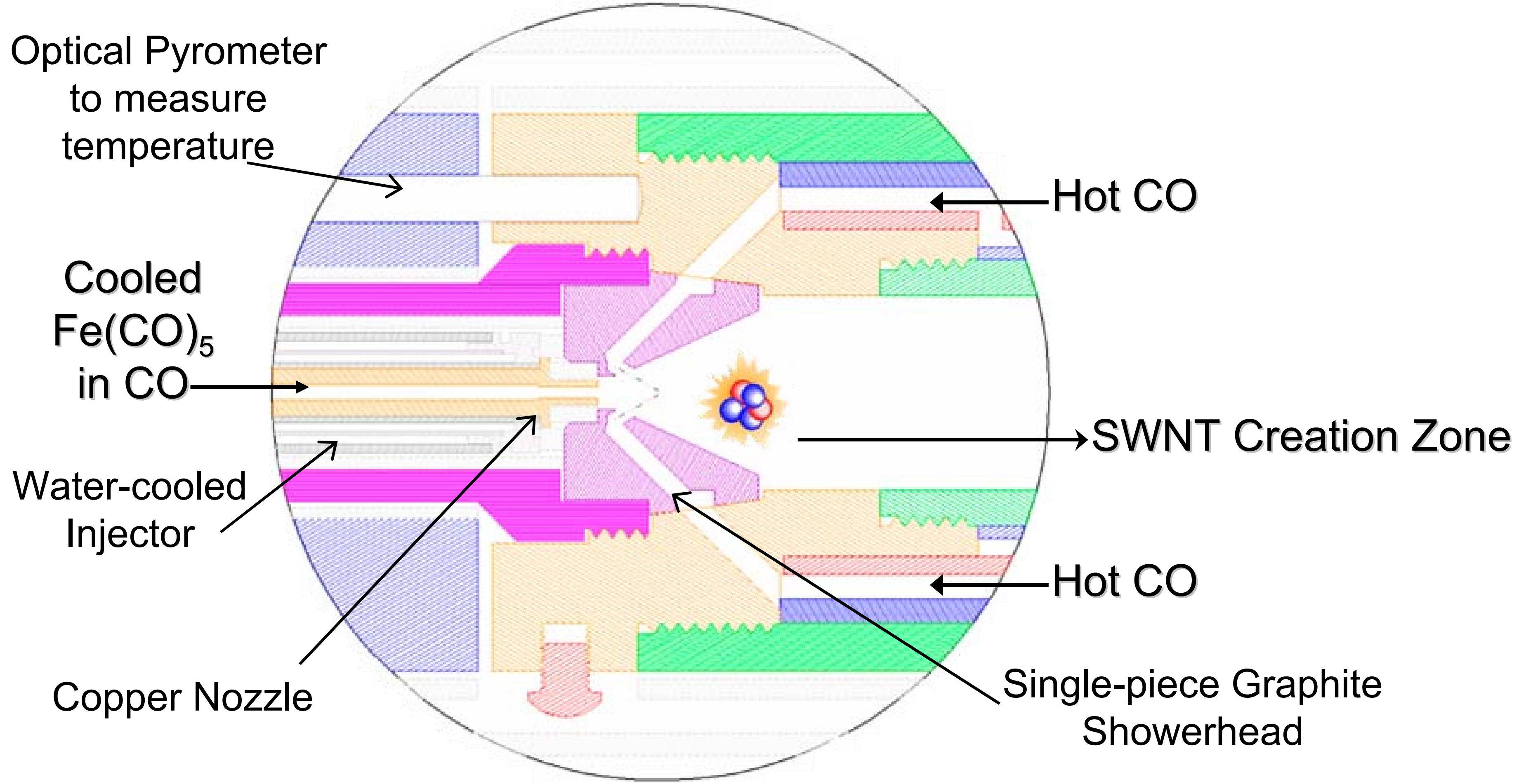
HiPCO: Gas-phase (floating catalyst CVD) method for SWNT production

Smalley et al. Chemical Physics Letters 313 (1999) 91–97



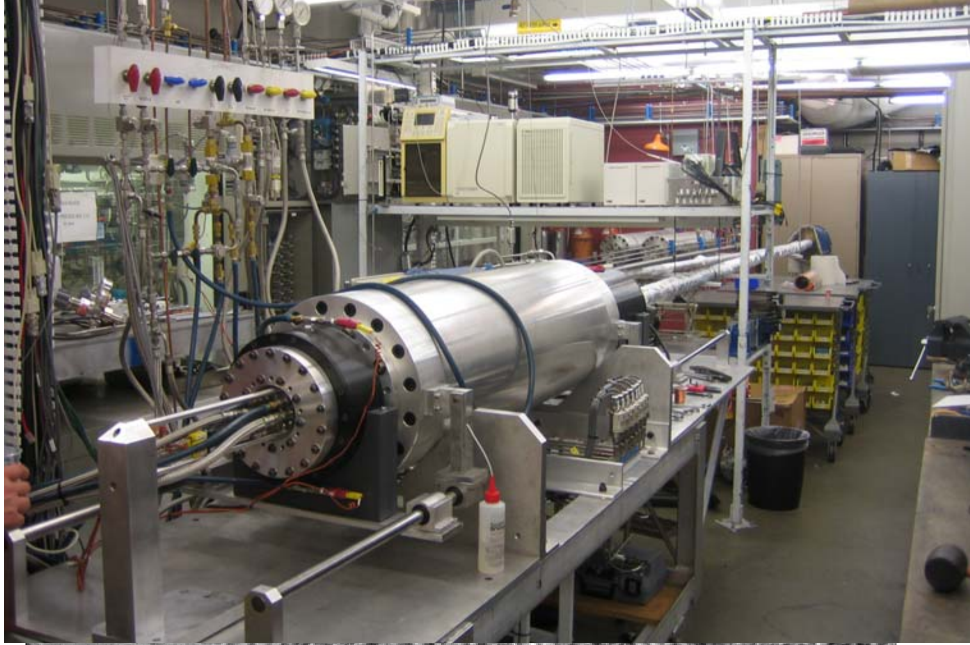
$Fe(CO)_5$ decomposition in high-pressure CO

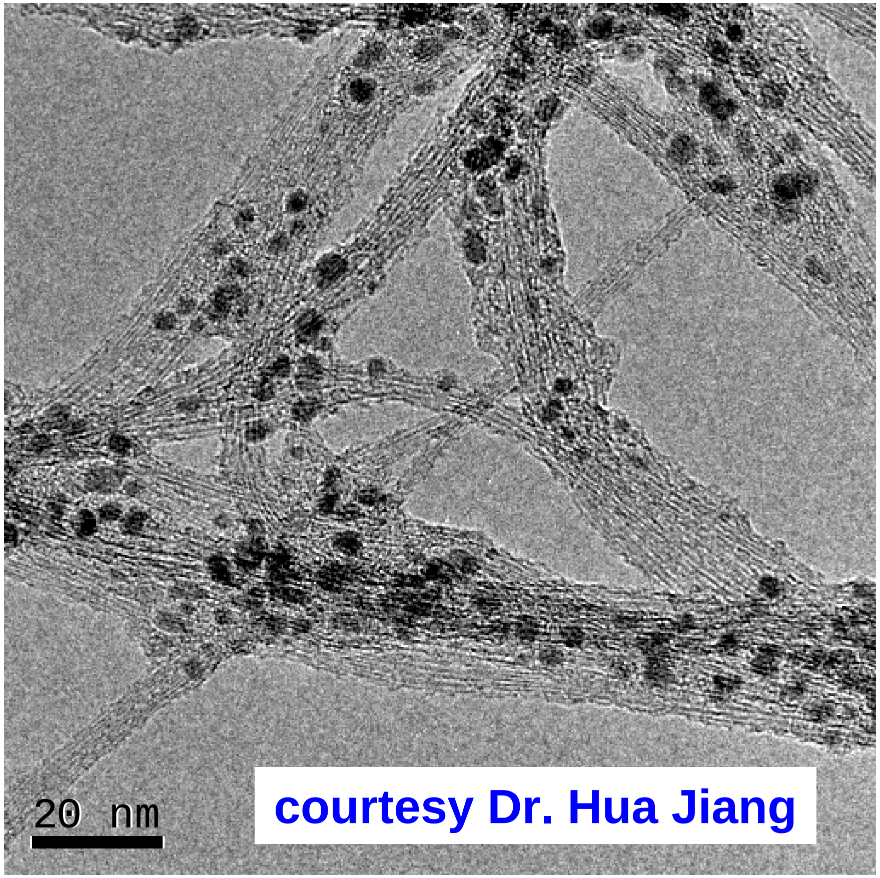
HiPco Mixing Zone



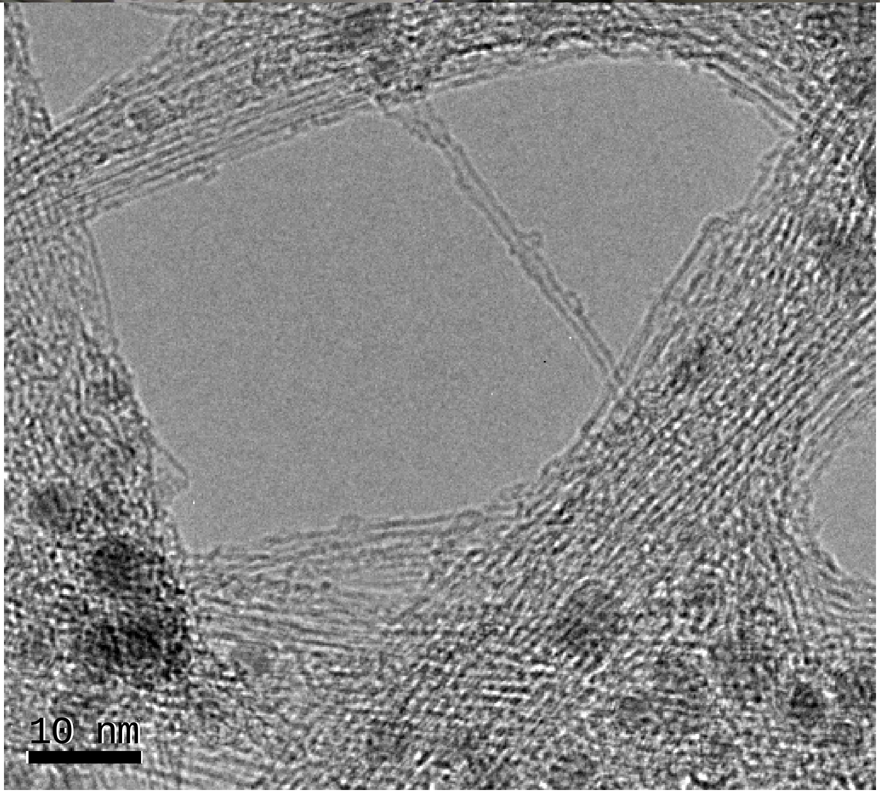
Courtesy R. Hauge

Commercial SWCNT’s made with traditional Floating Catalyst Method (HiPCO method, CNI)



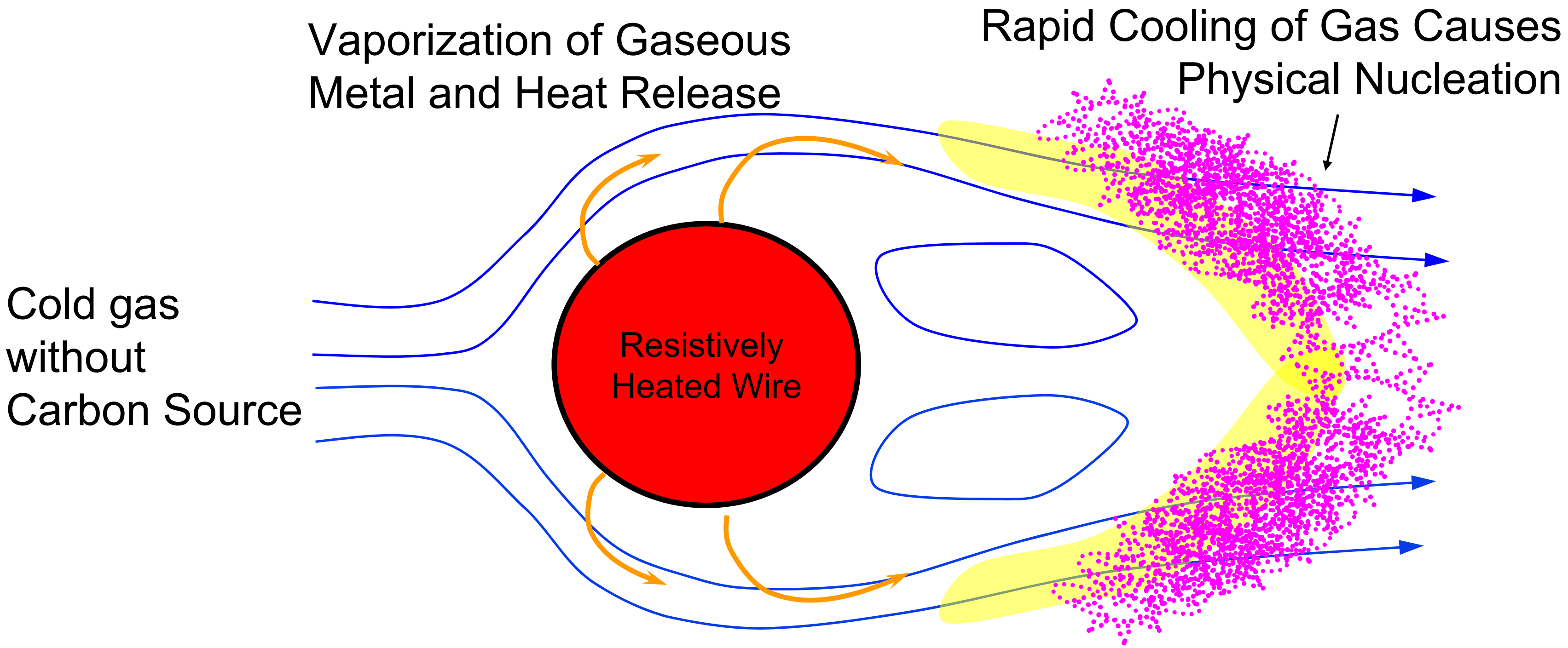


courtesy Dr. Hua Jiang



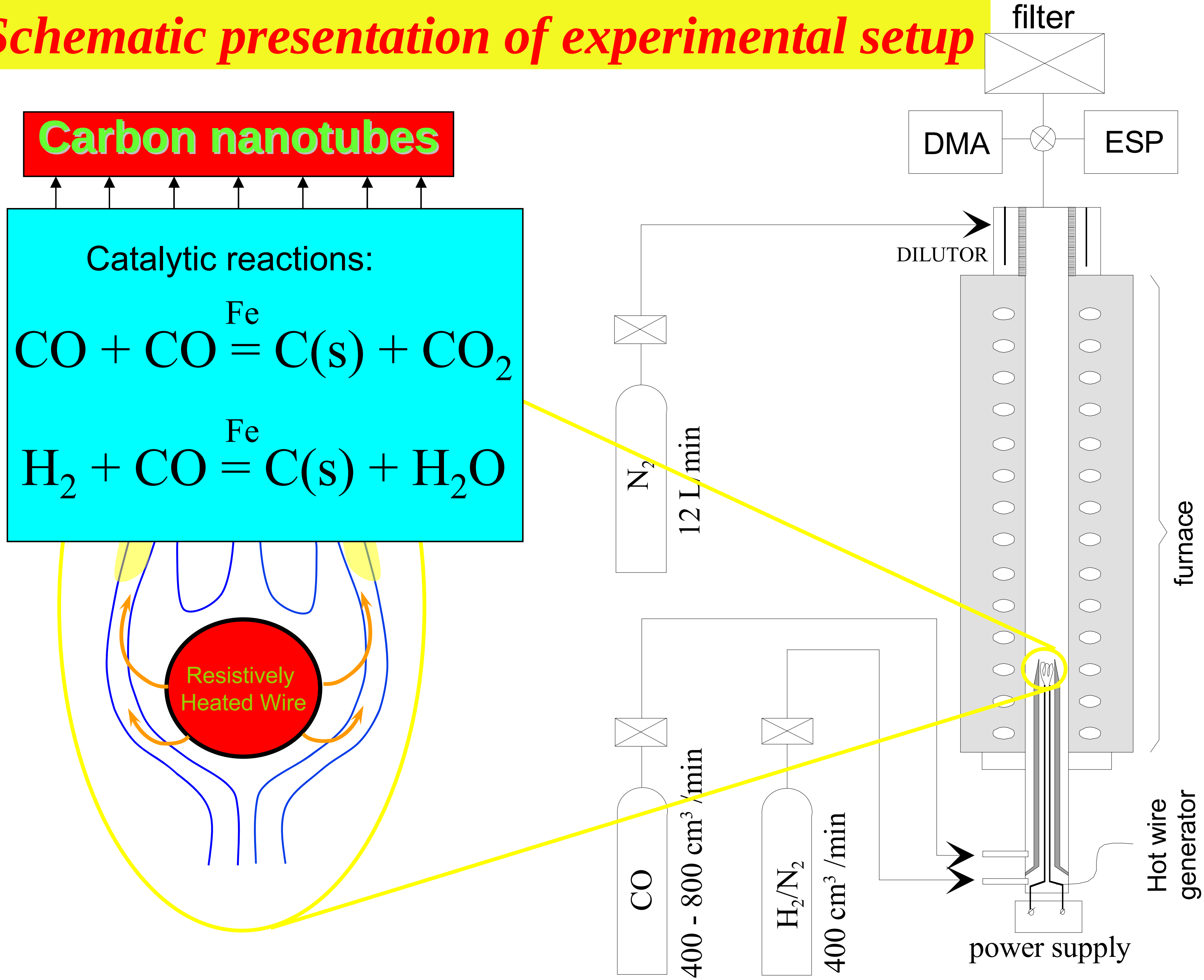
A novel floating catalyst method for SWCNT synthesis

Nasibulin, A. G., Moisala, A., Brown, D. P, Jiang, H. and Kauppinen, E.I. (2005) A novel aerosol method for single walled carbon nanotube synthesis. Chemical Physics Letters 402, 227 - 232.

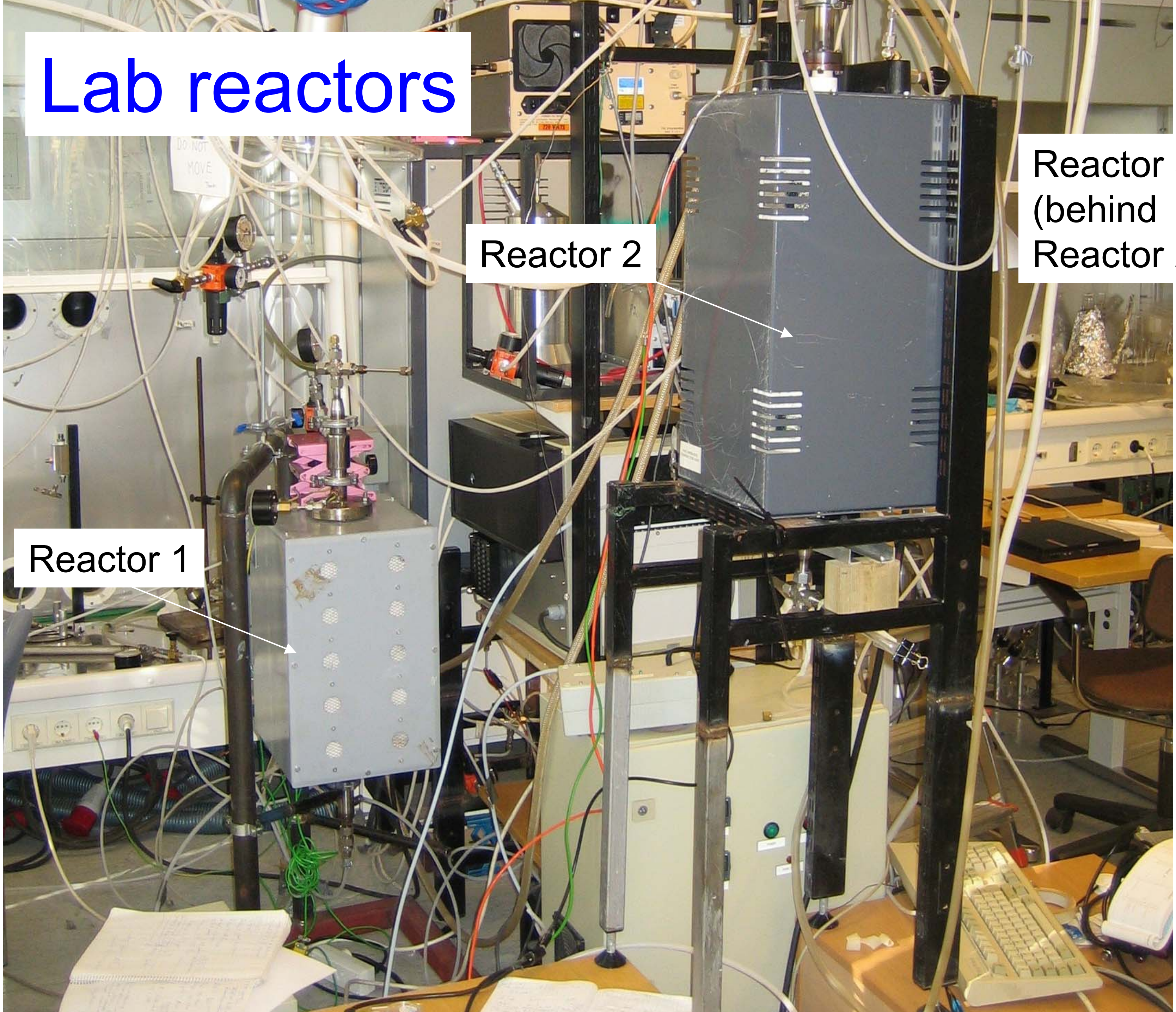


<u>Physical Production (PVD)</u> of Catalyst Clusters via Vapor Nucleation-Condensation using Hot Wire Generator (HWG)

Schematic presentation of experimental setup



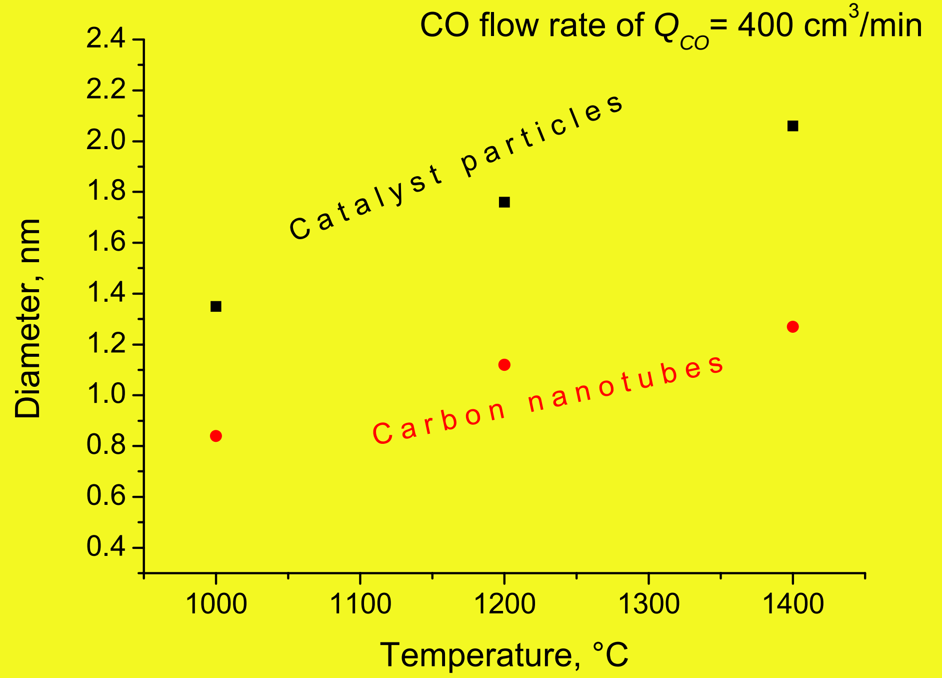
Lab reactors

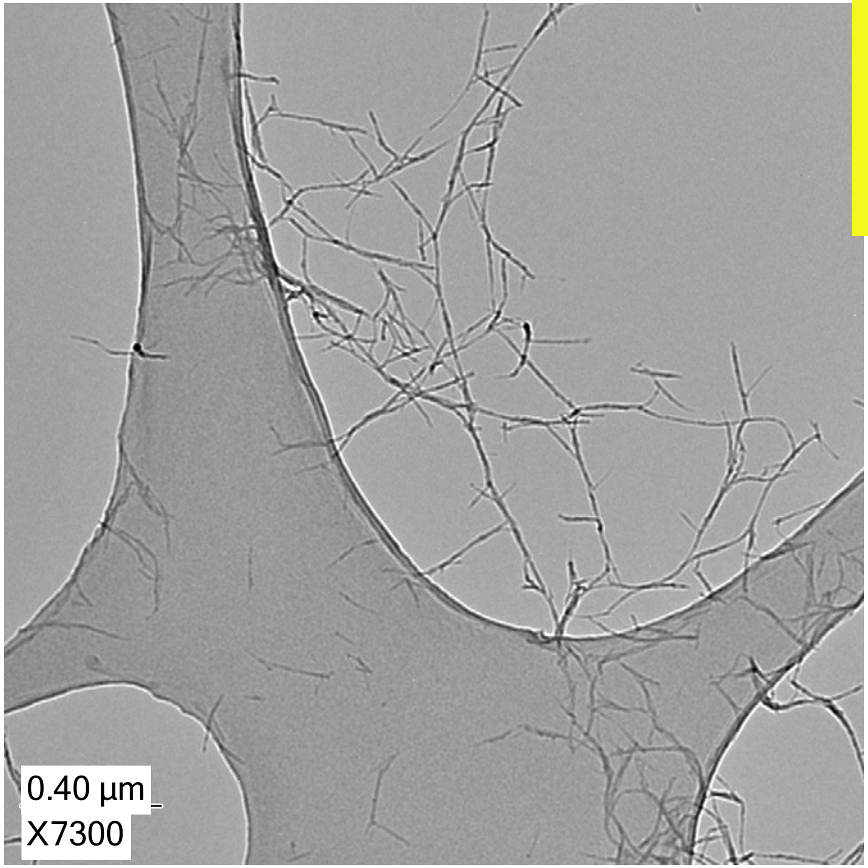


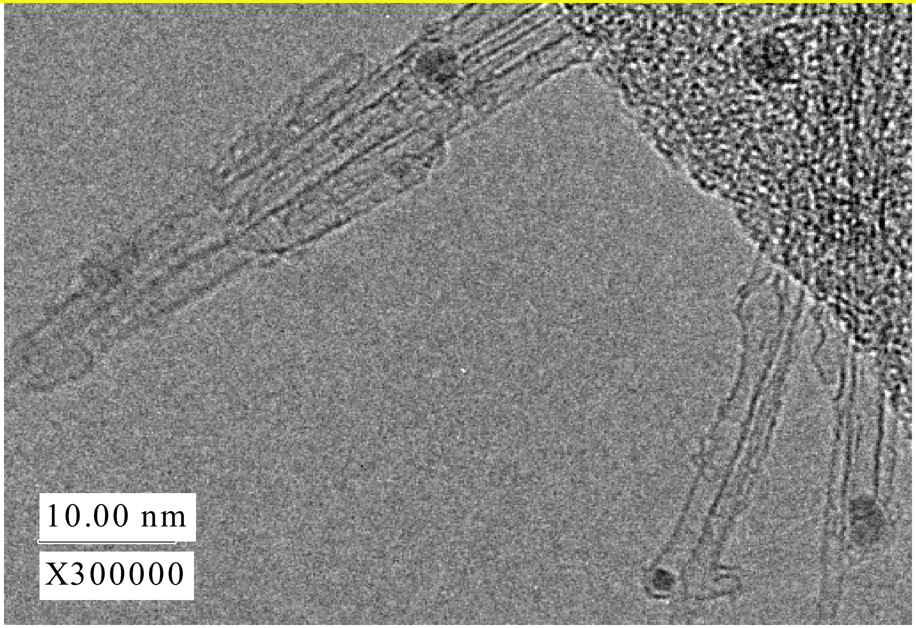
Early results -50 nm long SWNT's (1200 ºC)

$D_{part}/D_{CNT} = 1.6$

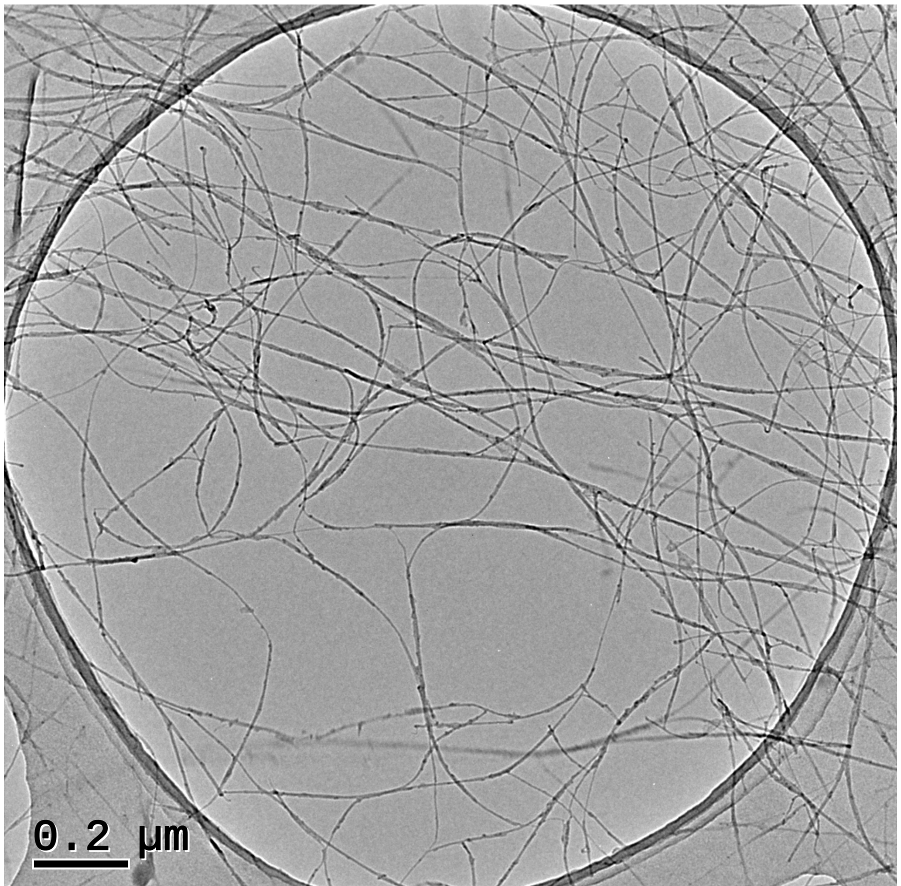
A.G. Nasibulin, P. V. Pikhitsa, H. Jiang, E. I. Kauppinen (2005). *Carbon.* **3**(11), 2251-2257.

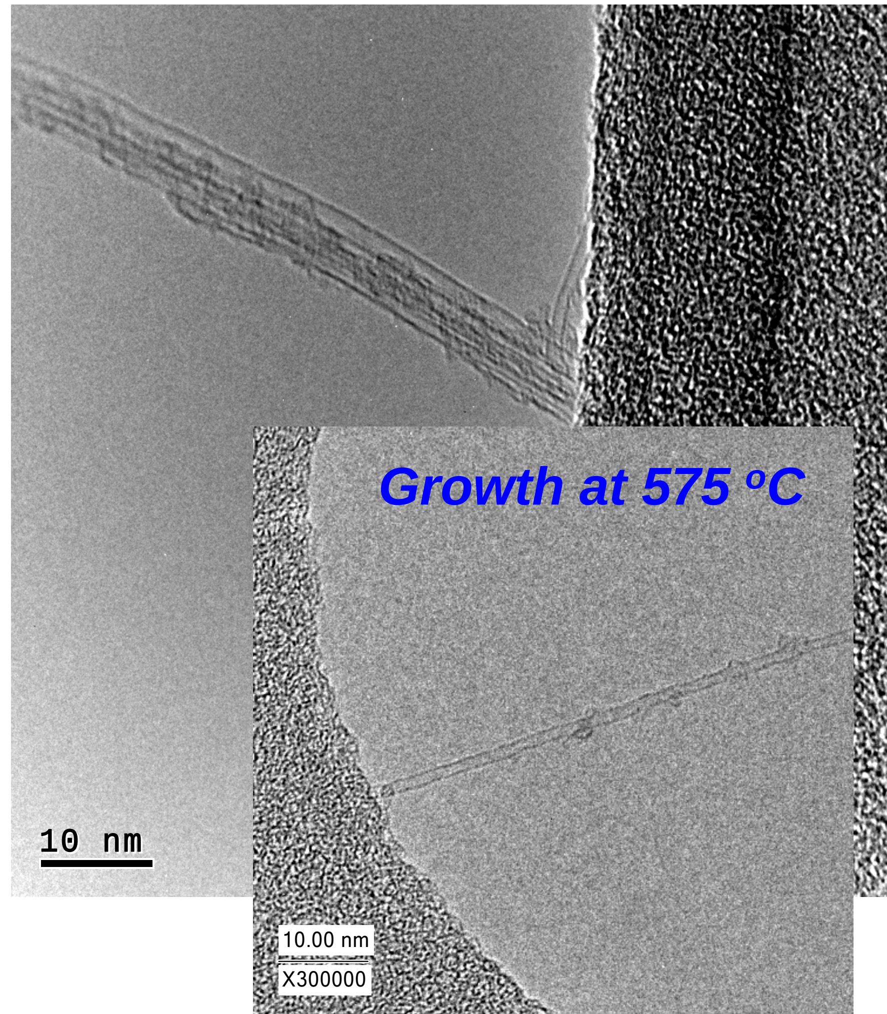






TEM images of longer SWCNT's at 924 ºC with stainless steel rector tube using CO as carbon source and H_2/N_2 mixture through the Fe catalysts cluster source.





When & where SWCNT's nucleate - *in situ* sampling.

Q_{tot}=800 scm³/min

⇒3150 cm³/min (at 900 ° C).

L=1.5 cm (894 - 908 °C)

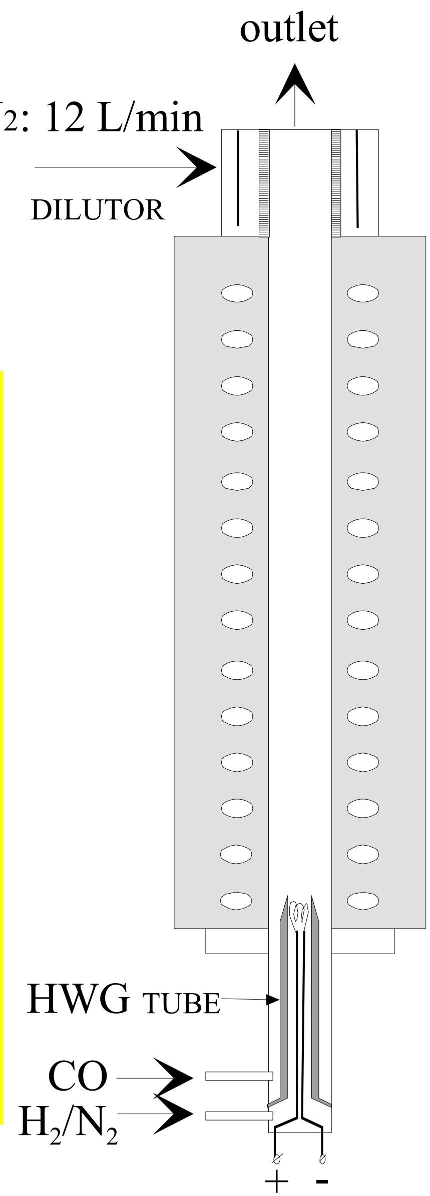
Centerline sampling:

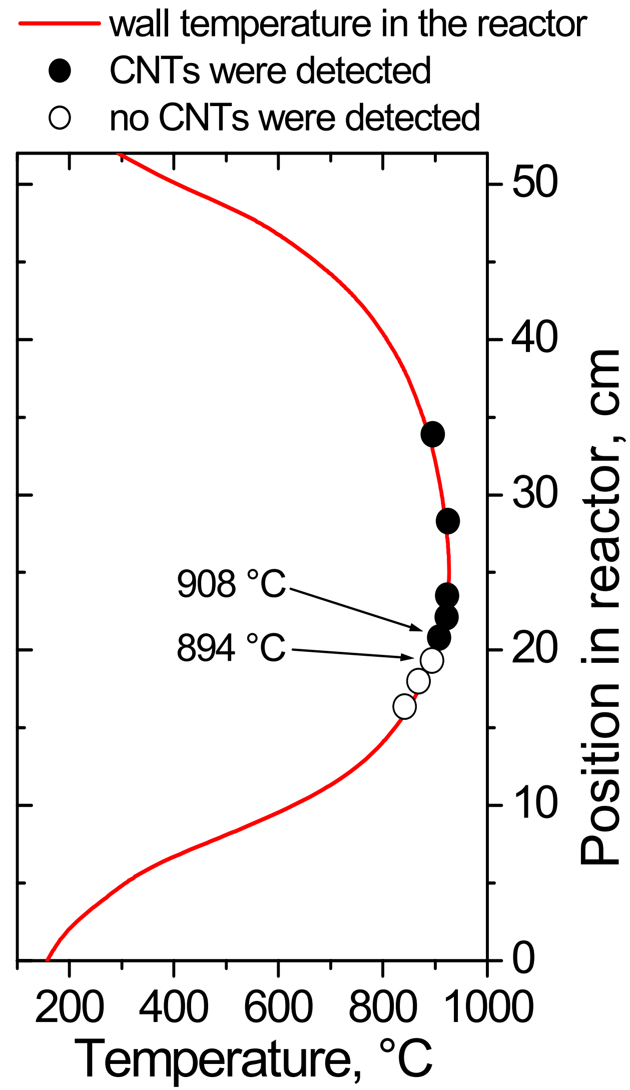
Residence time: τ = 0.054 s.

CNT length *l* = 60 nm.

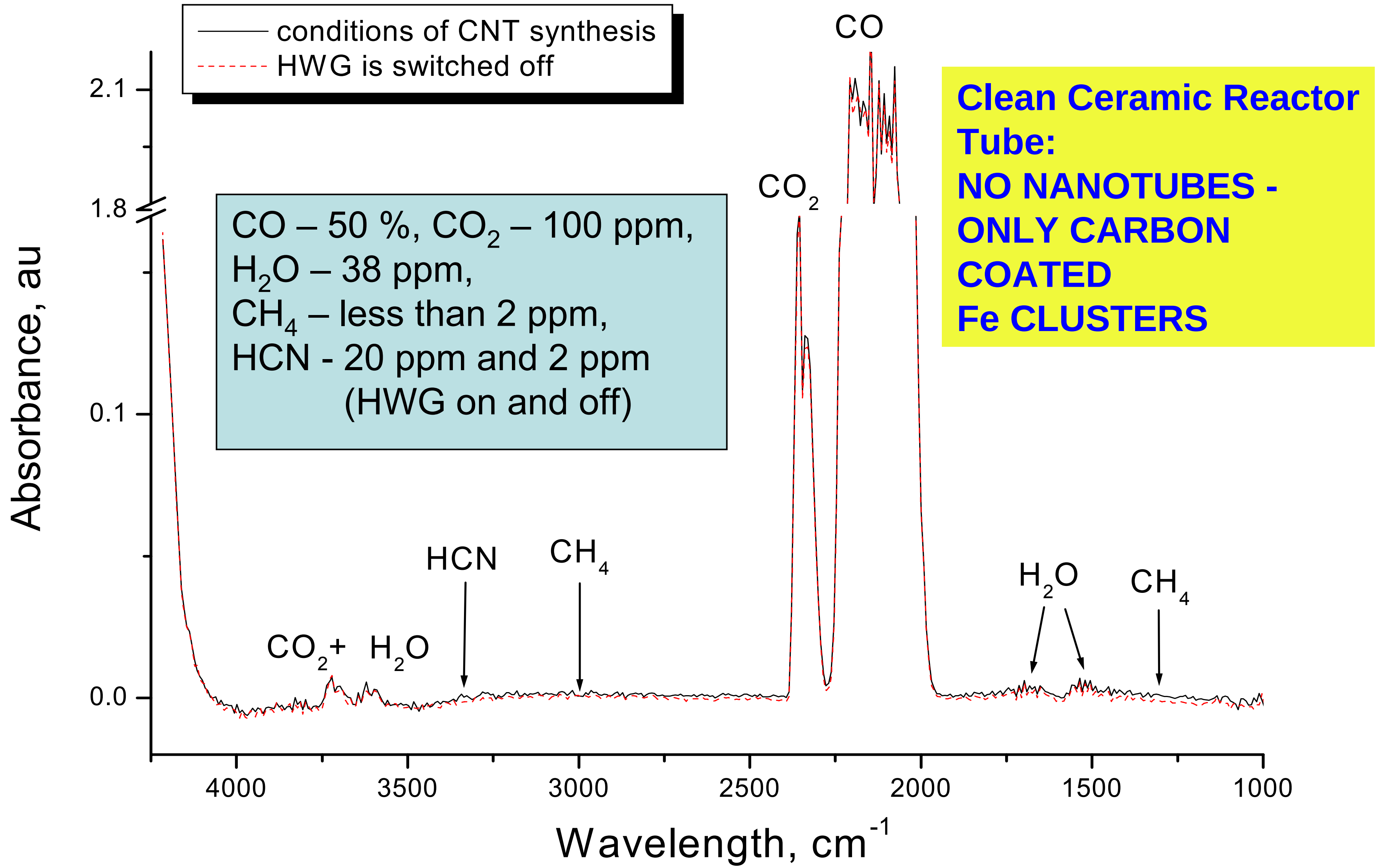
⇒ **CNT growth rate** exceeds

1.1 μm/s





Comparison of FT-IR spectra obtained at the conditions of CNT synthesis at 924 ºC and after switching HGW off - stainless steel reactor tube



Reactor wall conditions important due to the synthesis of small amount of H_2O and CO_2 at SS (or catalyst covered) reactor surfaces !

Similarly, adding oxidant to aid SWNT forest growth :

*** water - Hata et al.**

*** oxygen – Dai et al.**

*** alcohol – Maruyama et al., Windler et al. etc.**

CO_2 – 100 ppm,
H_2O – 38 ppm,
CH_4 – less than 2 ppm,
HCN - 20 ppm and 2 ppm (HWG on and off)

$$CO + CO \Leftrightarrow C(s) + CO_2$$

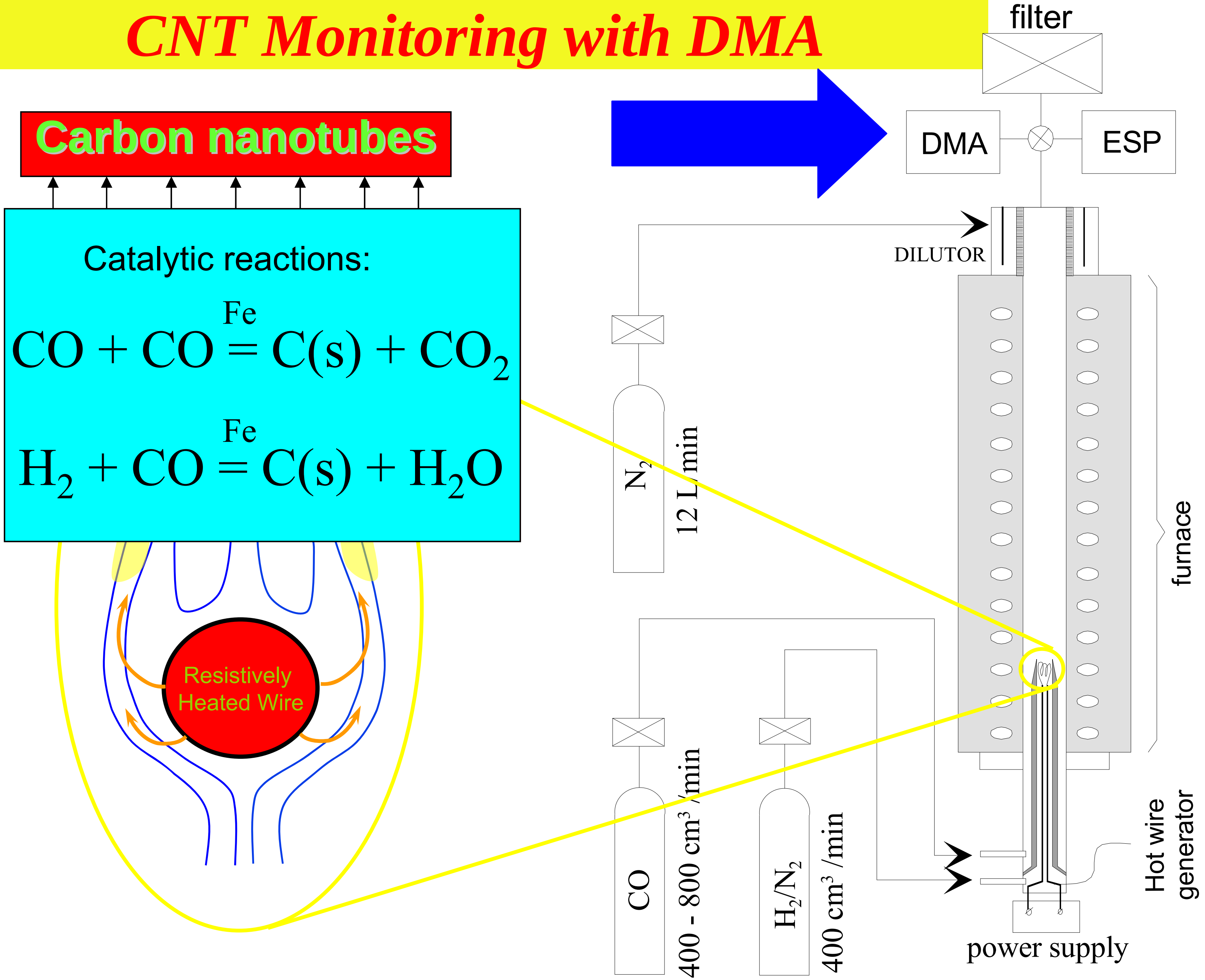
$$H_2 + CO \Leftrightarrow C(s) + H_2O$$

Effect of experimental conditions on the CNT length -

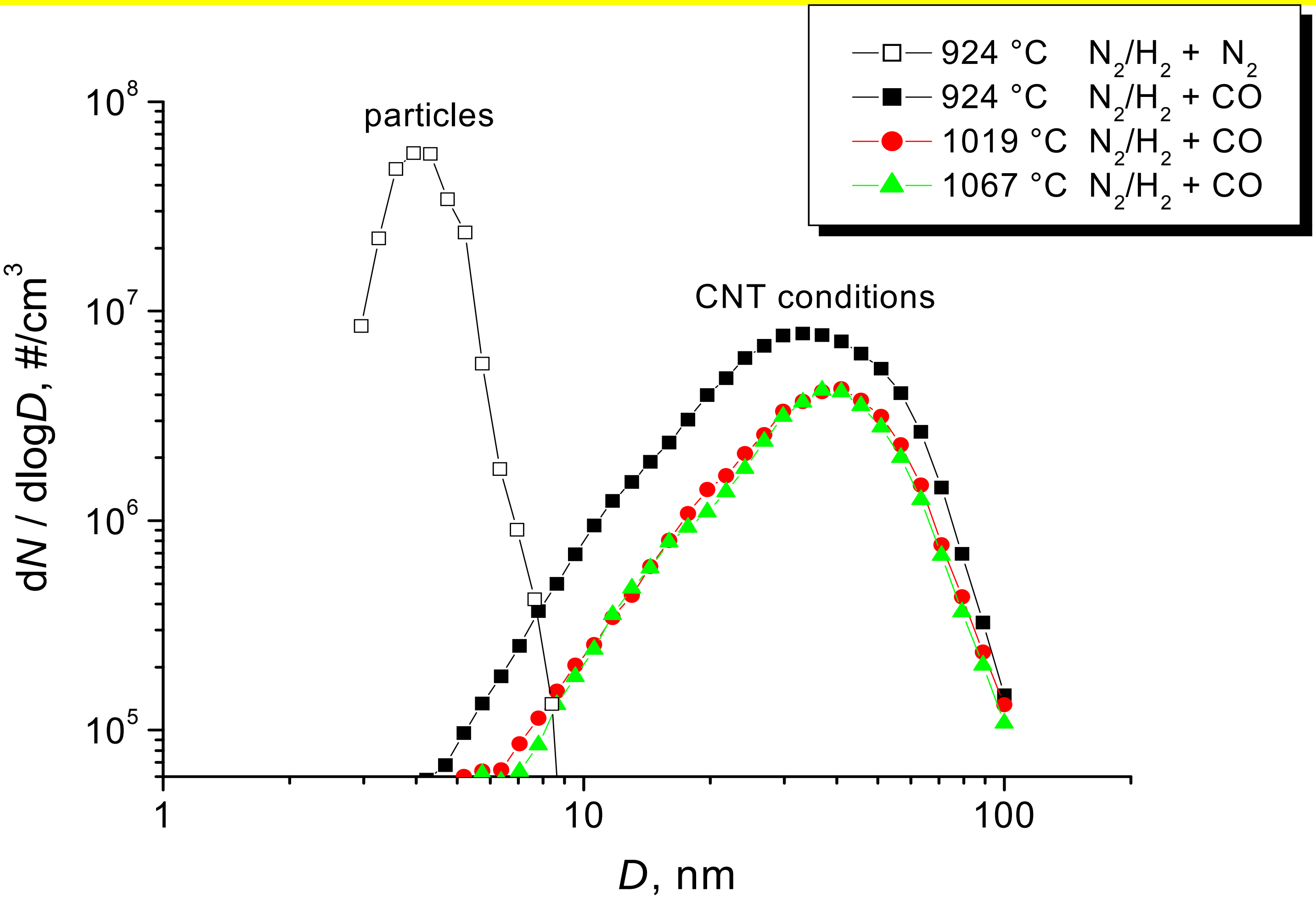
CNTs are 60 nm long in $CO+H_2/N_2$ with 2 s ave res. time

Additives	Concentration	Results
CH_4	1000 ppm	no effect on length
H_2O	0, 150, 330 ppm	up to 300 nm long
CO_2 (clean reactor)	1000 ppm	length up to 200 nm
H_2	50 %	up to 500 nm

CNT Monitoring with DMA

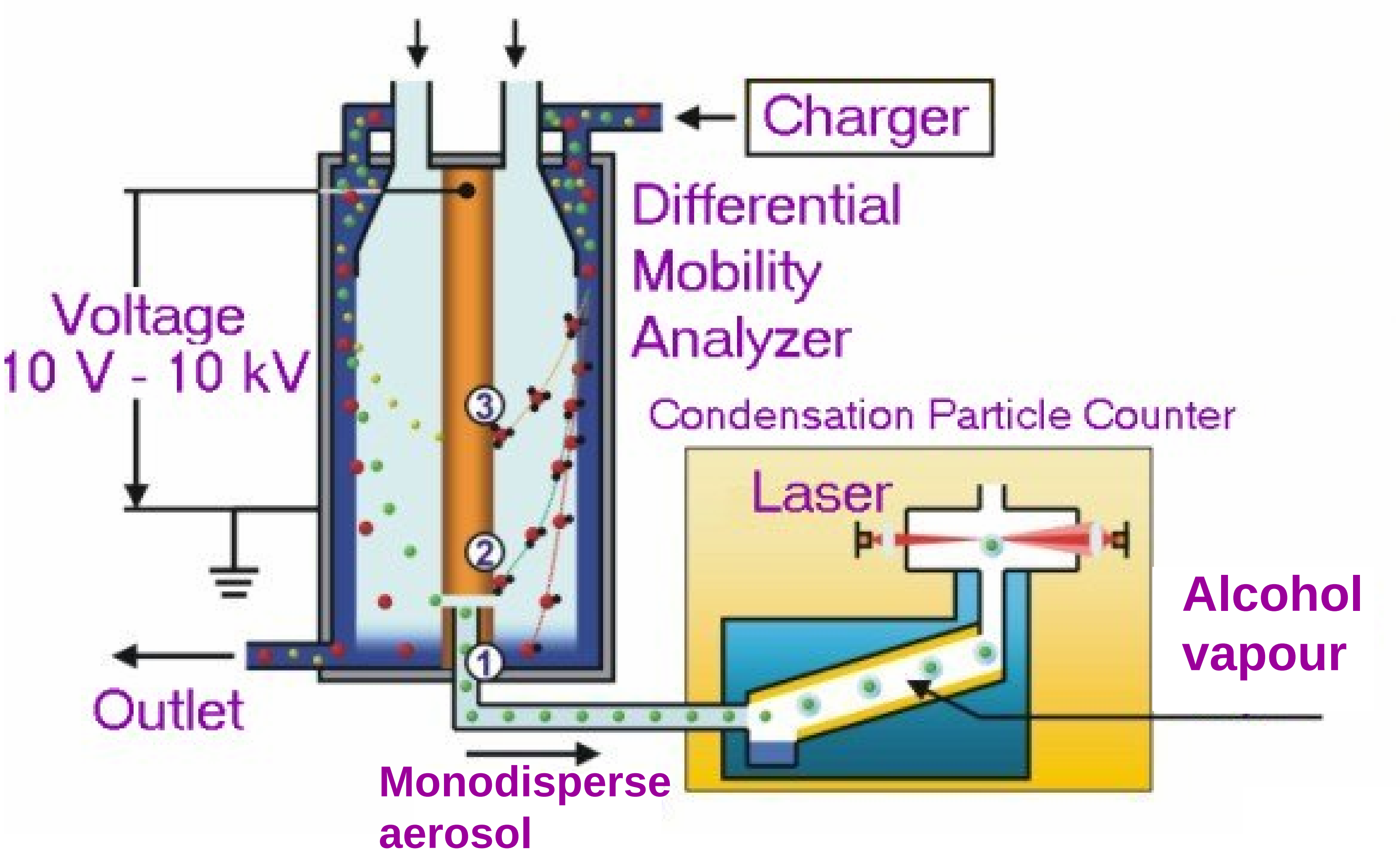


Monitoring SWCNT production via number size distributions of the aerosol product measured by DMA after the reactor (stainless steel tube)



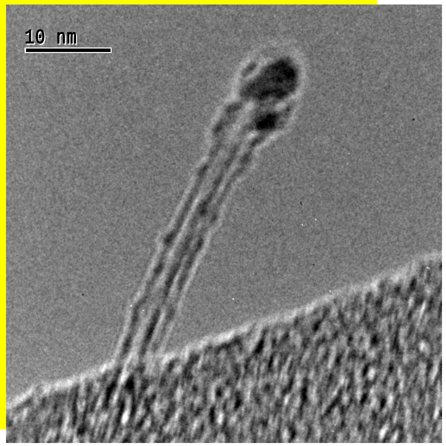
Moisala A., Nasibulin A.G., Shandakov S.D., Jiang H. and Kauppinen E.I. (2005) On-line detection of single-walled carbon nanotube formation during aerosol synthesis method. *Carbon* **43**, 2066-2074.

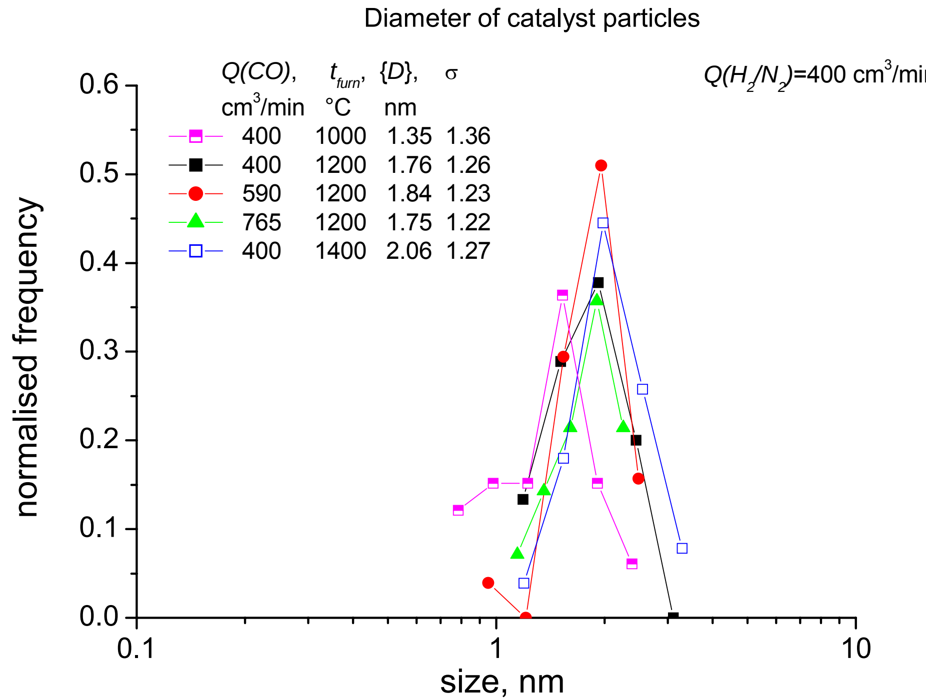
Real-Time Monitoring of CNT Formation: DIFFERENTIAL ELECTRICAL MOBILITY ANALYSER (DMA)

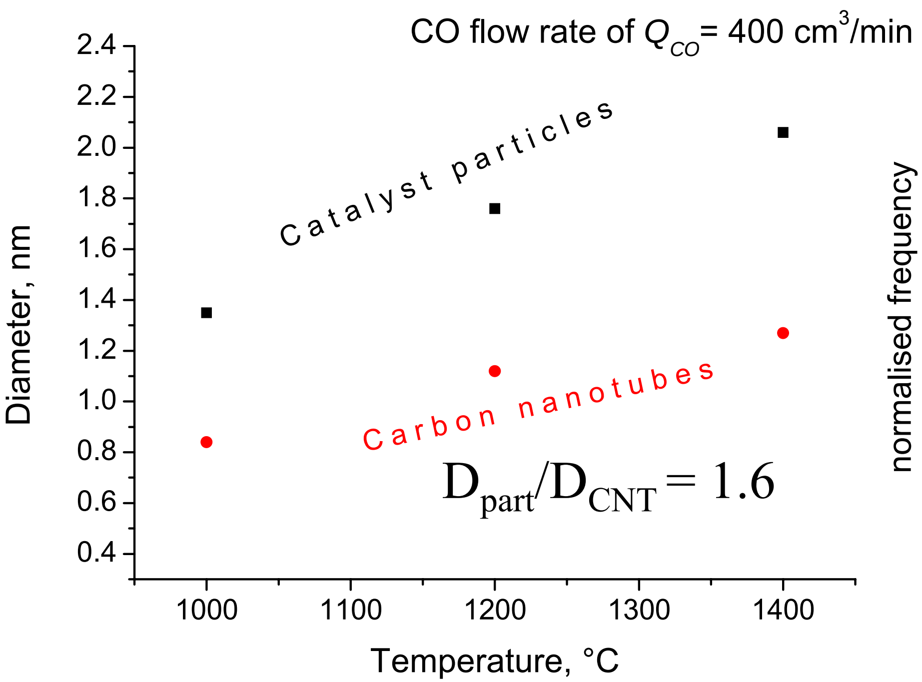


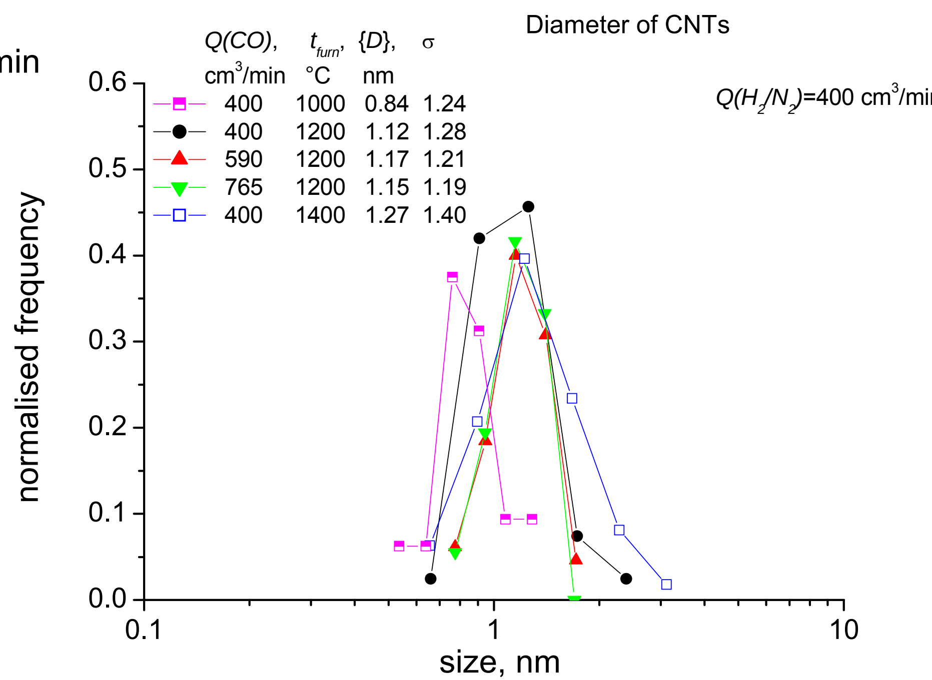
Potential difference (V)→ Mobility (cm^2/Vs)→ Particle size (nm)

Correlation between diameter of Fe particles and SWCNTs – controll of CNT and Catalyst size

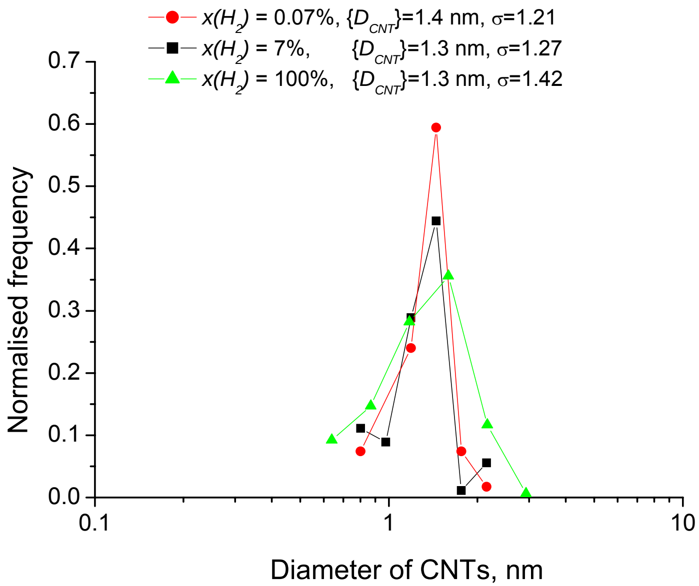






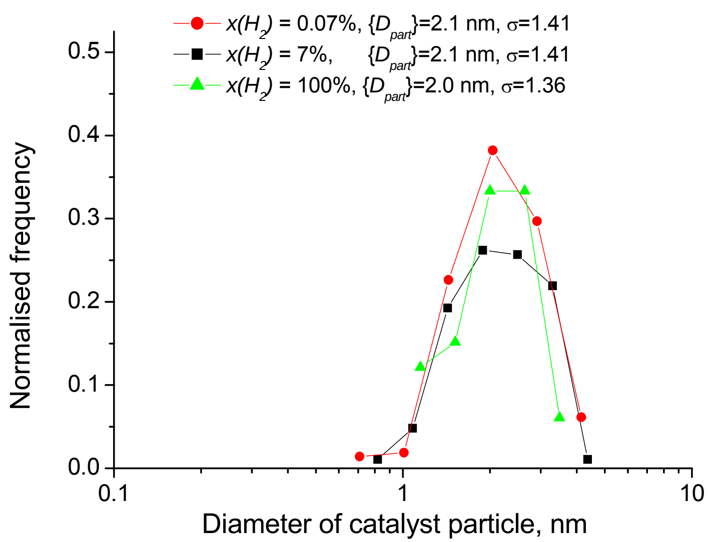


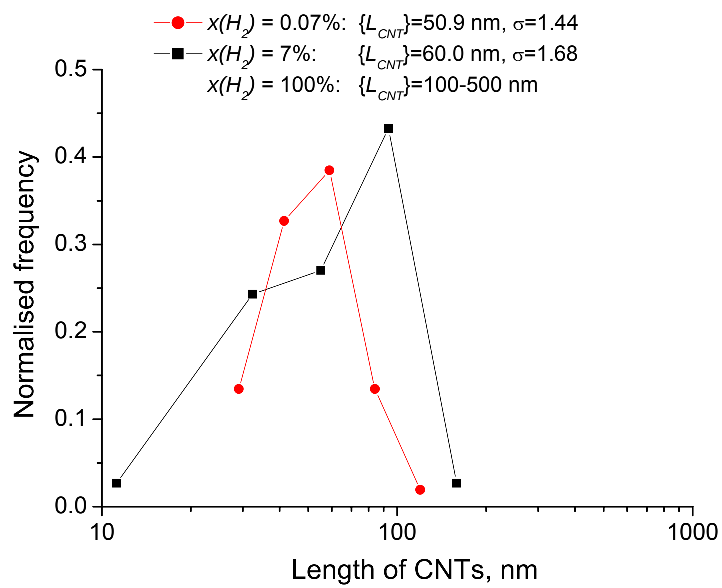
$D_{catalyst}/D_{CNT}$ ratio constant at higher growth rates ?



YES

Number distributions of CNT diamaters and lengths and catalyst particle diameters for different concentrations of H_2 at 924 ºC





Ratio between diameters of catalyst particles and CNTs

Pre-made Fe particles introduced in conditions of CNT formation

Experimental conditions		Ratio
t_{furn}, °C	Q_{CO}, cm³/min	D_{part}/D_{CNT}
1000	400	**1.60**
1200	400	**1.57**
1200	590	**1.57**
1200	765	**1.52**
1400	400	**1.62**

H_2 concentration	D_{CNT}, nm	D_{Fe}, nm	D_{part}/D_{CNT}
0.07	1.4	2.1	**1.50**
7	1.3	2.1	**1.62**
100	1.3	2.0	**1.54**

Ethanol, t_{furn}=1200 °C:
D_{CNT} = 1.7 nm, D_{Fe} = 2.4. D_{part}/D_{CNT} = **1.41**

In-situ CVD Synthesis of Particles :

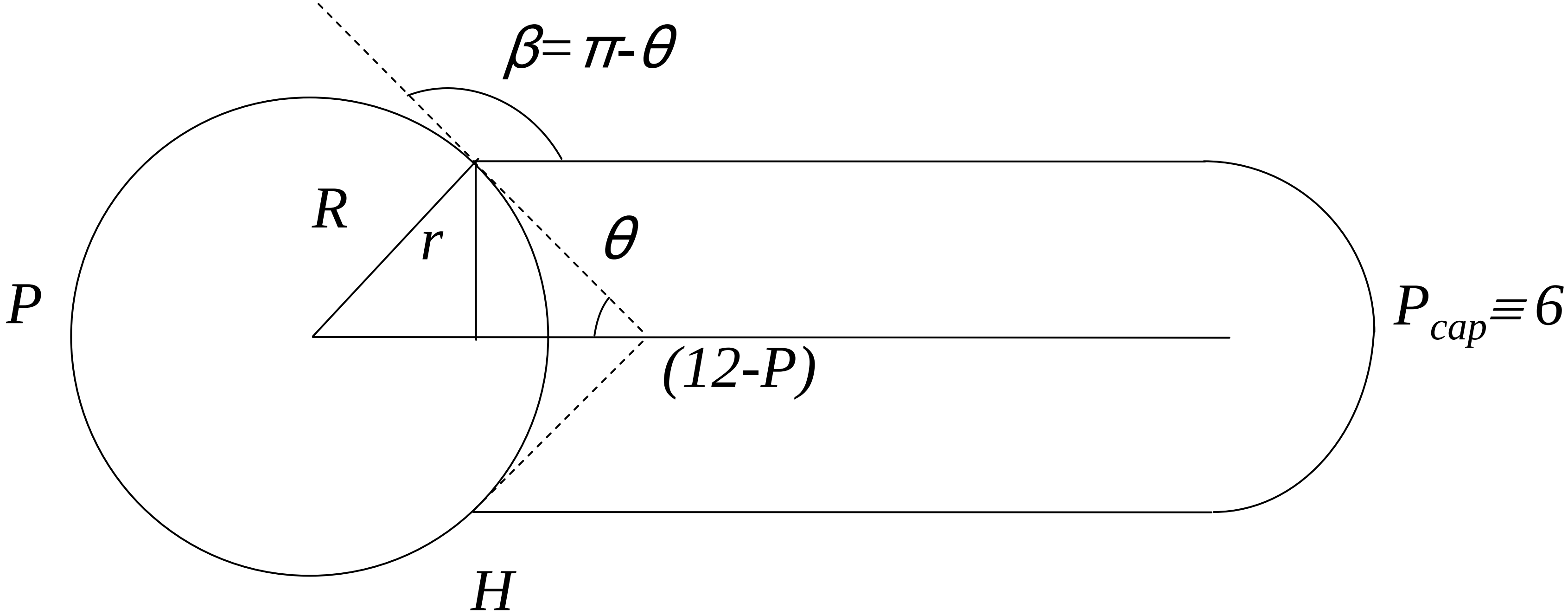
Ferrocene vapor decomposition in CO at 1150 °C
D_{CNT} = 1.3 nm, D_{part} = 3.1 nm
D_{part}/D_{CNT} = **2.4**
MORE DETAILS LATER

HiPco CNTs
(Nikolaev *et al.* ChemPhysLett 1999)
D_{CNT} = 0.7-1.4 nm, D_{part} = 5-10 nm
D_{part}/D_{CNT} > **3**

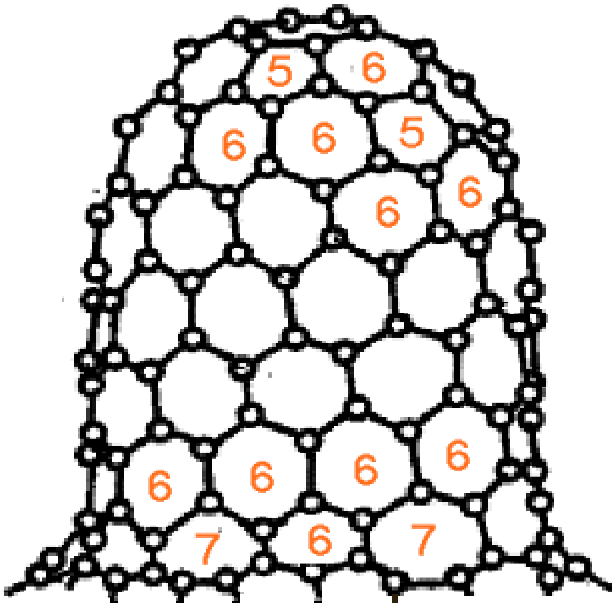
The schematic of the CNT growth geometry

(Nasibulin, Pikhitsa, Jiang, Kauppinen, “Correlation between catalyst particle and single-walled carbon nanotube diameters”, *Carbon* **43**(11), 2251-2257).

$$2R/2r = 1/\cos(\theta) = 1/\sqrt{1-(H/6)^2}$$



Examples of pentagon and heptagon defects



Schematic presentation of CNT topology: walls consist of hexagons (6); to close the tube six pentagons (5) are needed; to make negative curvature (to join a CNT and a particle) a number of heptagons (7) is required.

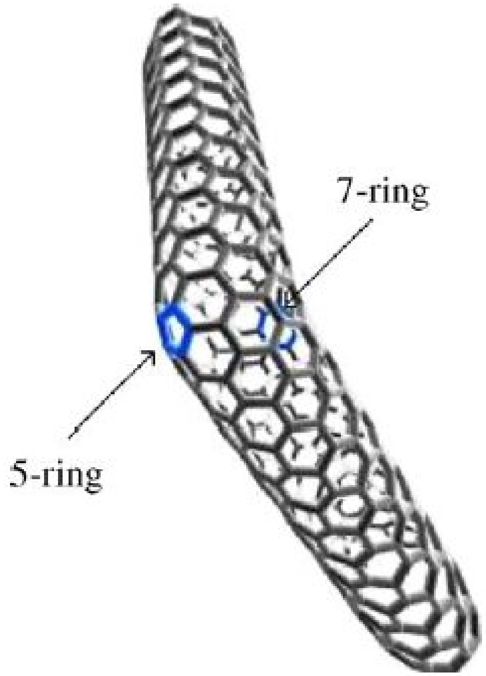


Fig. 10. Model of a nanotube kink junction, with 5- and 7-rings; the tube segment at the top can be metallic whereas the bottom segment is semiconducting [32].

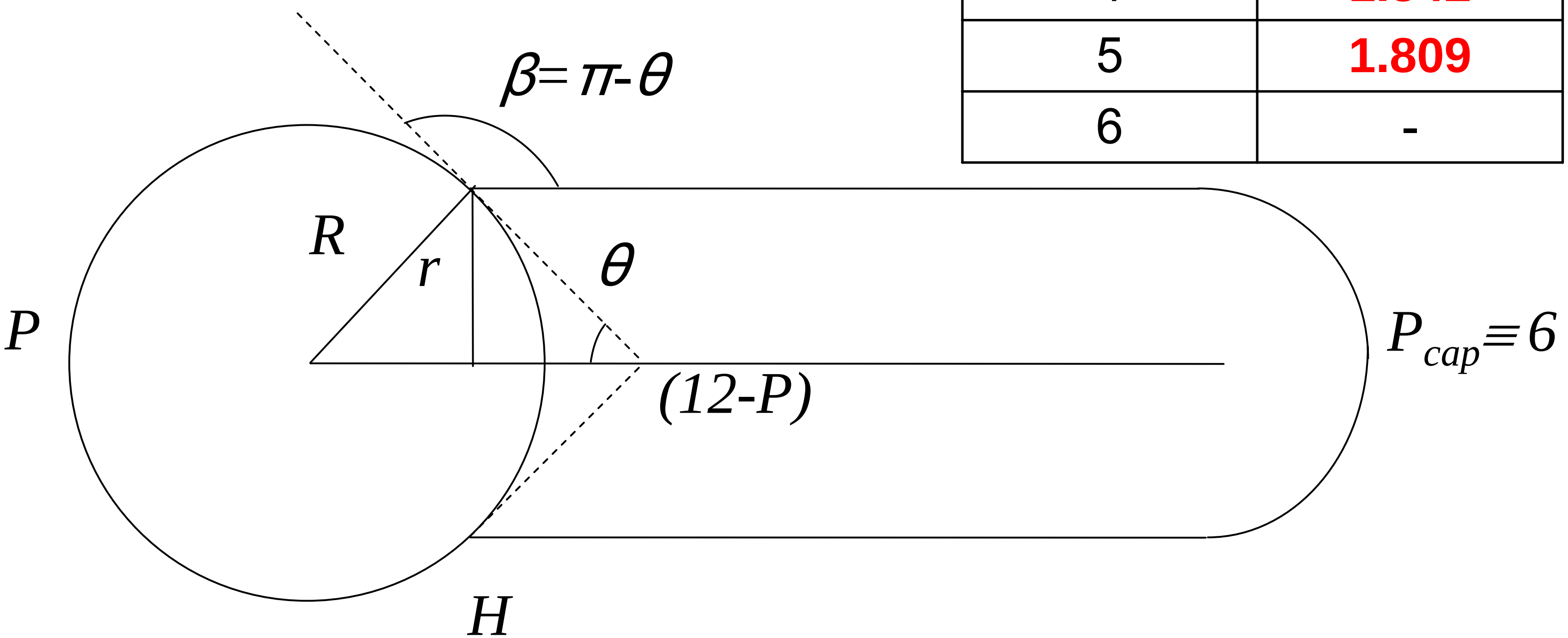
The schematic of the CNT growth geometry

H = number of heptagons at the root of CNT,

P = number of pentagons.

H	D_{cat}/D_{CNT}
0	-
1	1.014
2	1.061
3	1.155
4	**1.342**
5	**1.809**
6	-

$$2R/2r = 1/\cos(\theta) = 1/\sqrt{1-(H/6)^2}$$



Estimating the limiting stage in the CNT formation process

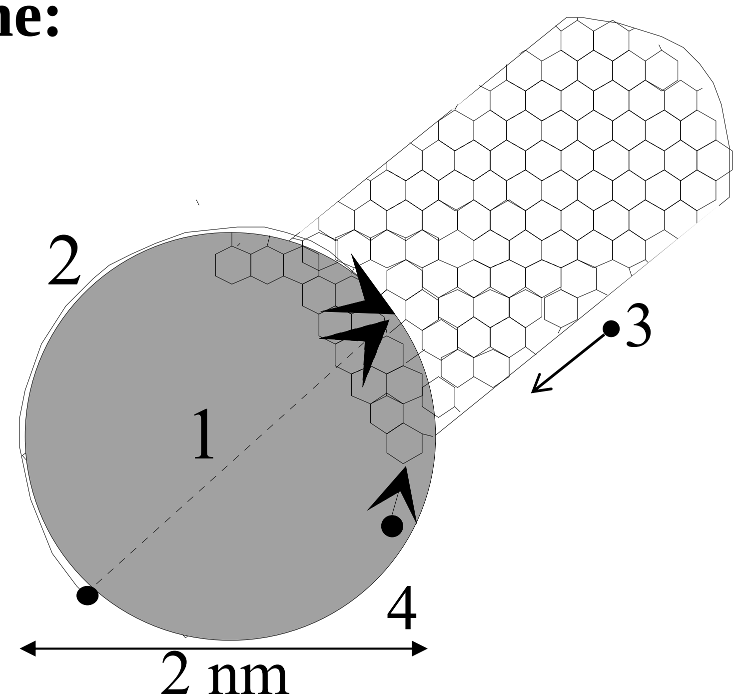
1. **Volume diffusion** of a carbon atom in a-Fe crystalline phase:
   $D_v = D_o \cdot \exp(-E_{av}/k_B T)$, $D_o = 7.9 \cdot 10^{-7}$ m^2/s; $E_{av} = 0.79$ eV.
2. **Diffusion** of carbon atoms on the iron **surface**:
   $D_s = a_o^2 \nu \cdot \exp(-E_{as}/k_B T)$, $a_o \cong 0.29$ nm, $\nu \approx 3.10^{13}$ Hz; $E_{as} = 0.35$ eV.
3. **Diffusion** of carbon atoms on the CNT **surface**:

Characteristic time:

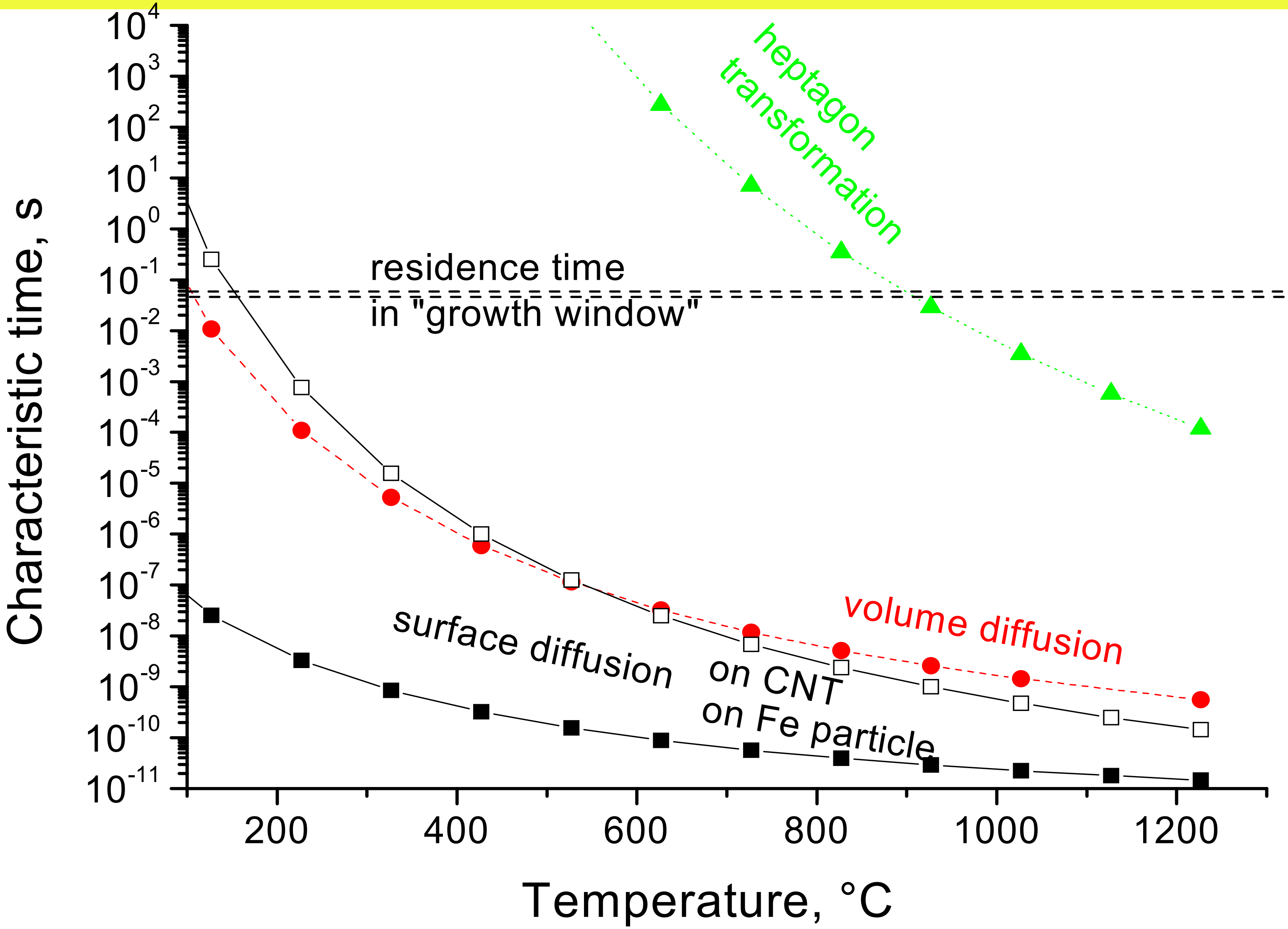
$$\tau = \lambda^2/(4D).$$

4. Process of **heptagon transformation**
$\tau = \nu^{-1} \cdot \exp(E_{ai}/k_B T)$,
where $E_{ai} = 2.8$ eV was found semiempirically

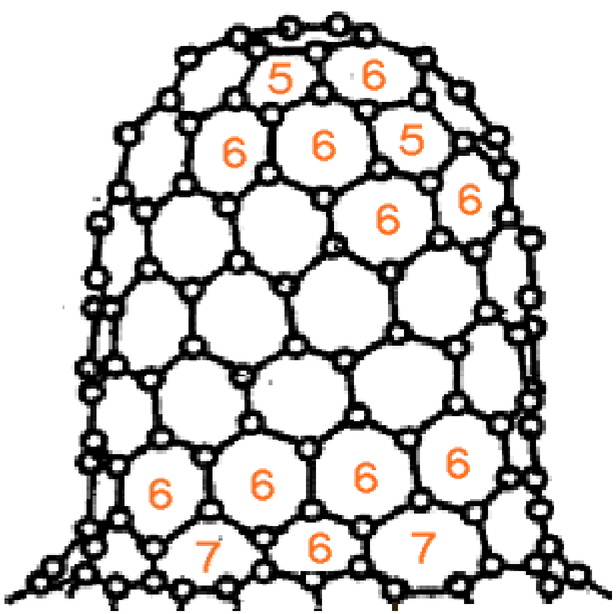
5. Nucleation of CNTs occurs in a nanosecond time scale
(Maruyama *et al.* and Ding *et al*.)

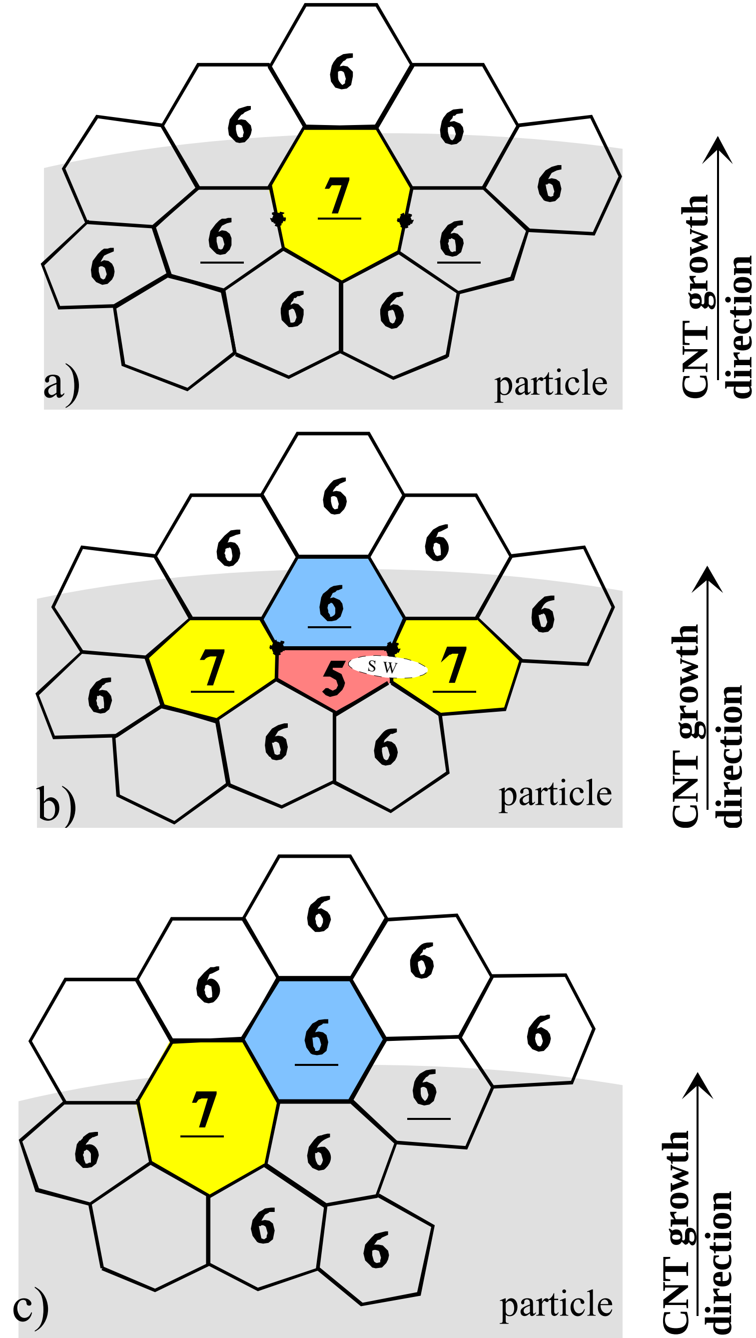


Characteristic times of surface and volume diffusions and carbon insertion into CNT. Kinetic data of CO disproportionation on the surface of iron particles.



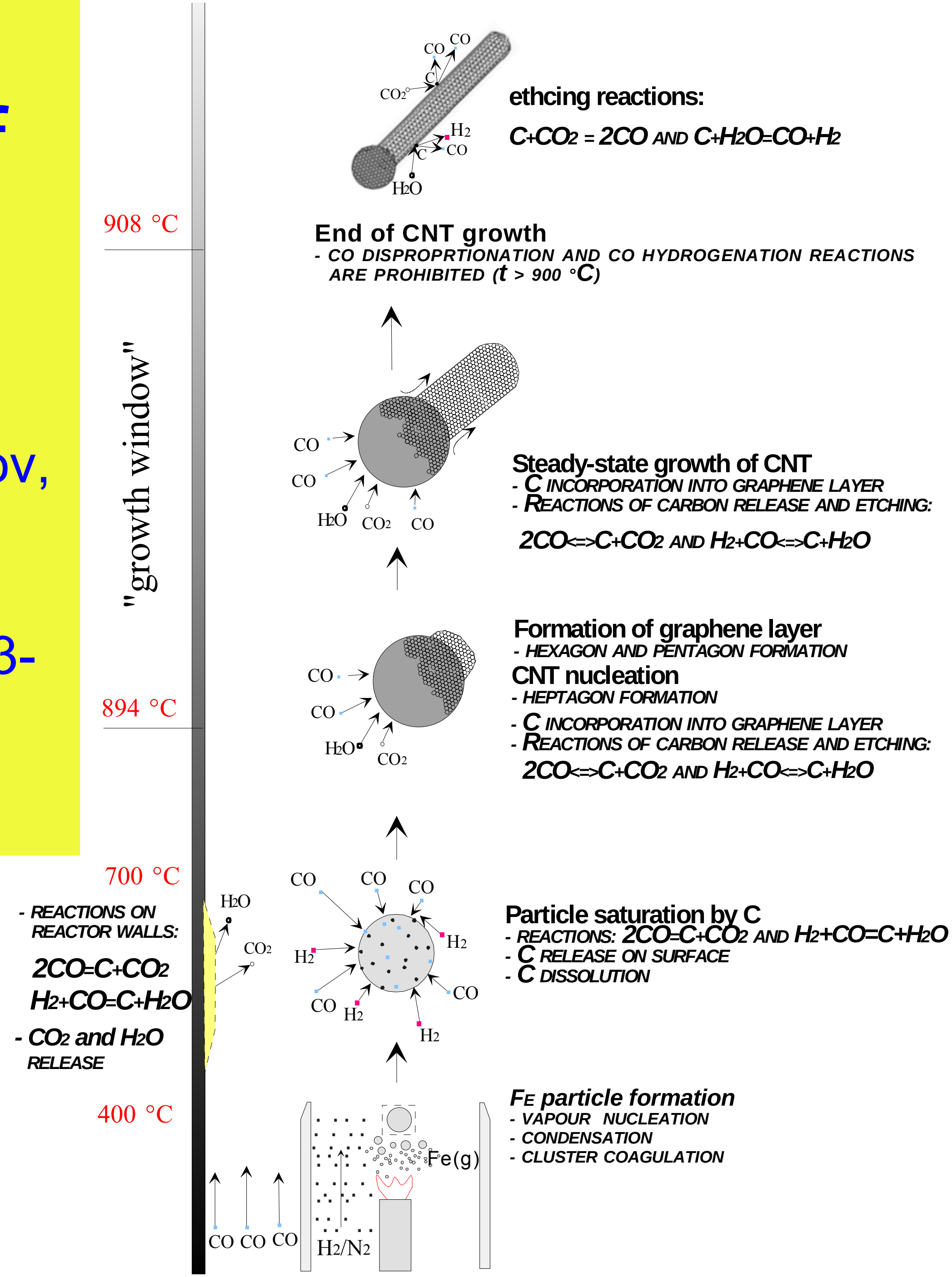
Schematic presentation of heptagon transformation (CNT growth)



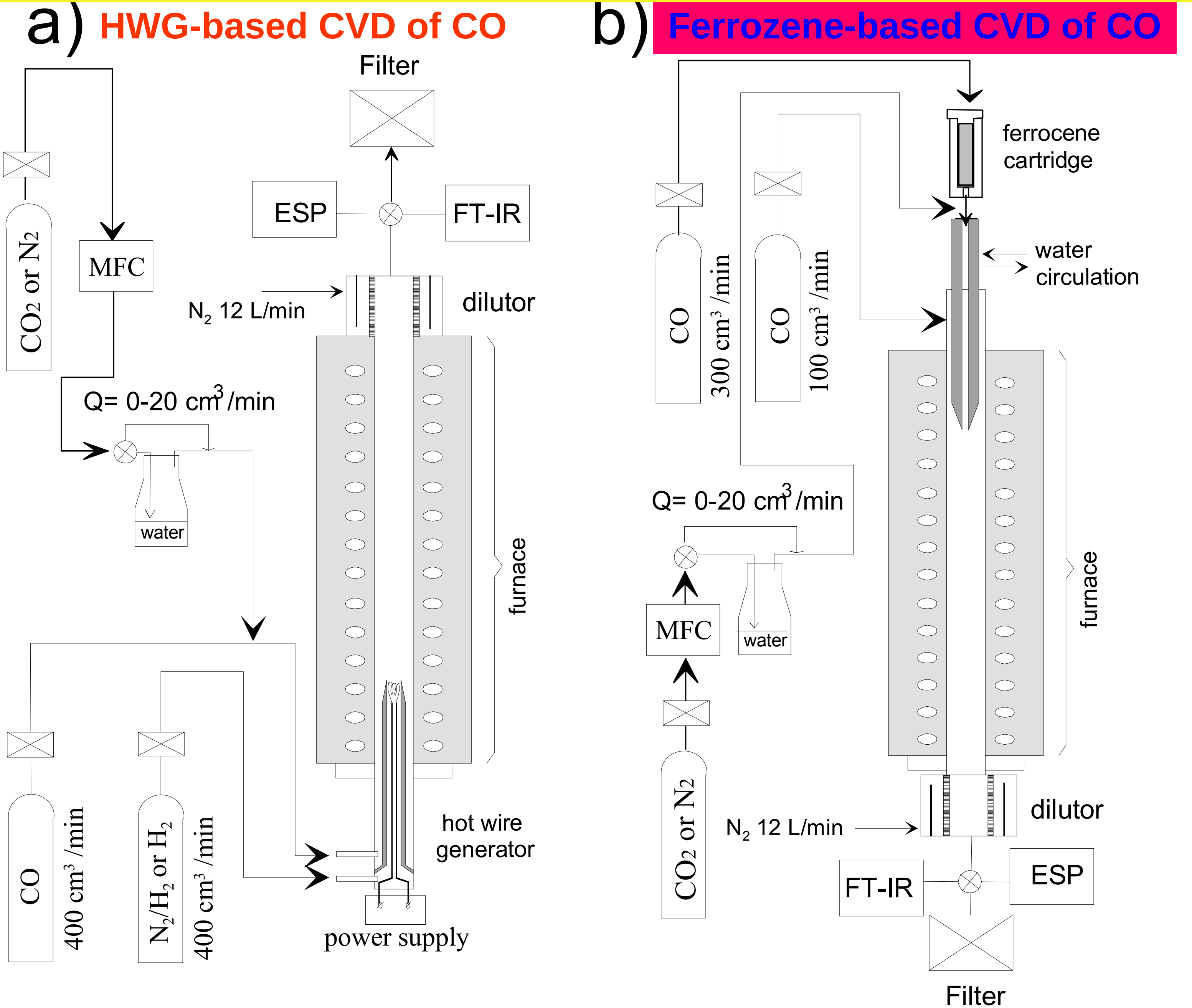


Schematic presentation of mechanism of CNT formation

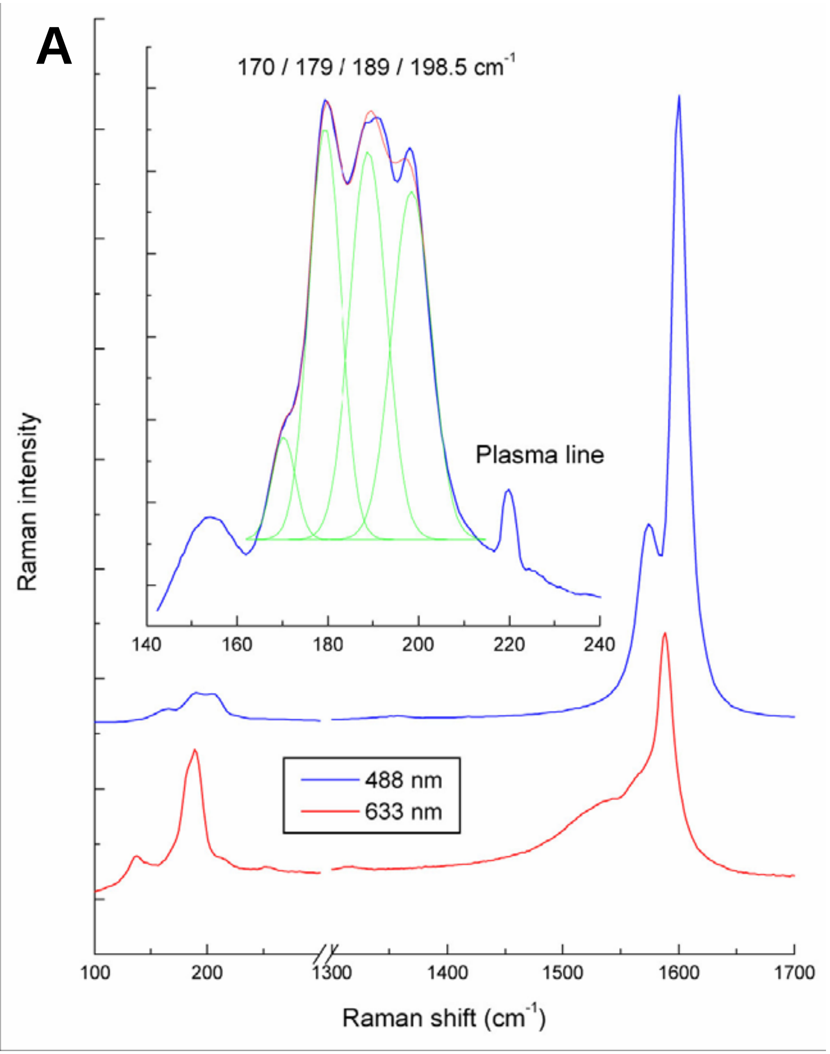
Nasibulin, Queipo, Shandakov, Brown, Jiang, Pikhitsa, Tolochko, Kauppinen, *J.Nanosci. Nanotech.* 6 1233-1246.

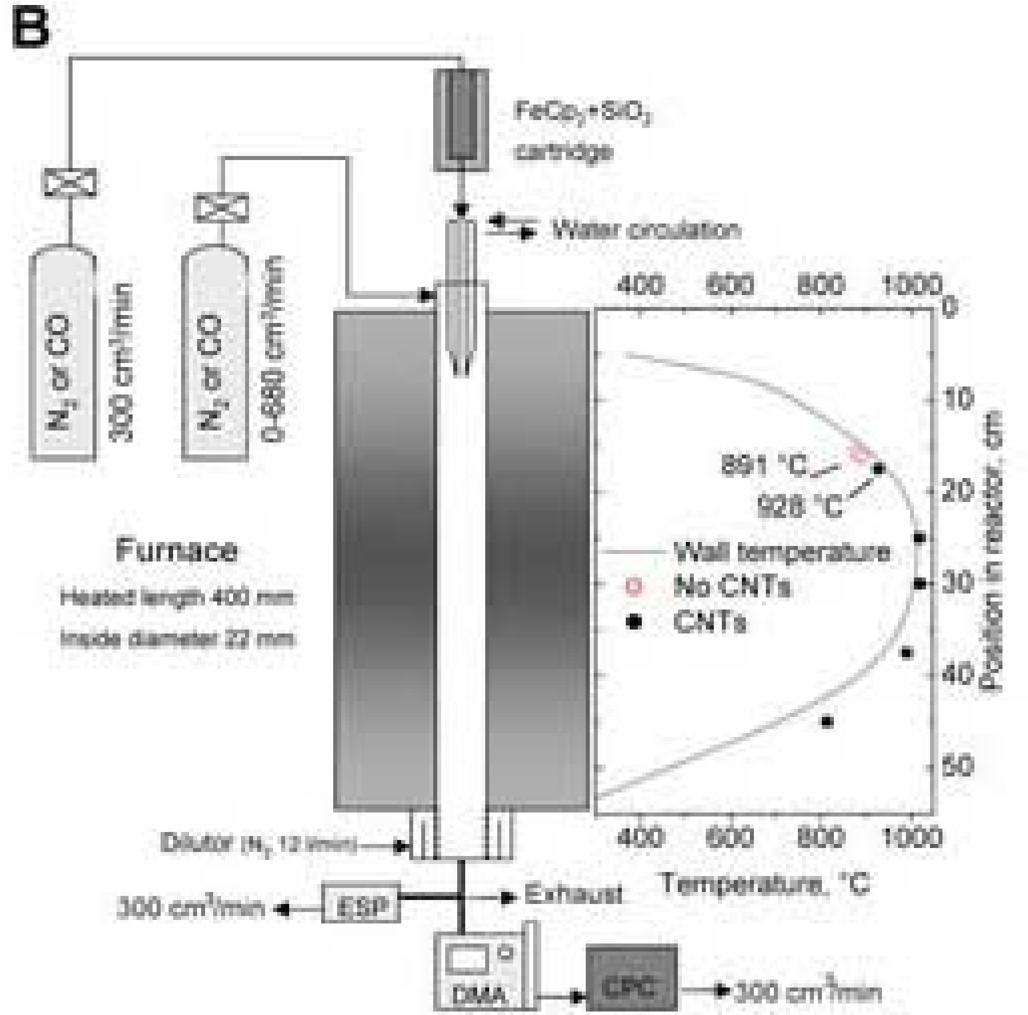


Floating Catalyst Methods for CNT Synthesis

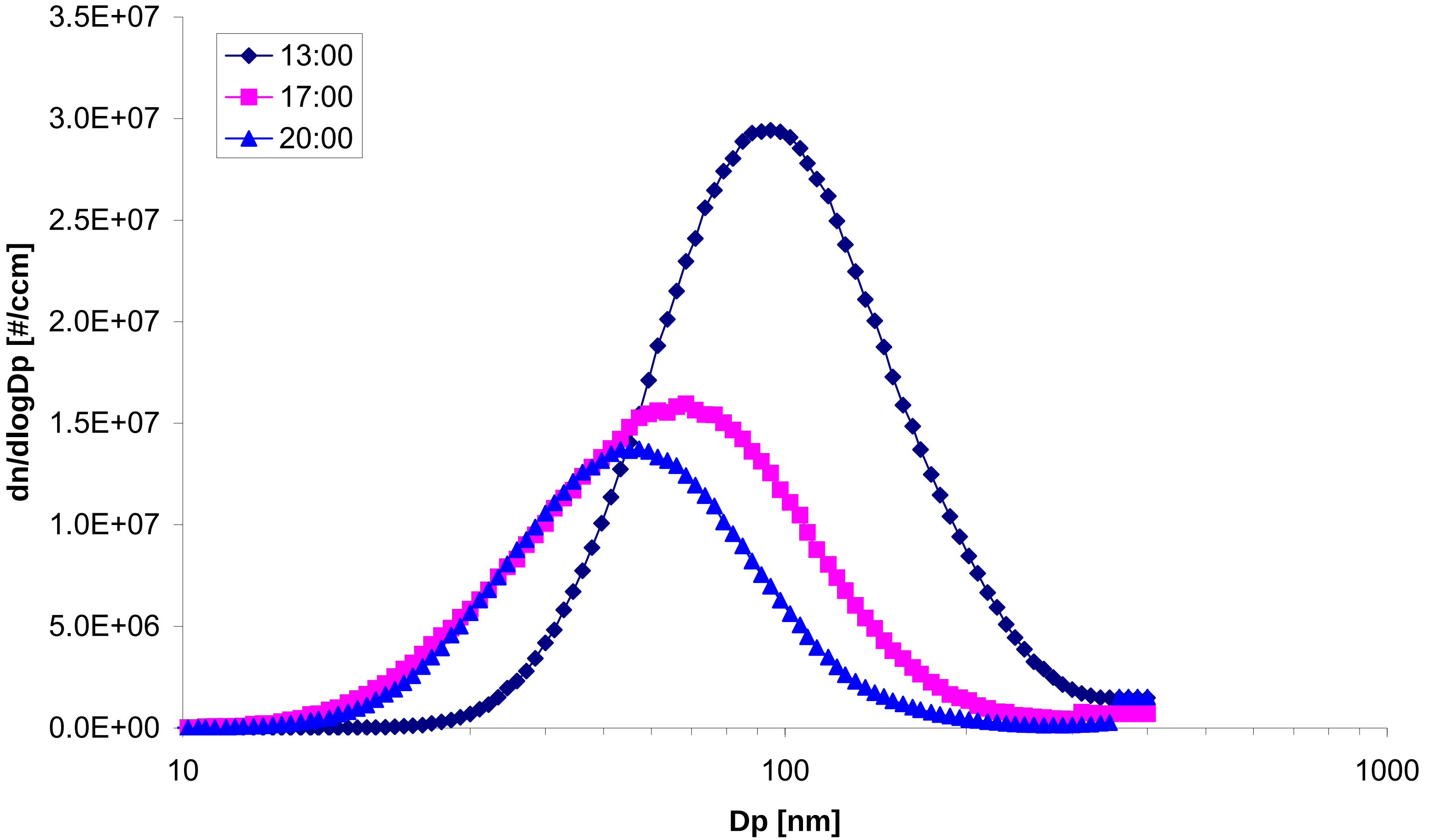


Raman (A) and In-situ sampling (B) – Ferrozene-based CVD of CO





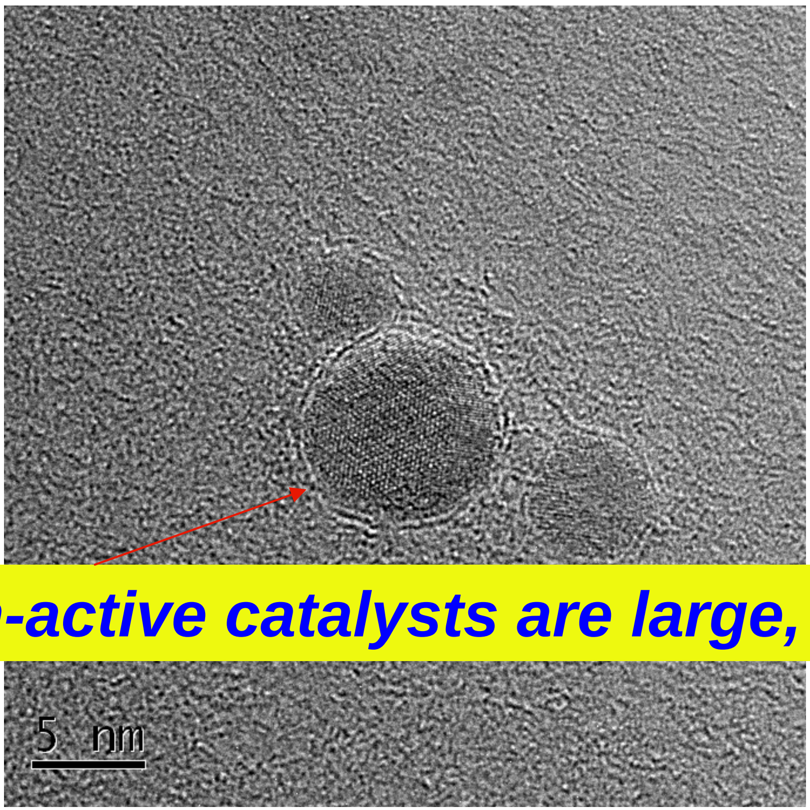
Size Distribution changes with Time at Fixed Reactor Conditions – e.g. $Fe(Cp)_2$ & CO at 1150 °C - similar for Fe from HWG & CO – Due to CO_2 formation at the reactor wall

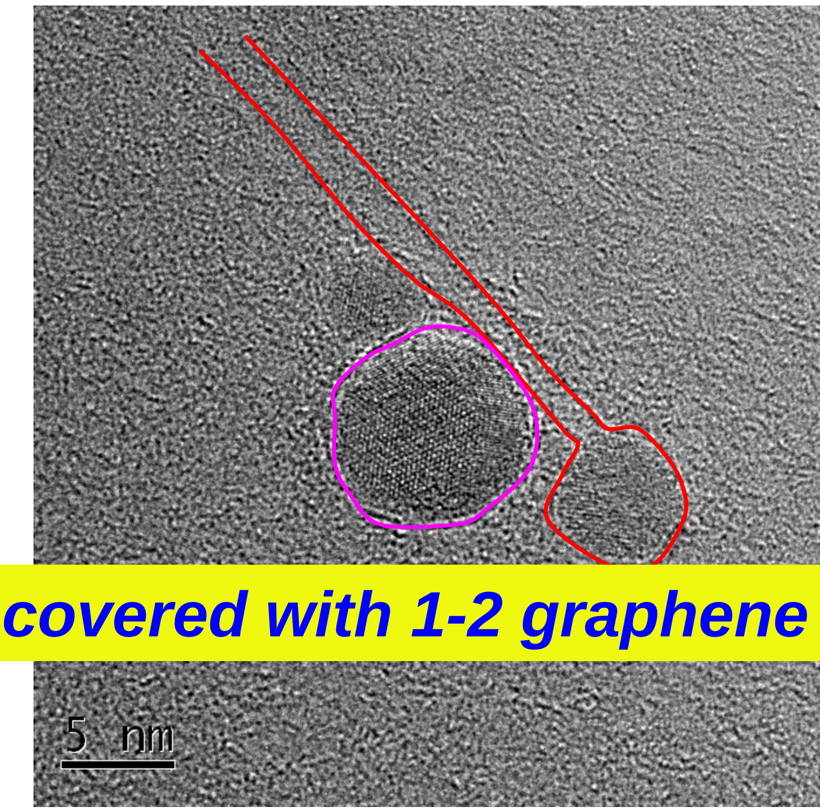


Cs-corrected TEM images of active catalyst clusters growing SWCNTs

Sample: **Ferrozene Reactor**
1000 C with $CO + H_2O$
Collected to TEM grid via ESP filter

Microscope: **FEI Titan™ 80-300**
High tension (HV): 300kV

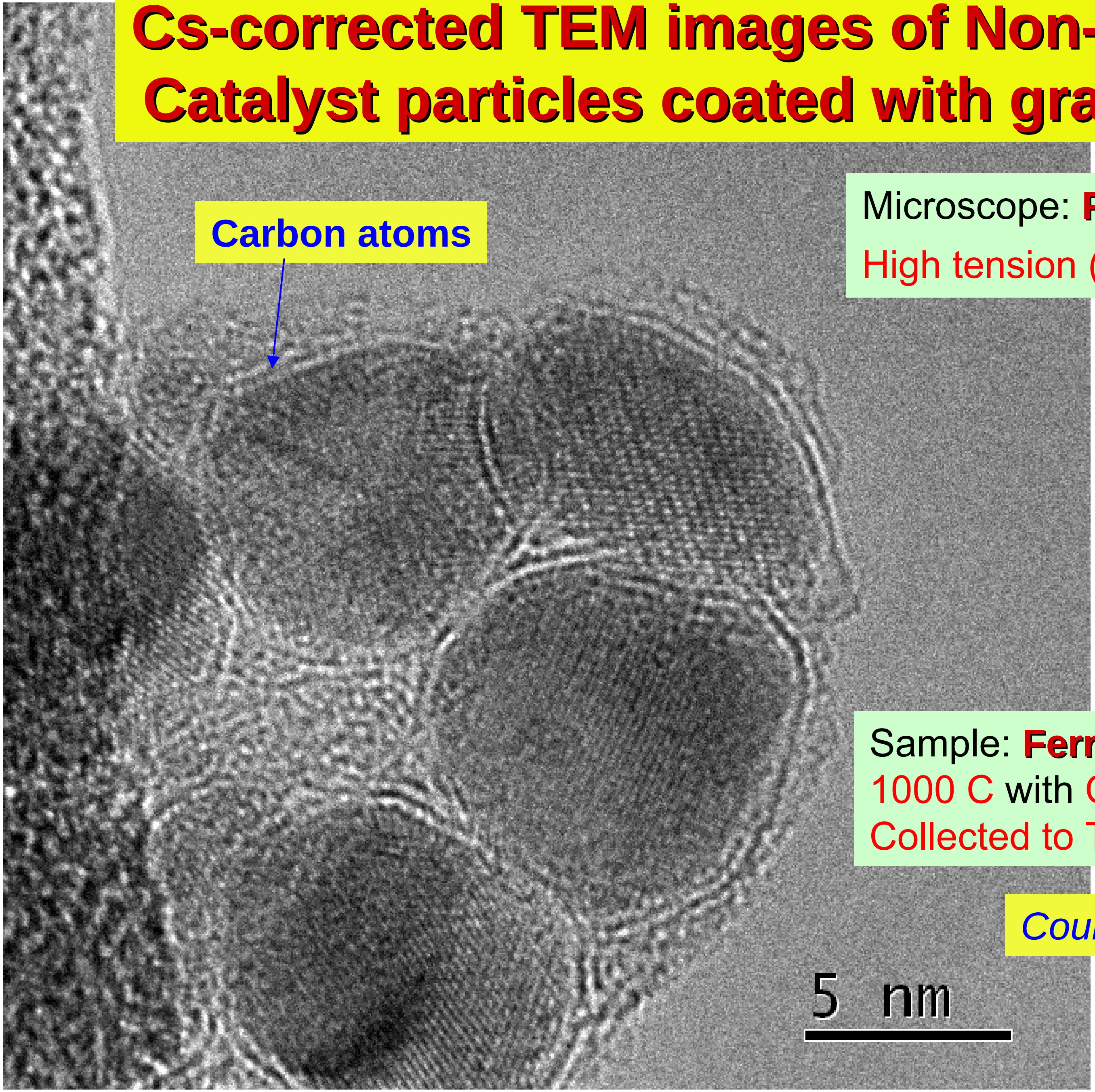




Non-active catalysts are large, covered with 1-2 graphene layer

Courtesy Dr. Bernd Freitag

Cs-corrected TEM images of Non-active large Catalyst particles coated with graphene layer



Microscope: **FEI Titan™ 80-300**

High tension (HV): **80 kV**

Large Non-active Catalyst Particles

Sample: **Ferrozene Reactor**

1000 C with CO + H_2O

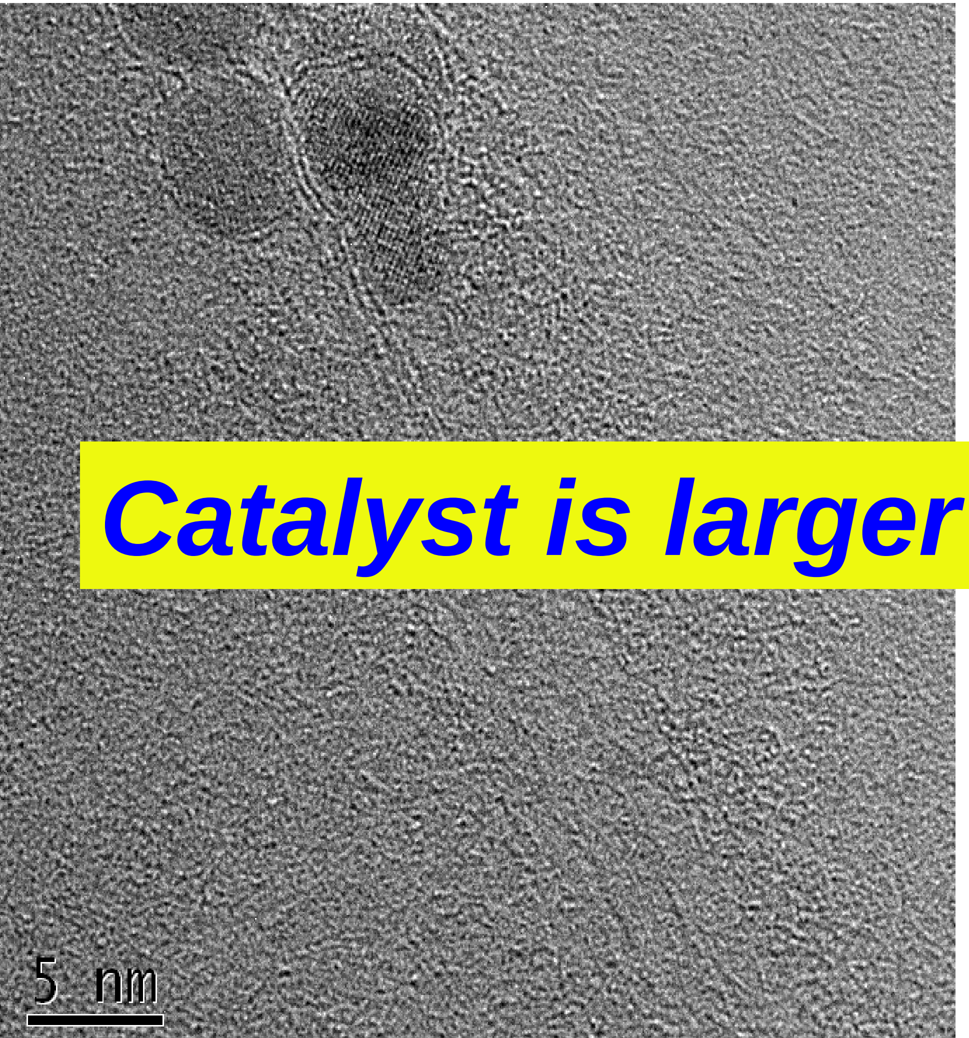
Collected to TEM grid via ESP filter

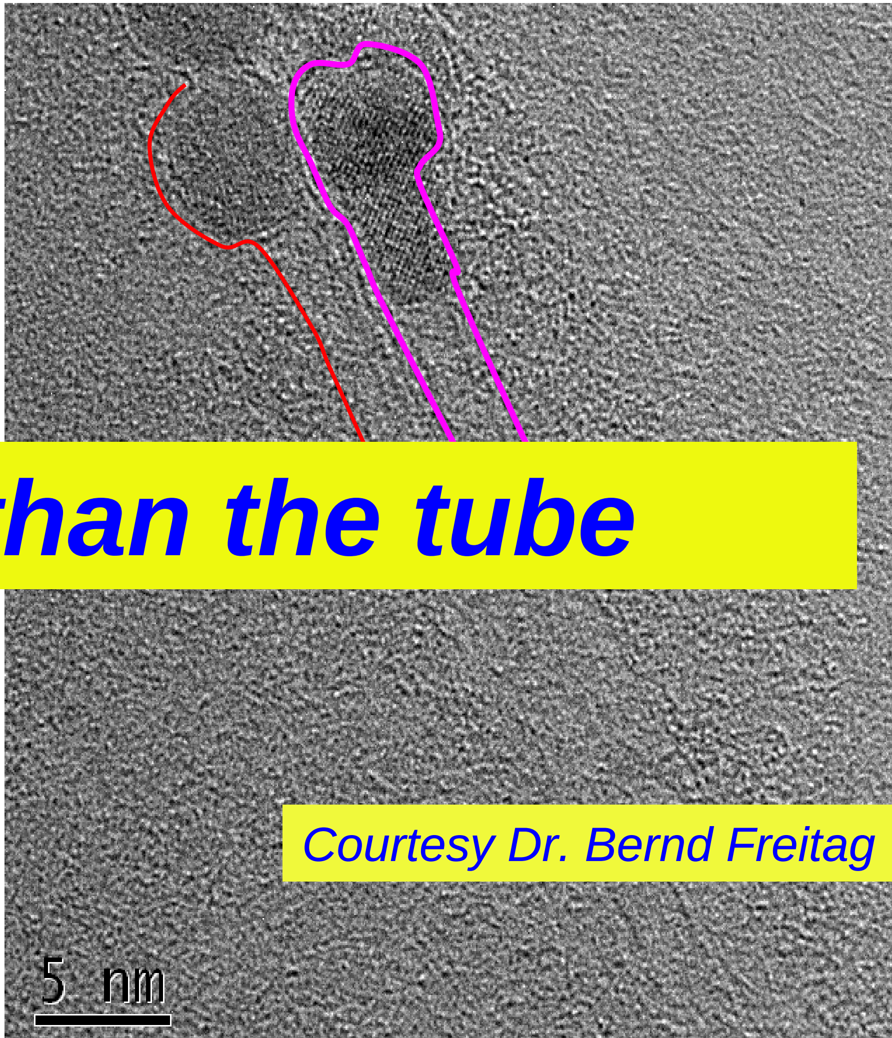
Courtesy Dr. Bernd Freitag

Cs-corrected TEM images of active catalyst clusters growing SWCNTs

Sample: **Ferrozene Reactor**
1000 C with $CO + H_2O$
Collected to TEMgrid via ESP filter

Microscope: **FEI Titan™ 80-300**
High tension (HV): **300 kV**





Catalyst is larger than the tube

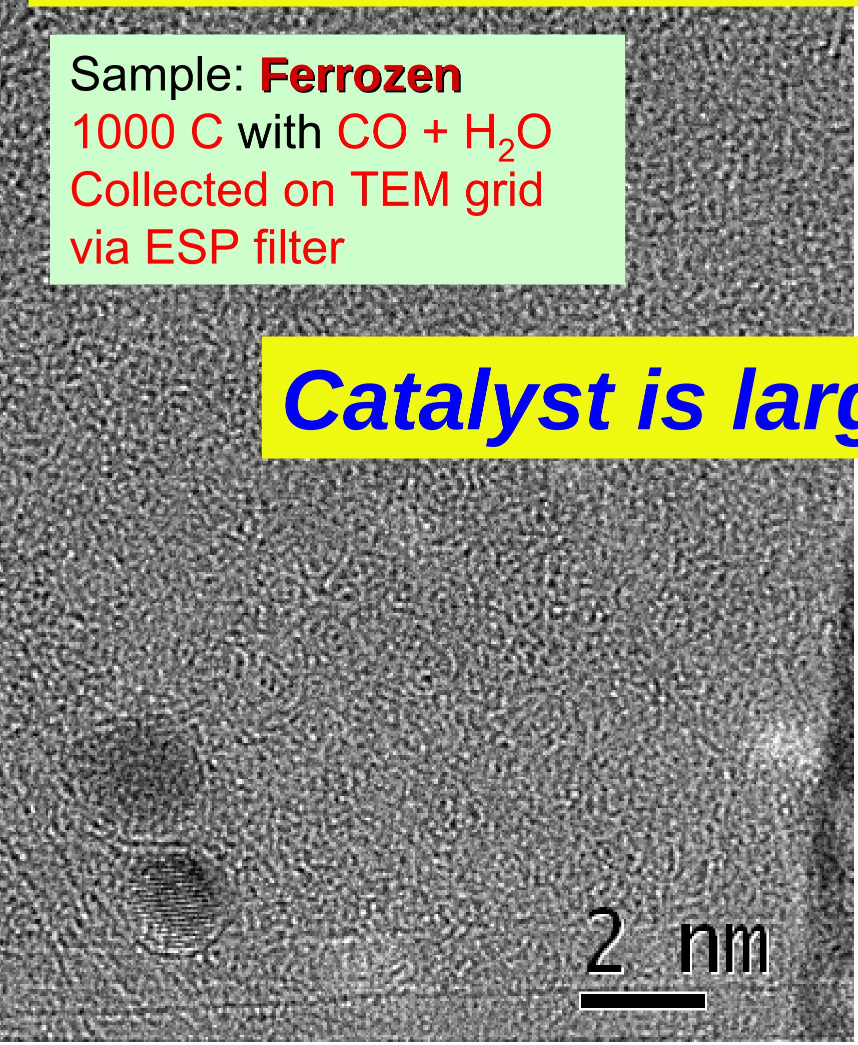
Courtesy Dr. Bernd Freitag

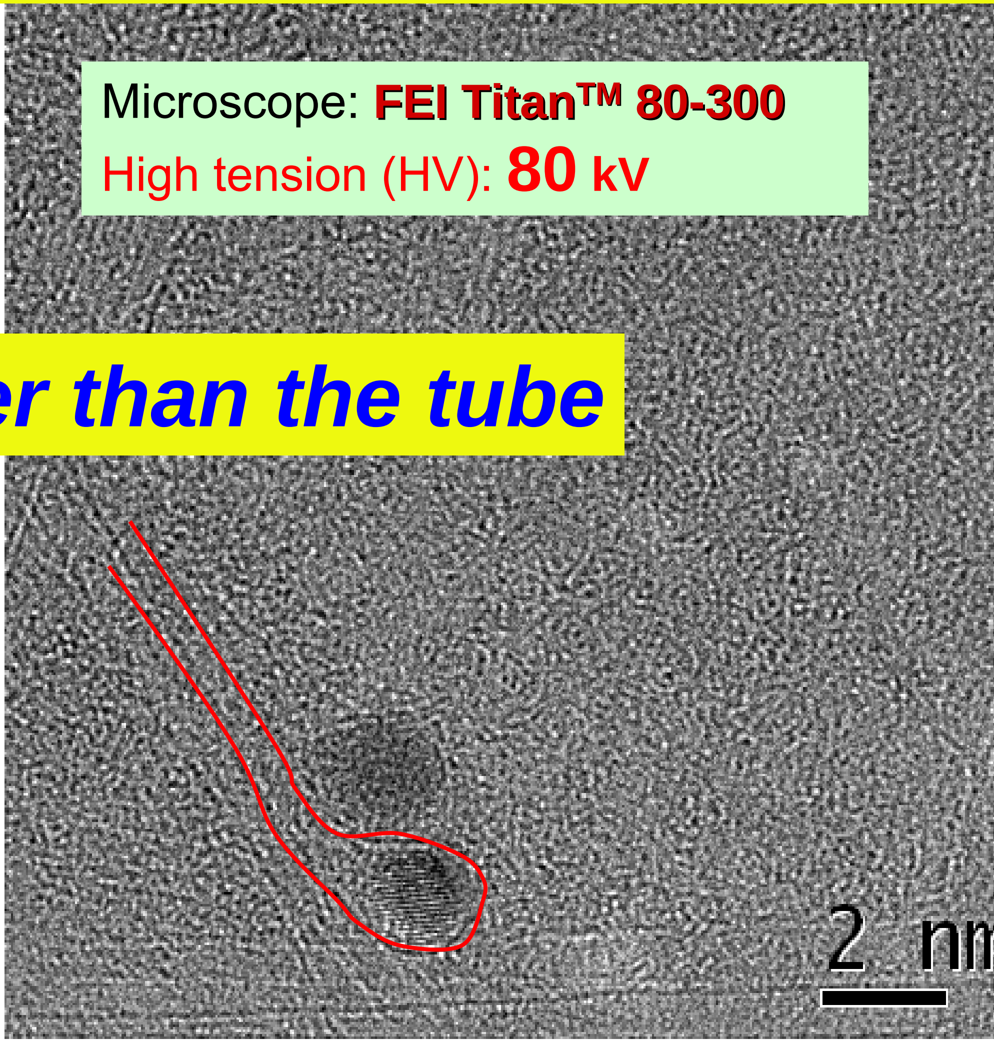
Cs-corrected TEM images of active catalyst clusters growing SWCNTs

Sample: **Ferrozen**
1000 C with $CO + H_2O$
Collected on TEM grid
via ESP filter

Microscope: **FEI Titan™ 80-300**
High tension (HV): **80 kV**

Catalyst is larger than the tube

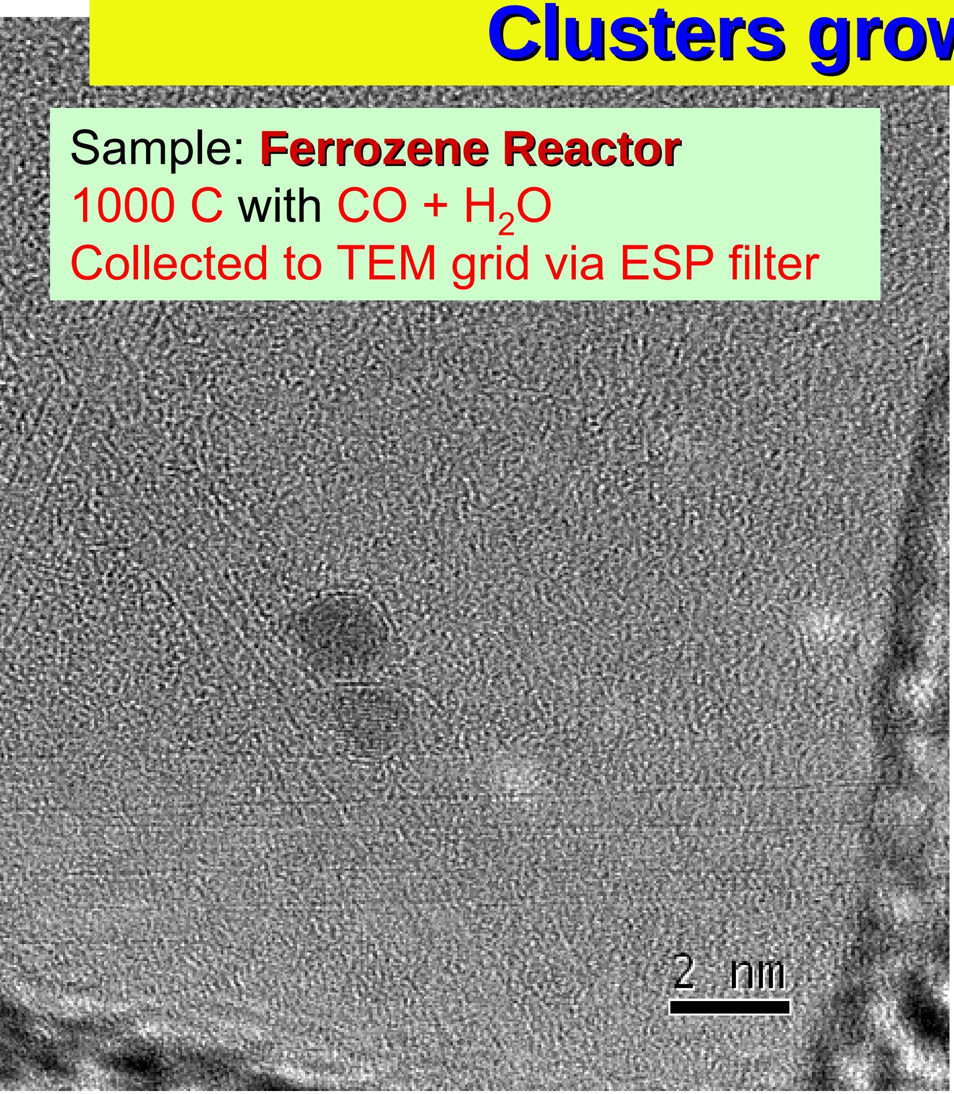




Courtesy Dr. Bernd Freitag

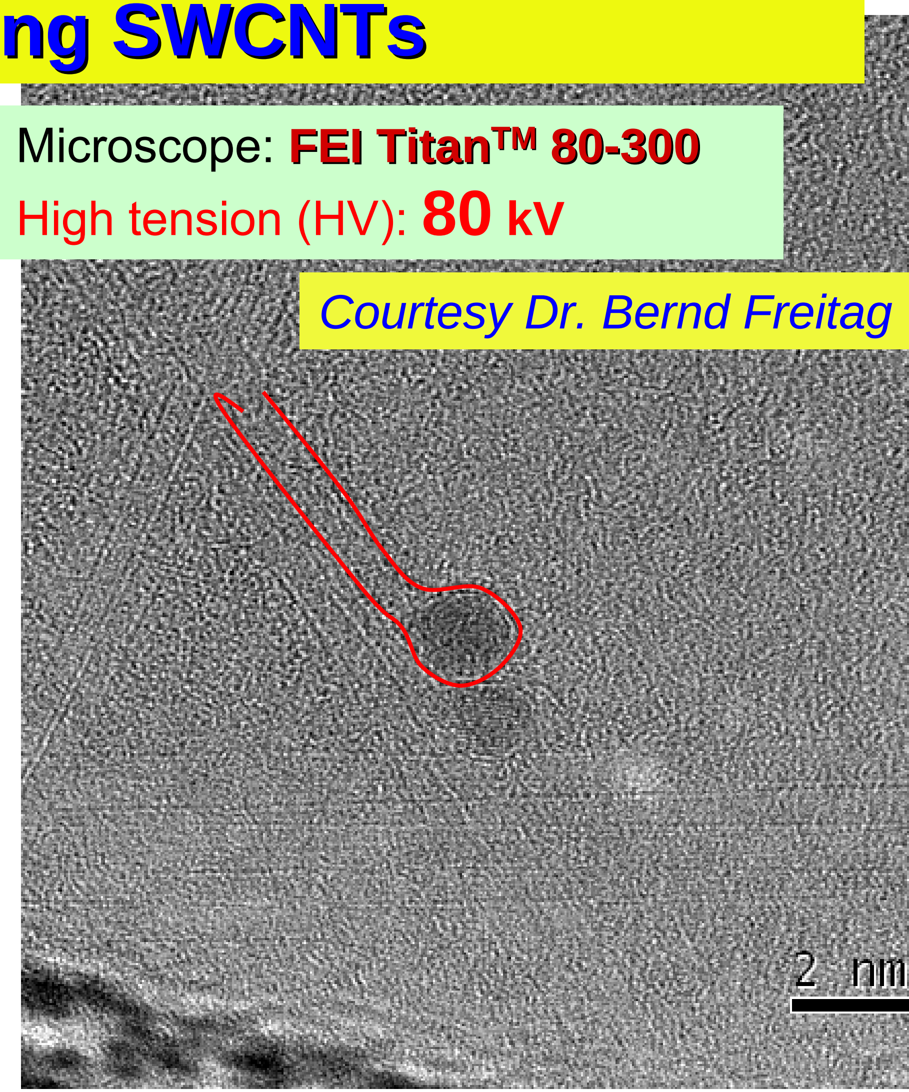
More Cs-corrected TEM images of active catalyst Clusters growing SWCNTs

Sample: **Ferrozene Reactor**
1000 C with CO + H_2O
Collected to TEM grid via ESP filter



Microscope: **FEI Titan™ 80-300**
High tension (HV): **80 kV**

Courtesy Dr. Bernd Freitag

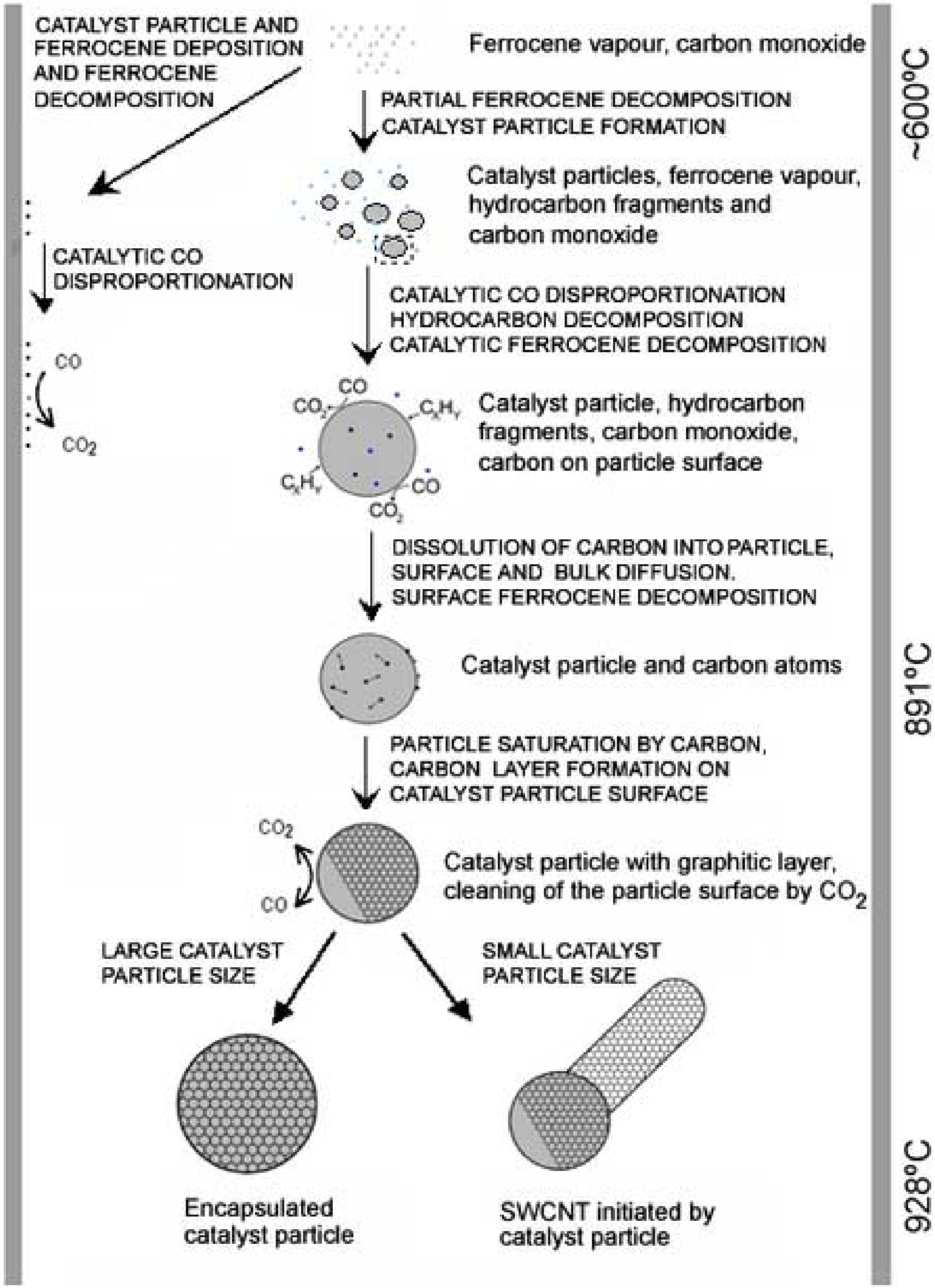


Catalyst is larger than the tube

Schematic presentation of SWCNT formation mechanism during ferrozene decomposition in CO

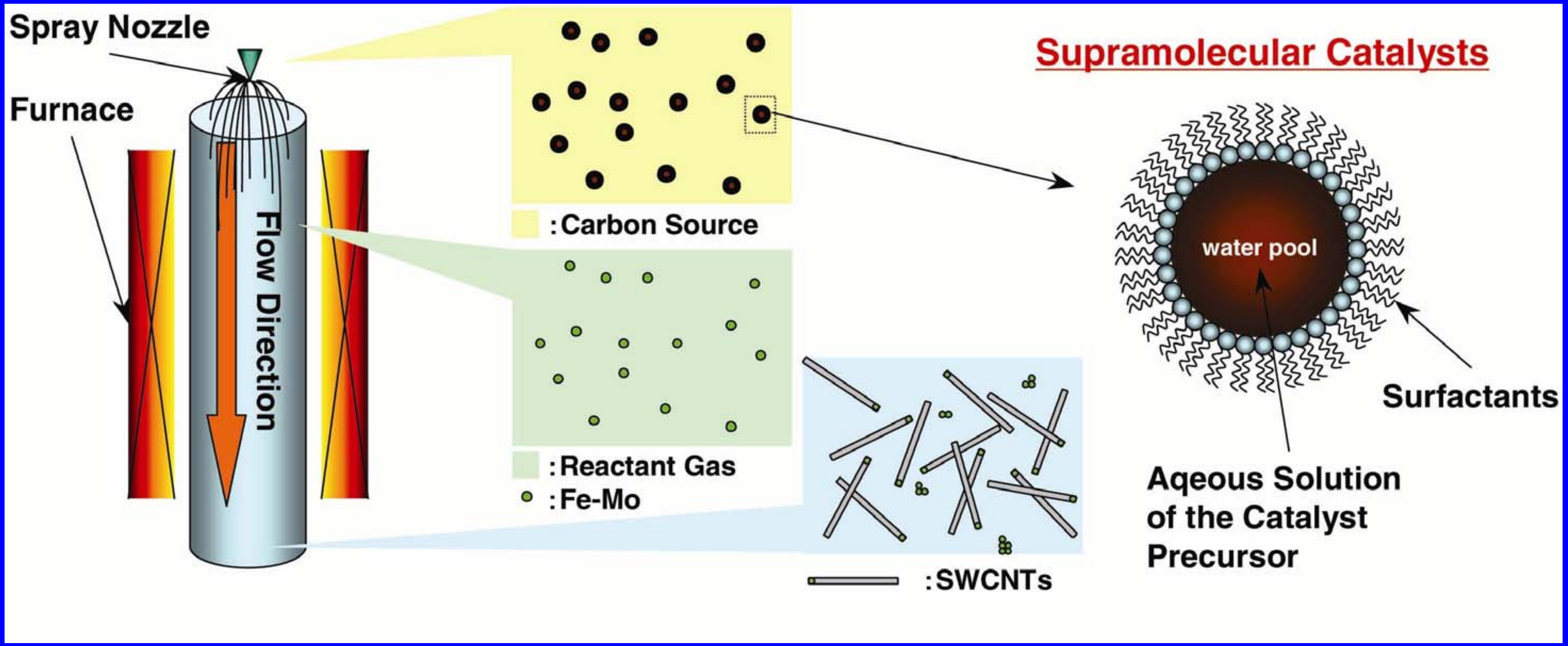
Moisala et al., CES 2006

Ferrozene decomposition slow – overlapp between CNT nucleation & growth and Ferrozene decomposition – CVD growth of catalysts



Another Interesting Floating Catalyst Method - Direct-Injection-Pyrolytic-Synthesis (DIPS)

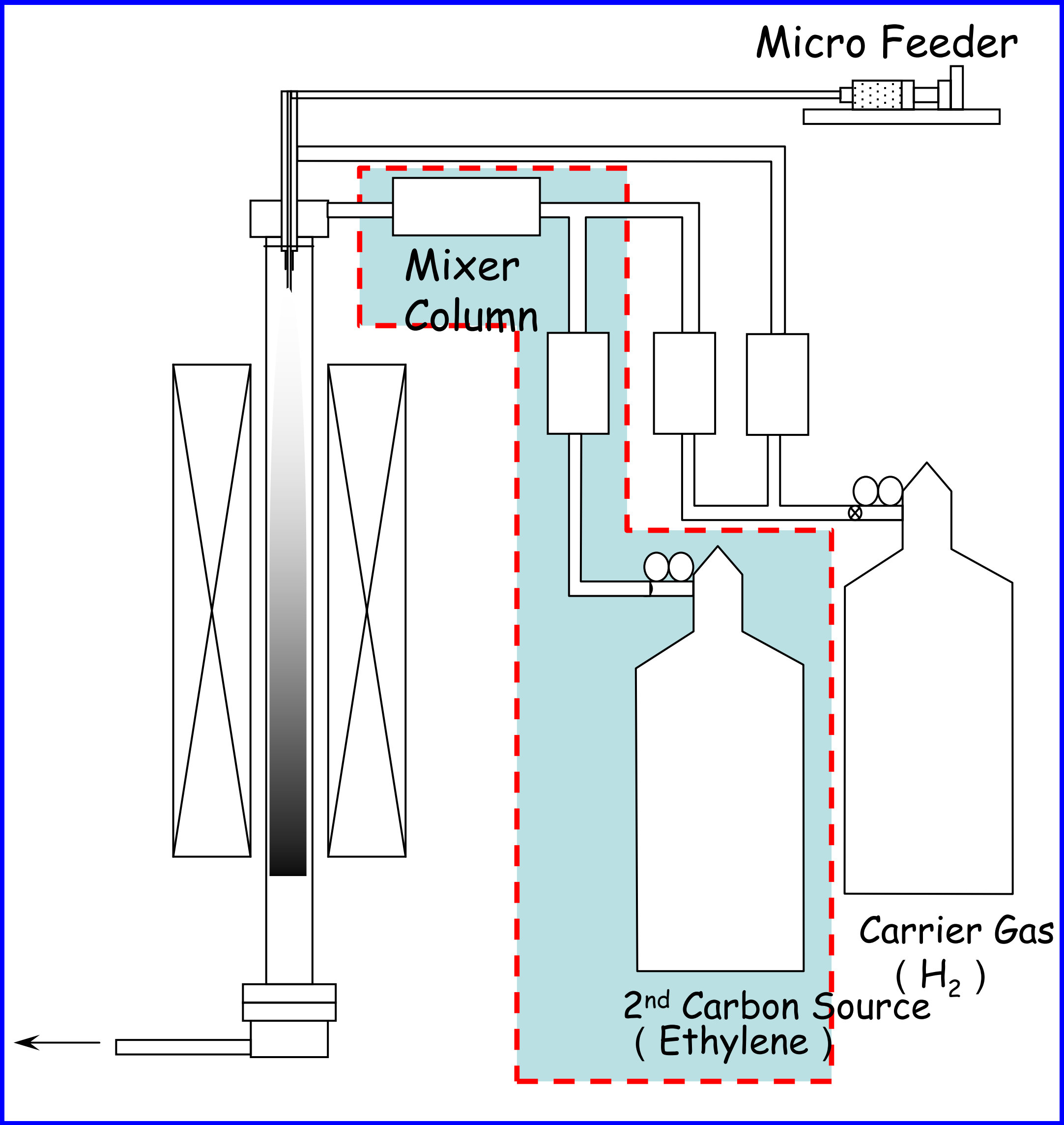
T. Saito,,S. Iijima et al,.J.Phys.Chem. 2005



Catalysts are injected into the furnace directly through the spray nozzle.

Courtesy Prof. S.Iijima

Set Up for the Diameter Control



Experimental Variables

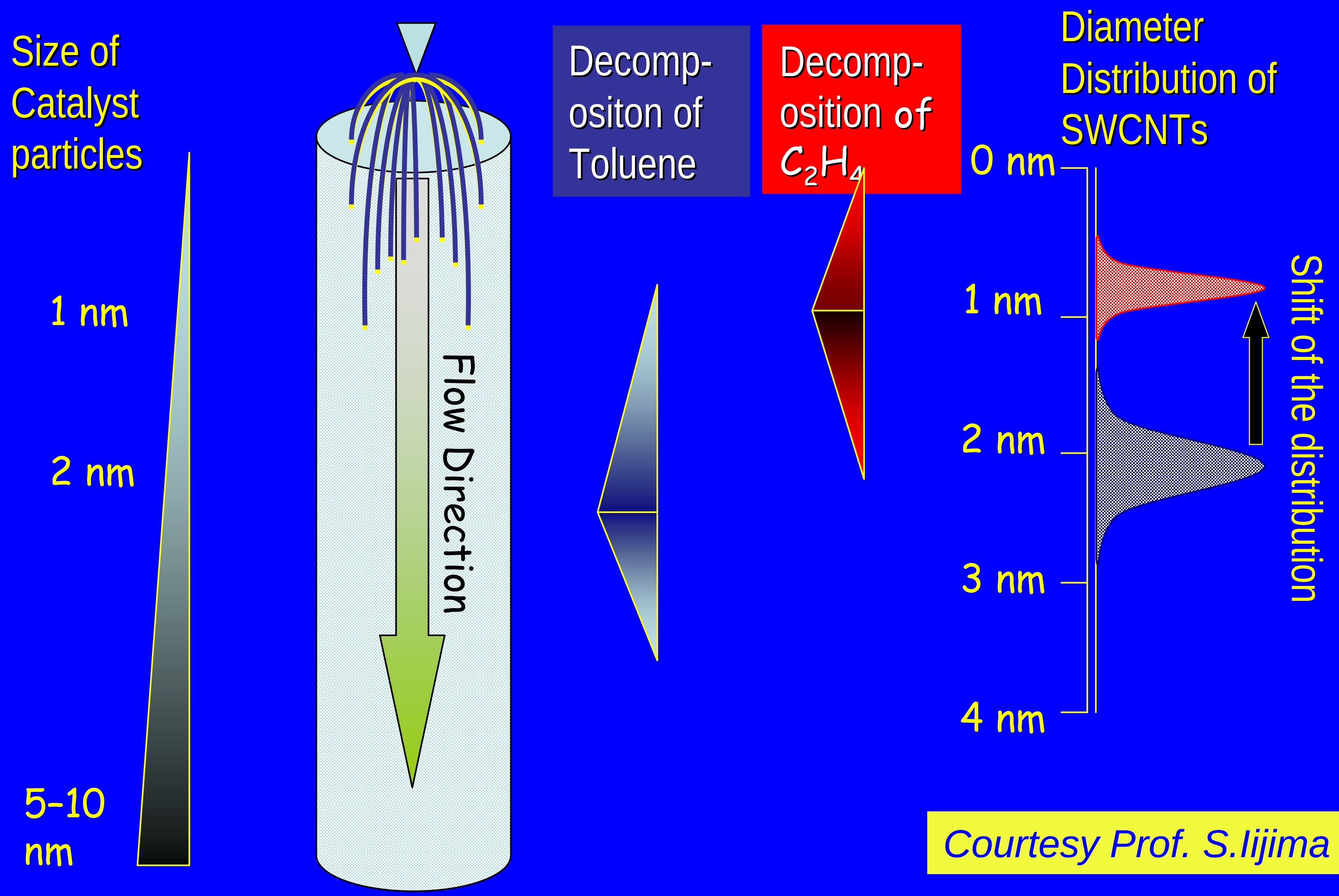
- Temperature 800 – 1200°C
- C_2H_4 flow rate 0 – 350 sccm

Fixed Constants

- Carrier Gas H_2
- H_2 flow rate 7.0 L/min
- feed rate 64 µL/min
- Catalyst Ferrocene or Supramolecular cat.
- Promoter Thiophene

Courtesy Prof. S.Iijima

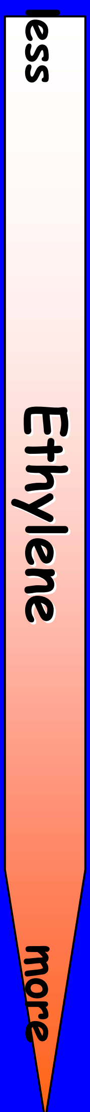
Diameter Control Mechanism

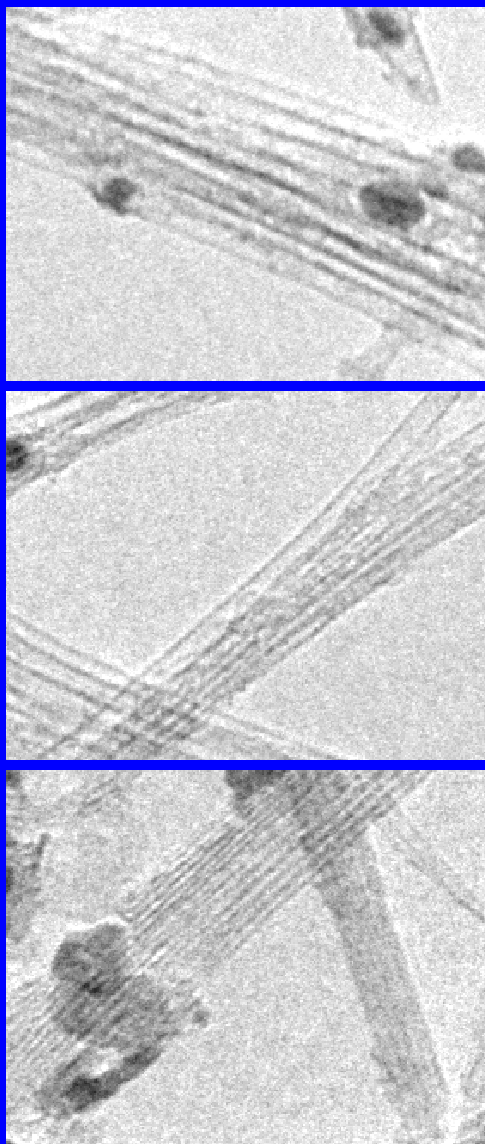


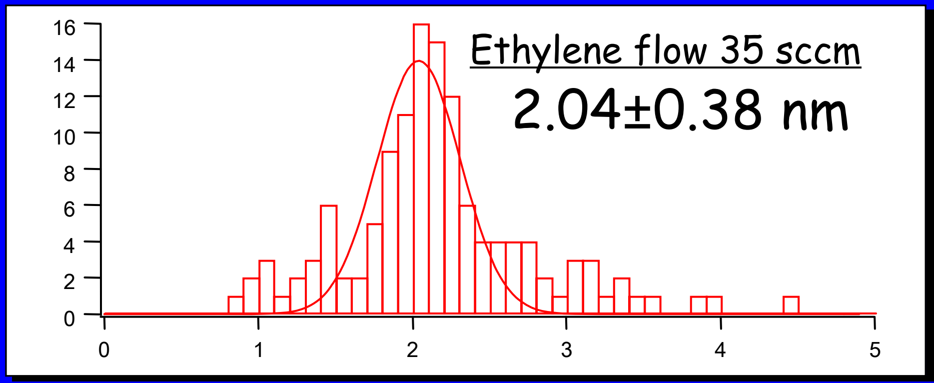
Courtesy Prof. S.Iijima

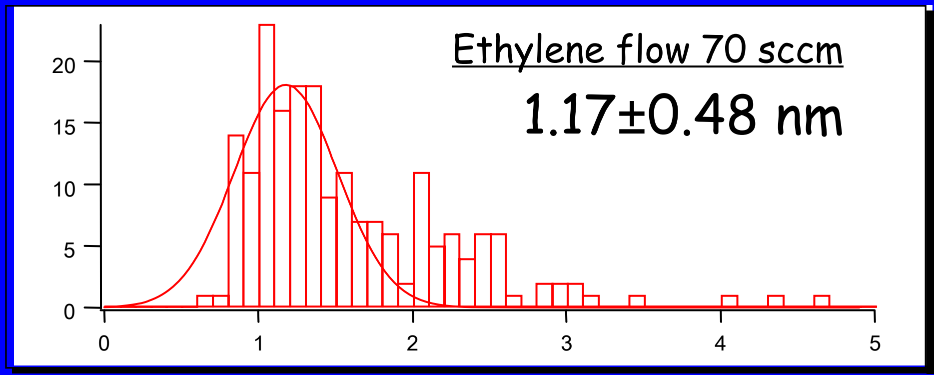
Diameter Distribution by TEM Observation

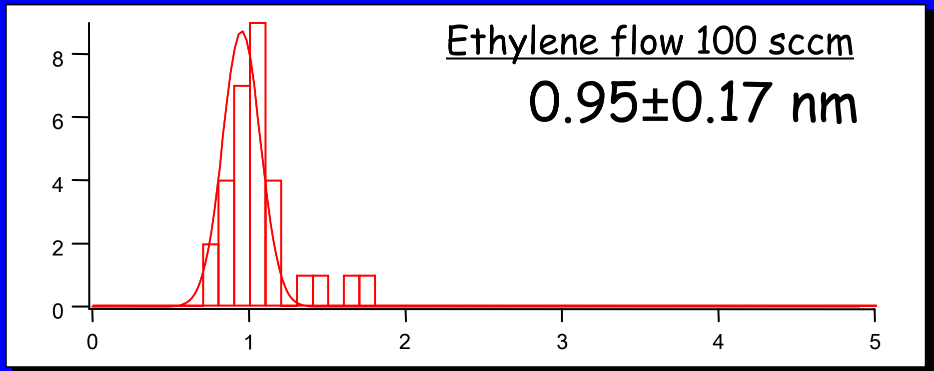
Courtesy Prof. S.Iijima

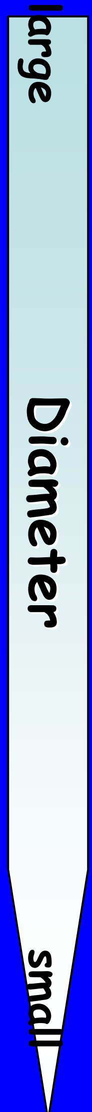




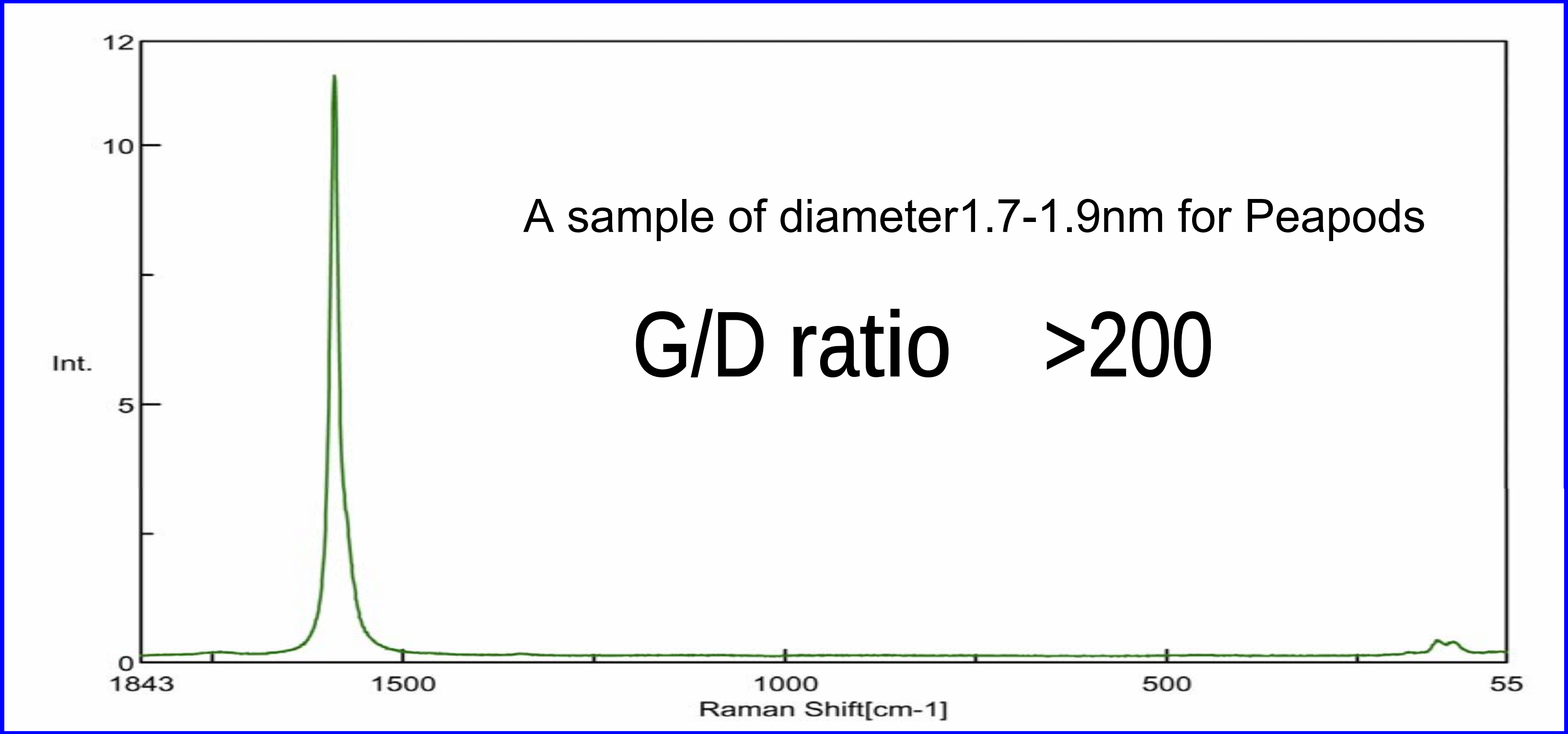


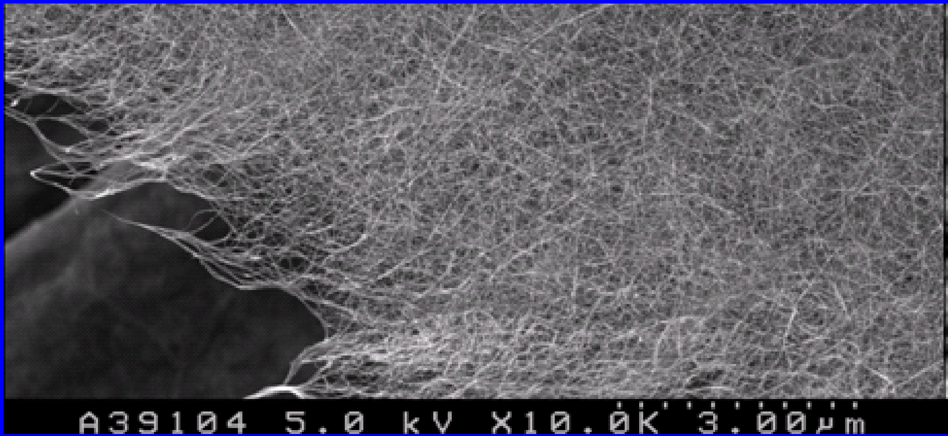


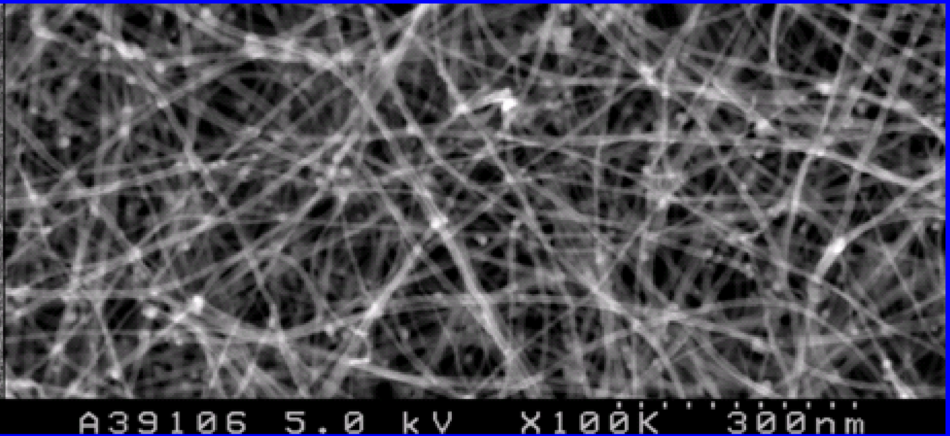




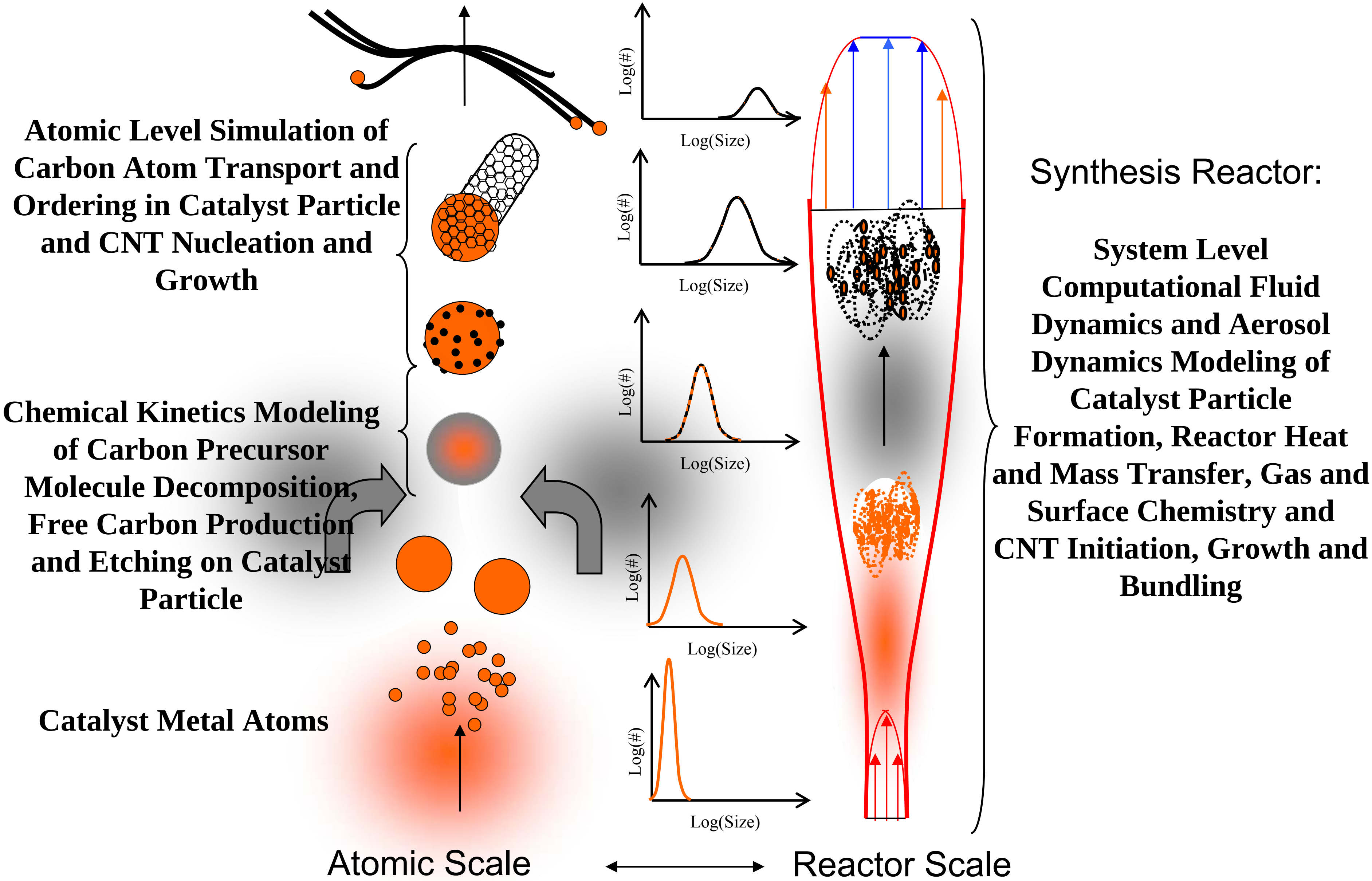
High Purity SWCNTs by DIPS Method



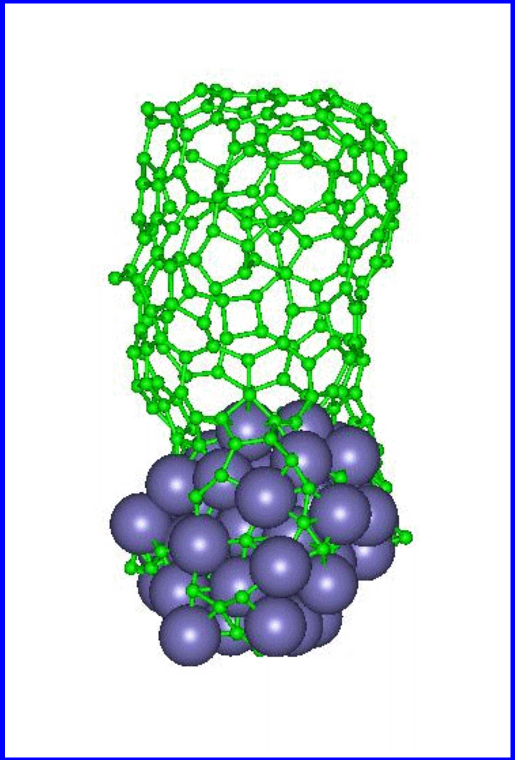




CNT Synthesis - Modeling at Different Length and Time Scales



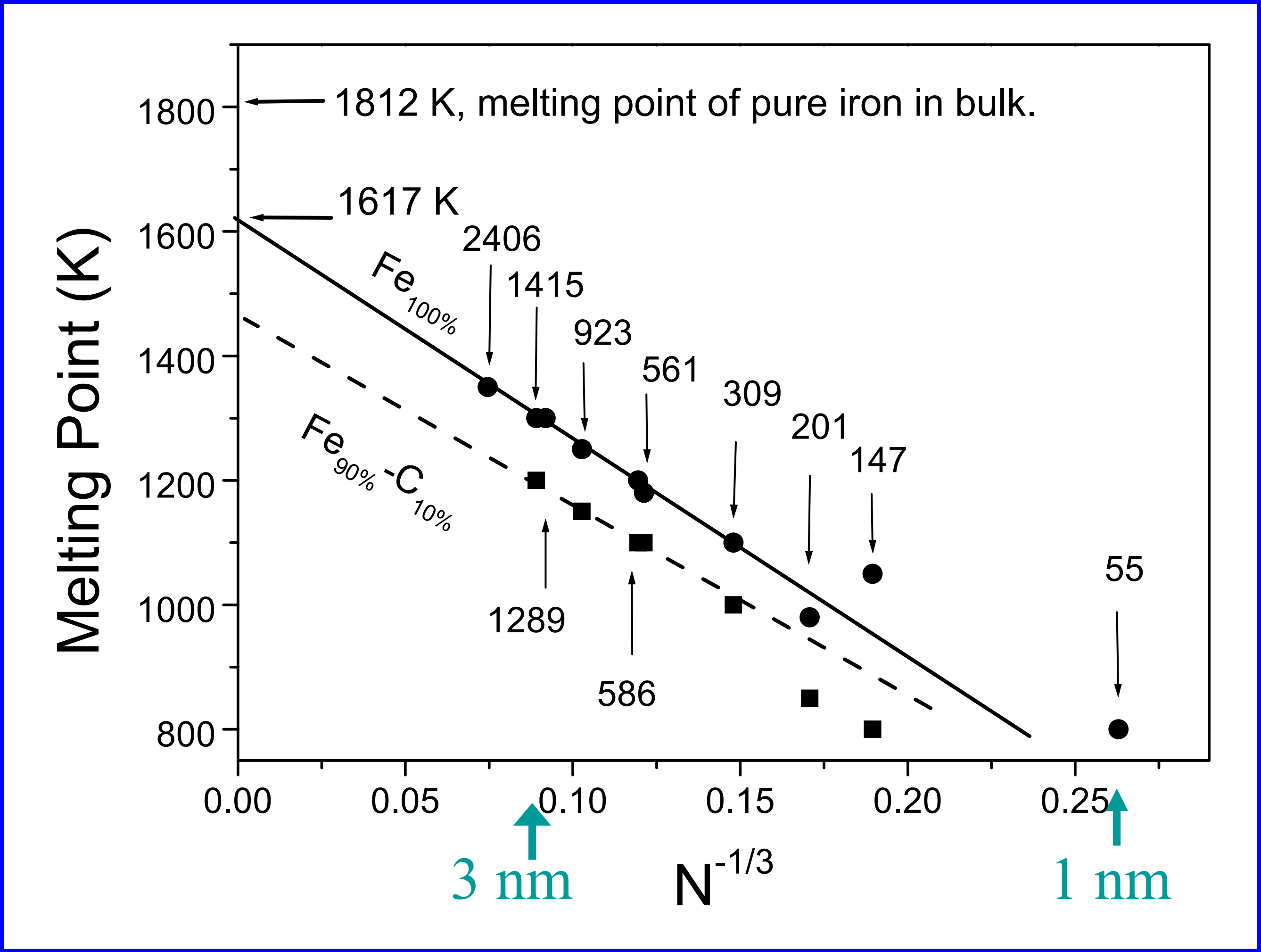
Dynamics simulation of metal cluster catalyzed SWNT nucleation: a review



Kim Bolton, Feng Ding, Arne Rosén

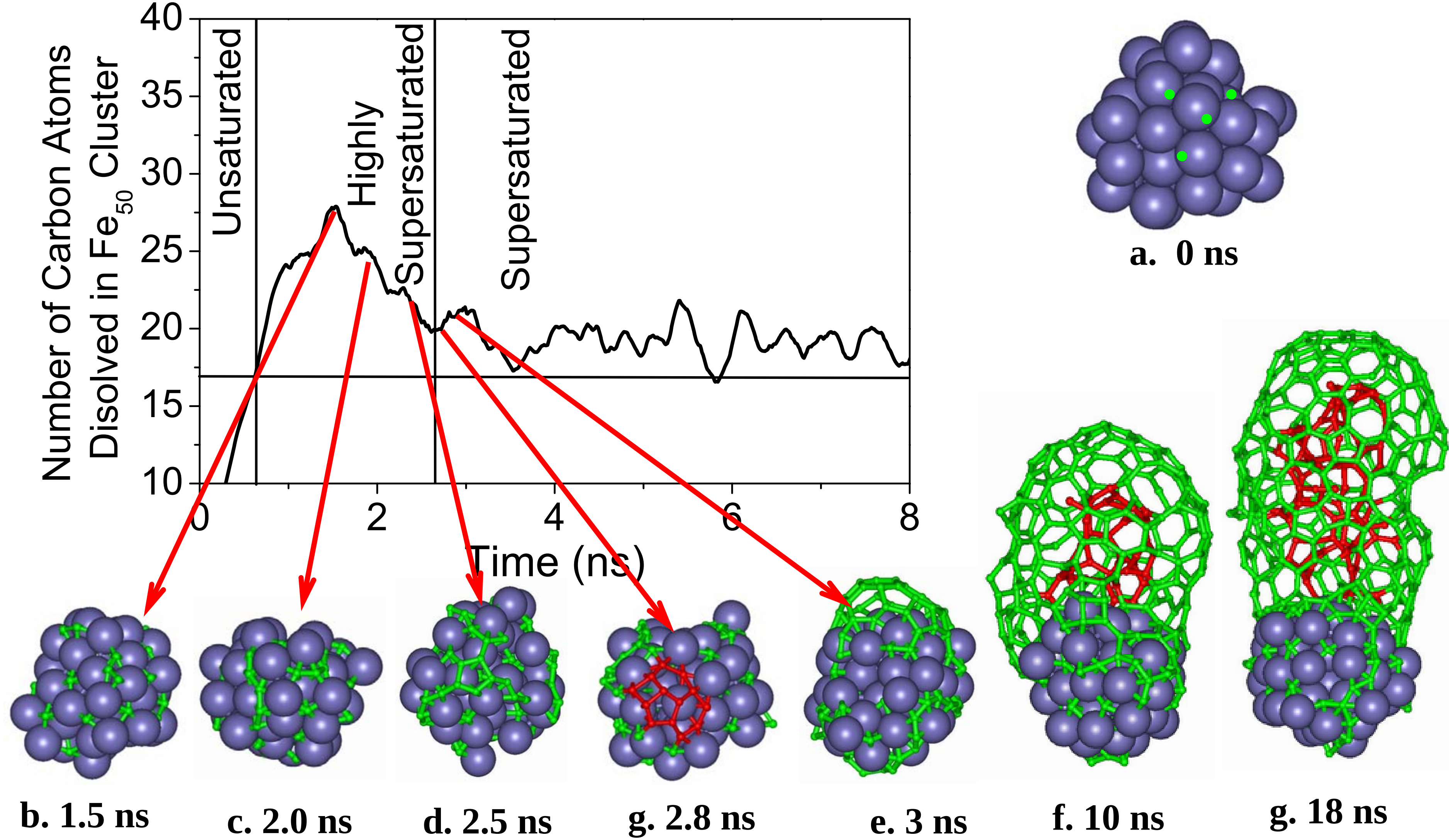
Göteborg University
University College of Borås
Sweden

Melting Temperature of Fe Cluster vs Size



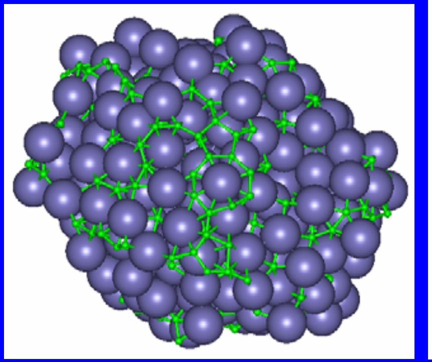
$N^{-1/3}$ dependence is also predicted by classical theories of nanocluster melting points

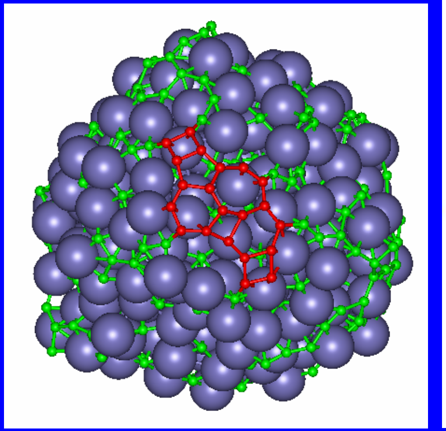
Fe_{50} (1 nm), 900 K, 1 C atom per 40 ps

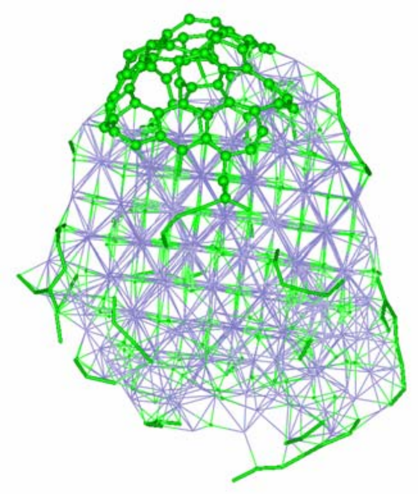


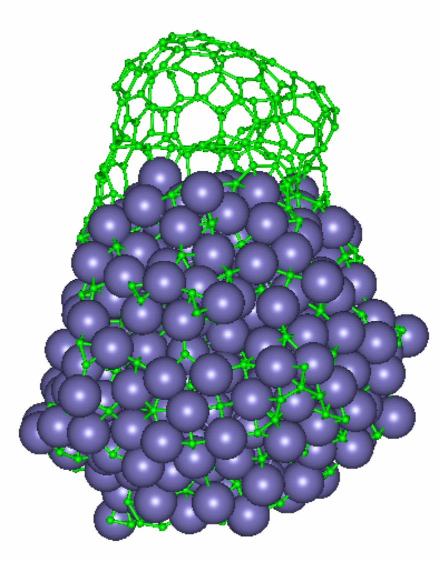
SWNT growth on ‘solid’ particles

Fe_{300} (Mpt = 1100 K), Temp = 1000 K



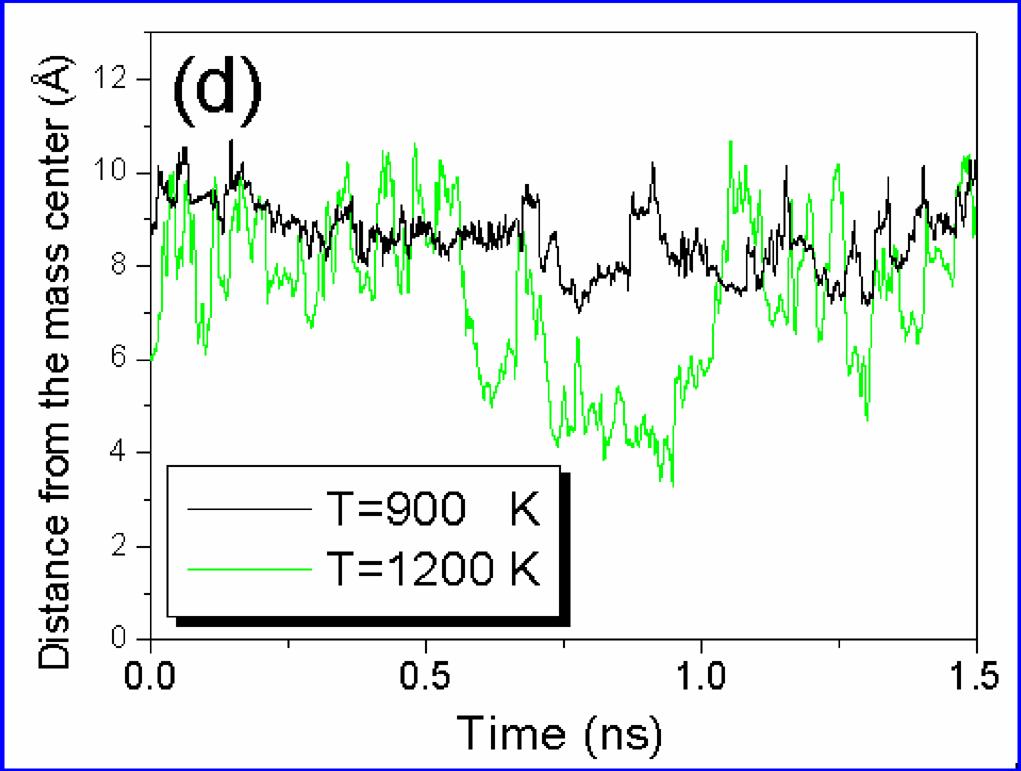




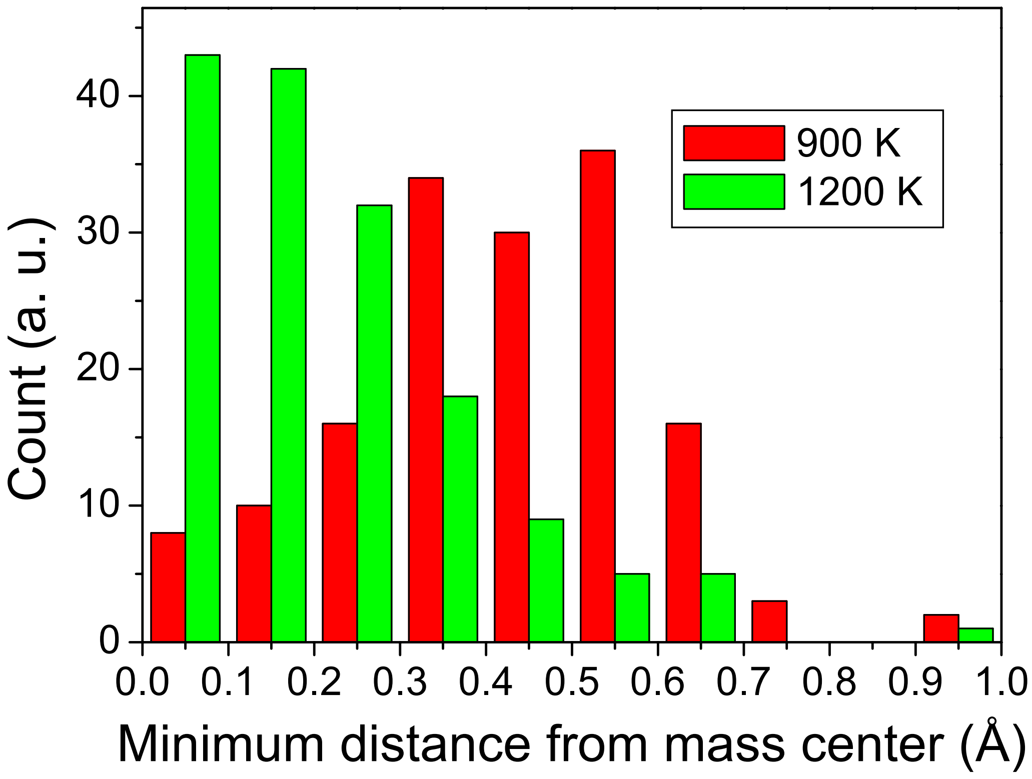


Route of C diffusion from addition on the surface to the SWNT end

Fe_{300} (Mpt = 1100 K)

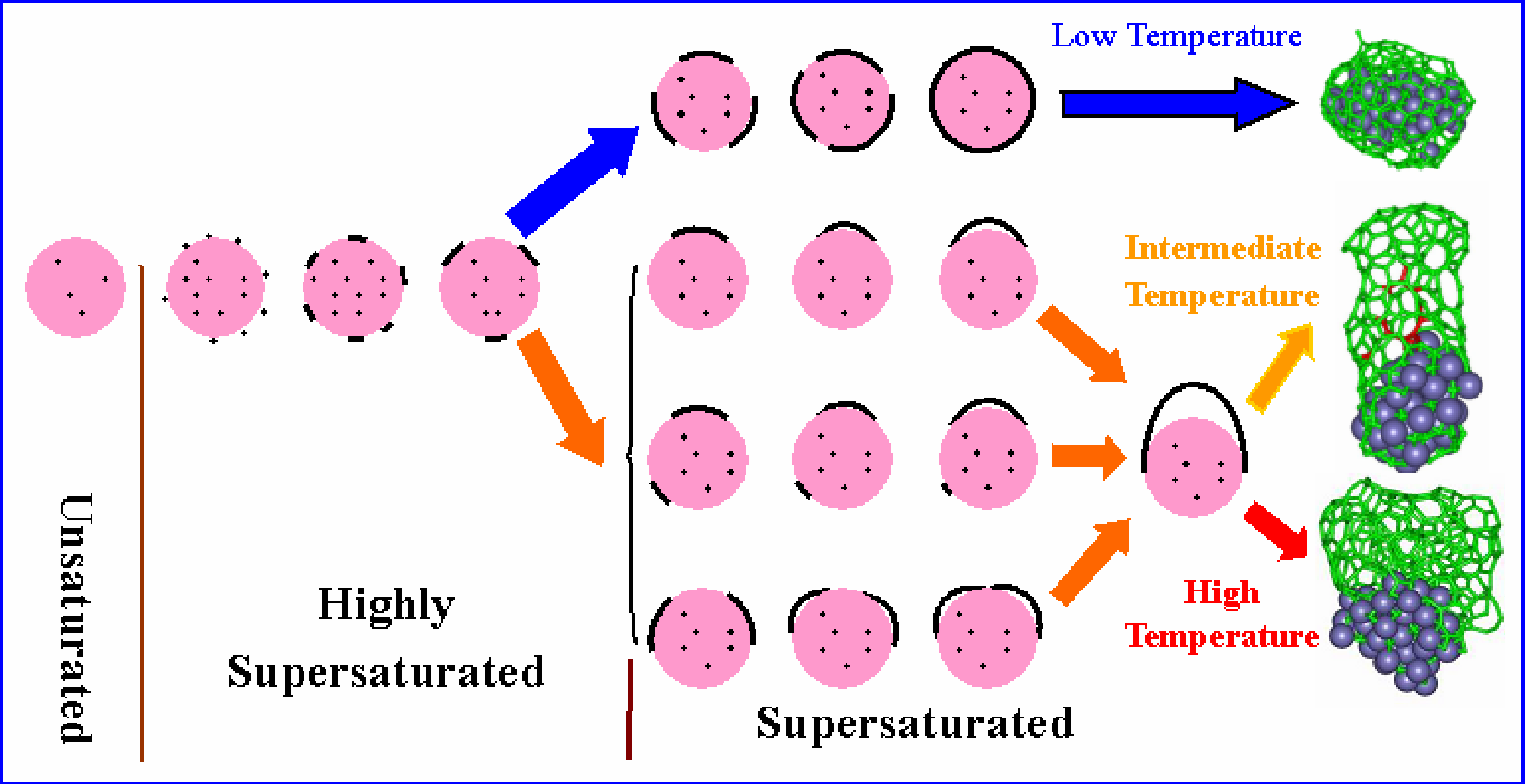


Liquid versus solid particles



Fe_{300} (Mpt = 1100K)

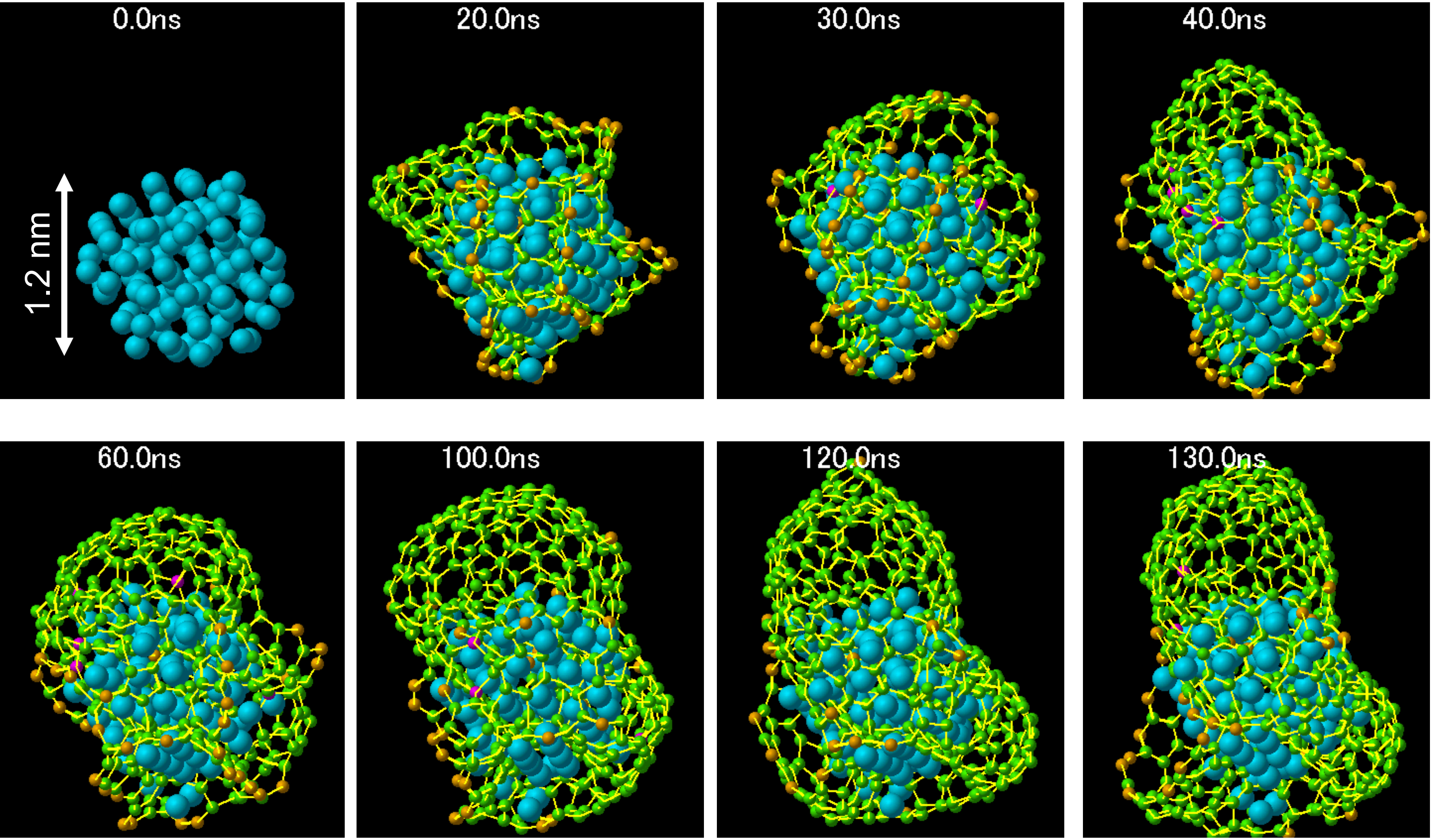
Summary by Bolton et al.



Molecular Dynamics Simulation for Mechanism

500 Carbon & Ni_{108} : 2500K

Y. Shibuta, S. Maruyama et al., CPL 382(2003)381.



Macroscopic modellig of catalyst particle dynamics important, as (based on exp. evidence) catalyst size during NT nucleation determines NT diameter

- Catalyst nucleation (physical or chemical)
- Growth by metal vapor condensation (and via surface reaction of precursor molecules)
- Growth by collisions (coagulation and coalescence)
- Losses to reactor walls by diffusion and thermophoresis
- Fluid flow fields needs to be modelled simultaneosly
- Example: Fe catalyst particle growth via collisions in HWG floating catalyst reactor (pre-made catalyst particles)

Catalyst Particle Dynamics

- General Dynamic Equation (GDE) for the time rate of change of catalyst cluster number concentration

$$\frac{Dn}{Dt}+\frac{\partial(Gn)}{\partial v}-I_{nuc}(v*)\delta(v-v*)-I_{rxn}$$

$$=\frac{1}{2}\int_0^v \beta(v-\tilde{v},\tilde{v})n(v-\tilde{v},t)n(v,t)d\tilde{v}-n(v,t)\int_0^\infty \beta(v-\tilde{v},\tilde{v})n(v,\tilde{v})n(\tilde{v},t)d\tilde{v}$$

$\frac{Dn}{Dt}$ = Change in number concentration with respect to time and space

$\frac{\partial(Gn)}{\partial v}$ = Rate of change in number concentration due to condensation/evaporation

$I_{nuc}(v*)\delta(v-v*)$ = Rate ofnucleation of new particles of critical volume v^*

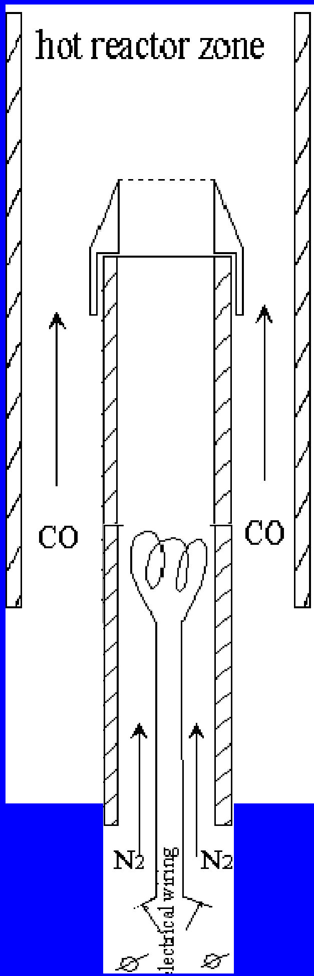
I_{rxn} = Rate of formation of new particles due to chemical reaction

$\frac{1}{2}\int_0^v \beta(v-\tilde{v},\tilde{v})n(v-\tilde{v},t)n(v,t)d\tilde{v}-n(v,t)\int_0^\infty \beta(v-\tilde{v},\tilde{v})n(v,\tilde{v})n(\tilde{v},t)d\tilde{v}$

= Rate of change of number concentration due to coagulation

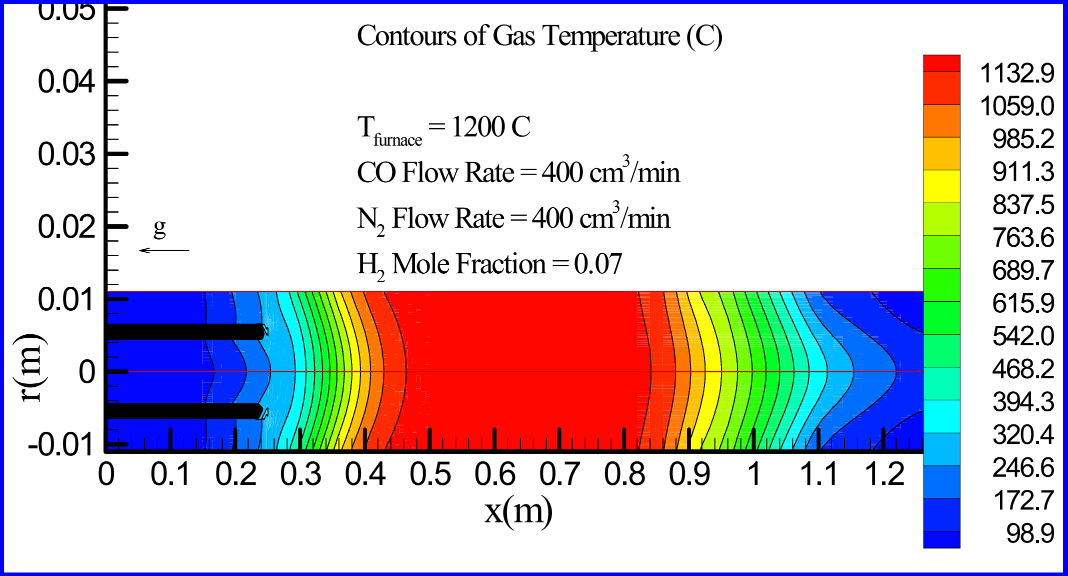
Assumptions and Boundary Conditions for 1.78 nm Premade Catalyst Particles

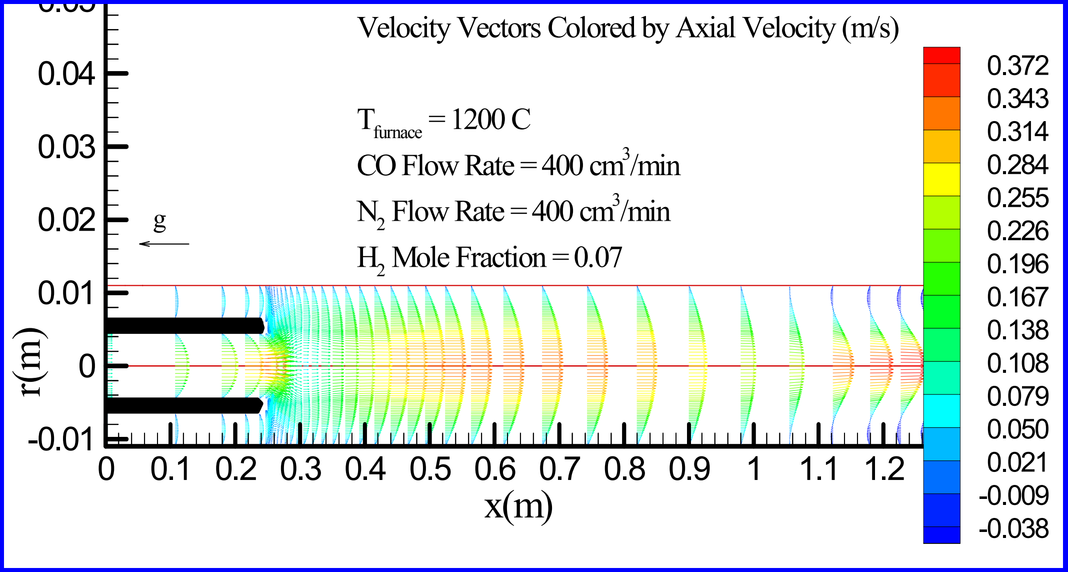
- Inflow boundary conditions
  - 50% mixture of CO and N_2 gases with 7% mole fraction of H_2 gas through inner tube
  - 400 cm^3/s inner and outer flows at 298 K
  - 1e14, 1e16 and 1e18 particles/m^3 with a GSD of 1.26 and mean diameter of 1.78 nm
- Wall boundary conditions
  - Temperature linearly interpolated from measurements, 1200 °C set wall temperature
  - Saturated with iron vapor
- Outflow boundary conditions
  - Atmospheric pressure



Brown, Nasibulin, Kauppinen (2006)

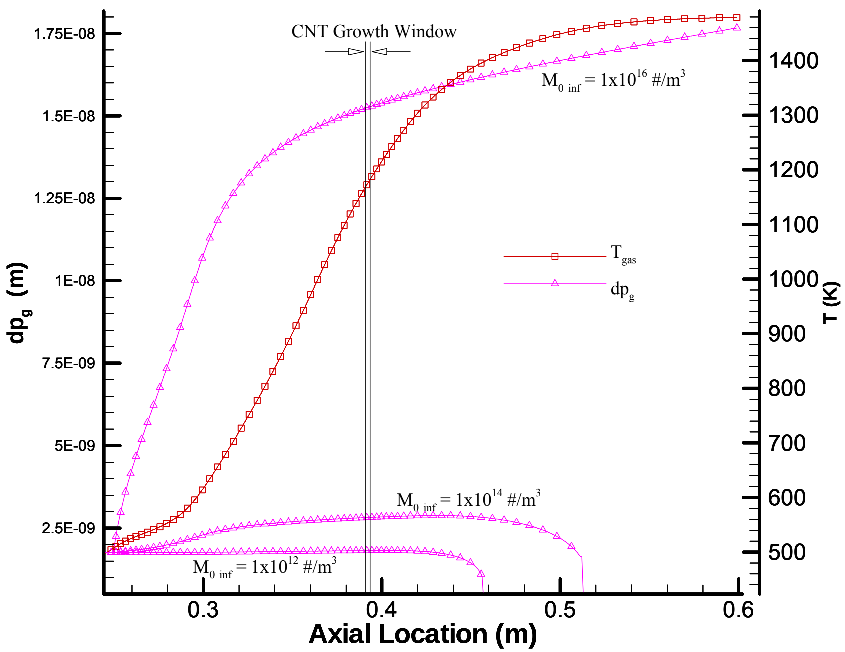
CFD Calculations of Gas Conditions





Combined CFD - Particle Dynamics Assuming 1.78 nm Premade Catalyst Particles- Mean Particle Diameter – Catalyst Growth when High Concentration

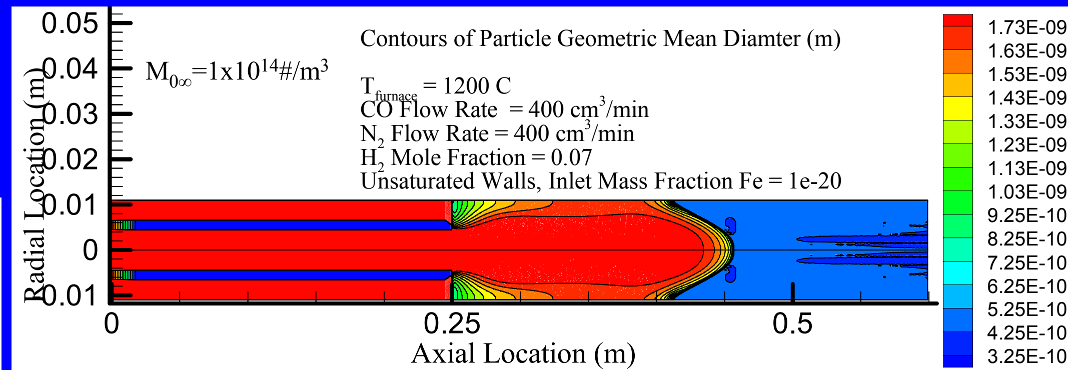
Centerline Particle Mean Diameter and Gas Temperature

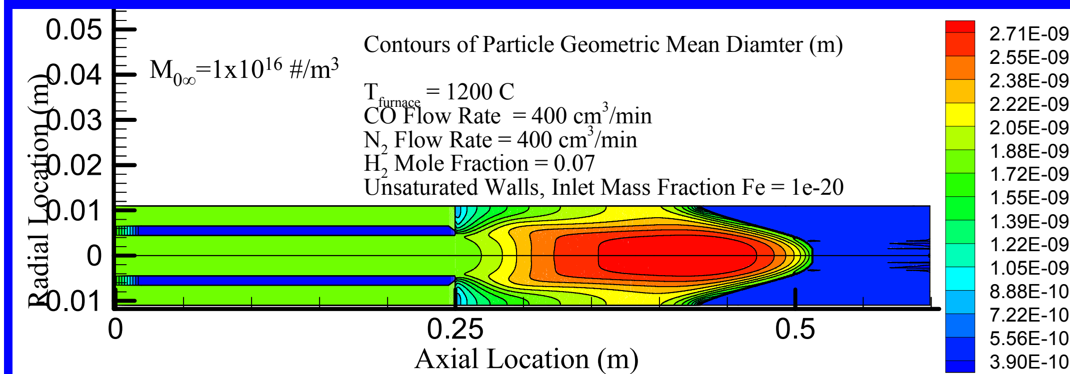


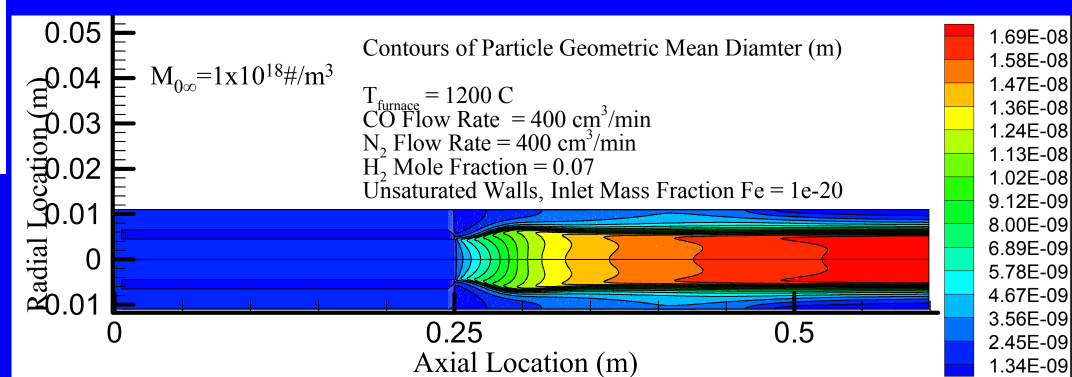
Coagulation Effects

Evaporation Effects

High conc – too large catalysts

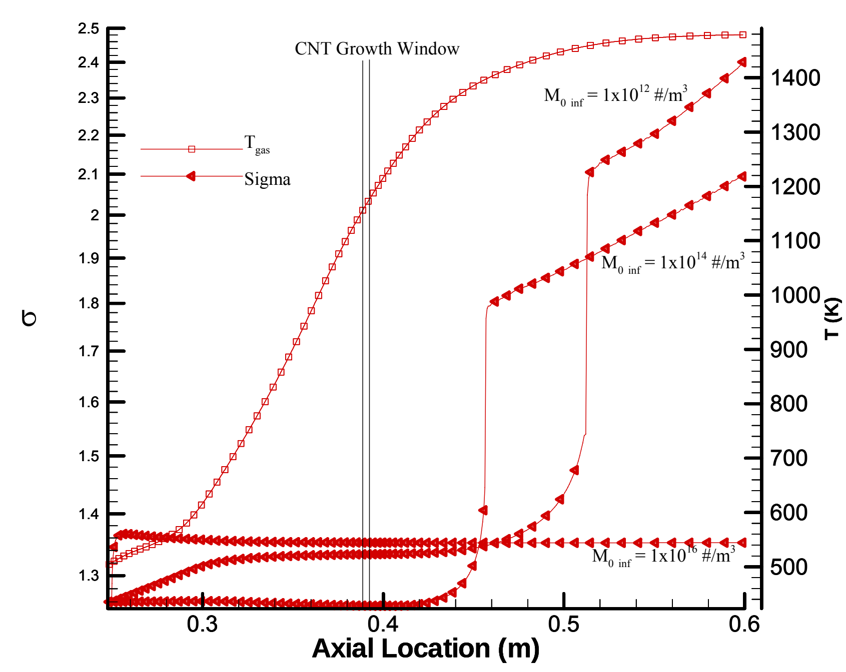






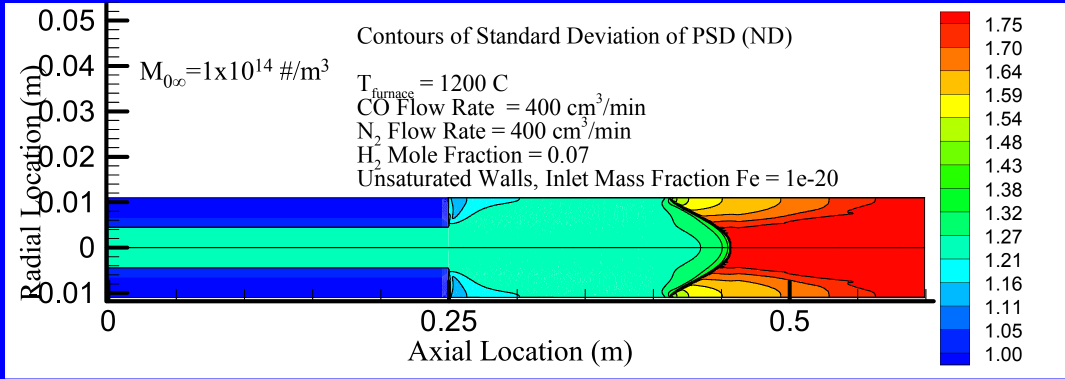
Particle Dynamics Assuming 1.78 nm Premade Catalysts- Std. Dev. of PSD

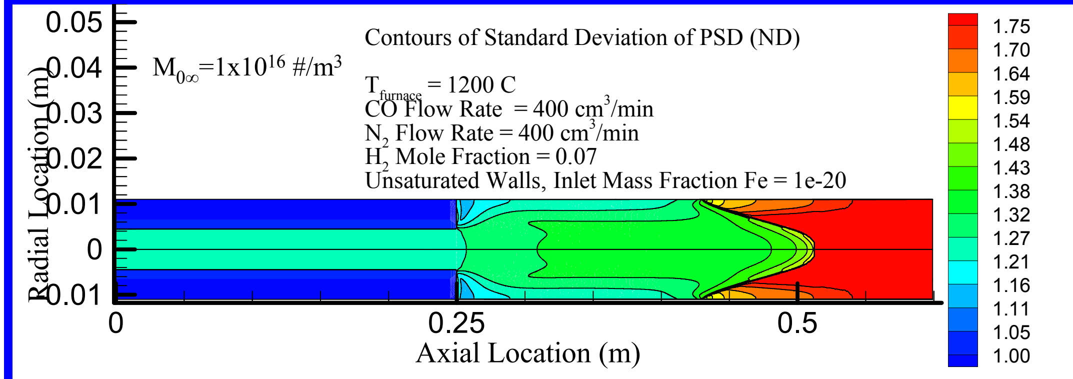
Centerline
Std. Dev. of Particle Size Dist. and Gas Temperature

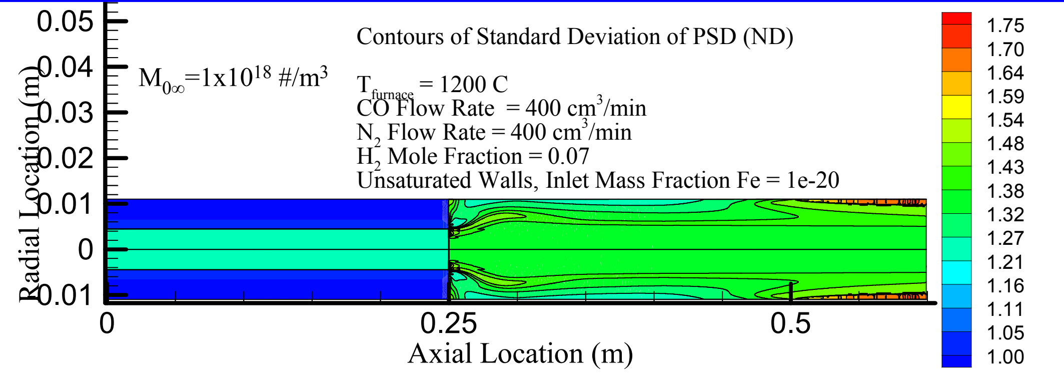


Coagulation Effects

Evaporation Effects







High conc – broad catalyst distr.

SUBSTRATE CVD METHODS

1 Catalyst

Transition metals: Fe, Co, Ni… or their mixtures

- Ability to decompose gaseous C-containing molecules
-Correlation between the SWNT Ø and the catalyst particle size
- Normally prepared by **wet chemical** routes or by depositing **thin metal film** on substrates by sputtering or evaporation

2 Substrate

Silica, alumina, zeolite…

- Strong metal-substrate interactions: reduce diffusion and prevent metal species for aggregating and forming unwanted large clusters

-Stabilisation of particles size distribution; **catalyst cluster dynamics important**

3 Carbon source

CO, EtOH, CH_4,… SWNTs synthesis

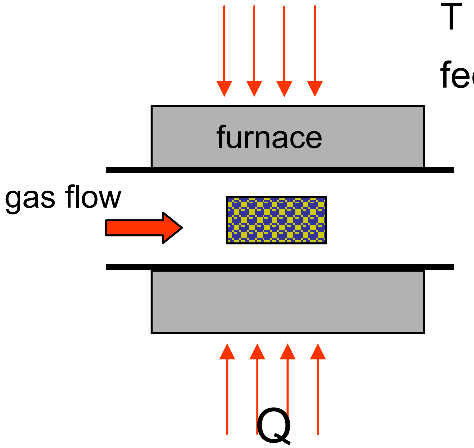
Acetylene, benzene,…precursors for MWNTs

Oxidazing trace gases

4 Operational conditions

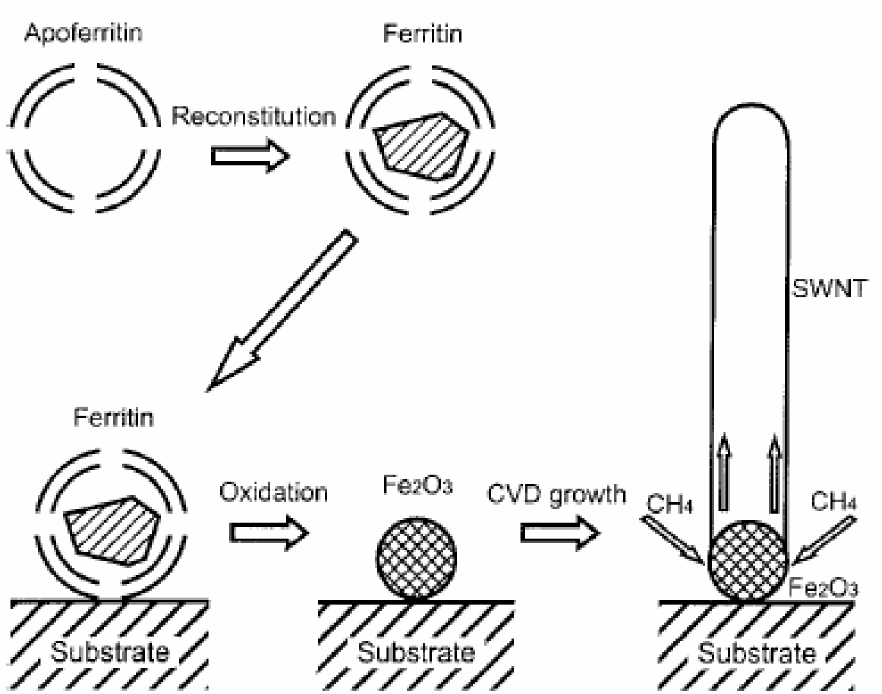
T (600-1200 ^{o}C)

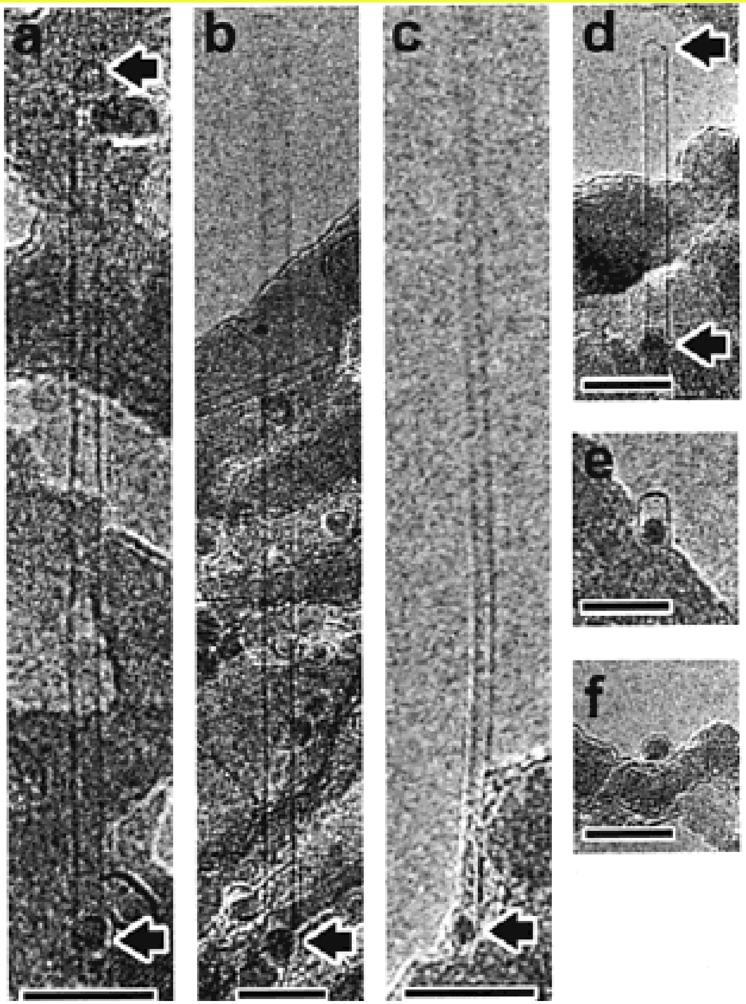
feed rate, t…



Preparation of discrete Catalytic nanoparticles of various sizes

Y. Li, H. Dai *et al.*, J. Phys. Chem. B 2001, 105 , 11424-11431





10 nm

Discrete catalytic iron oxide nanoparticles with tunable diameters using an iron storage protein: ferritin

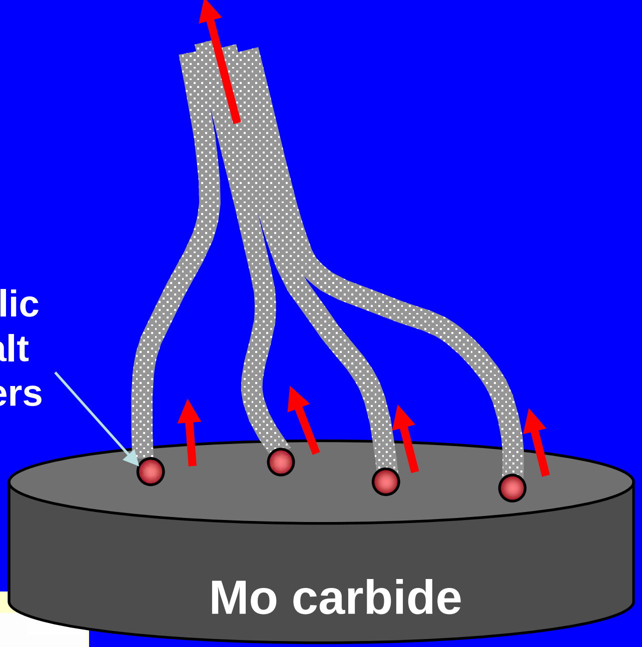
Growth of isolated SWNTs by CVD (900 ^{o}C, CH_4,5 min) method with diameters controlled by the sizes of the catalytic particles:

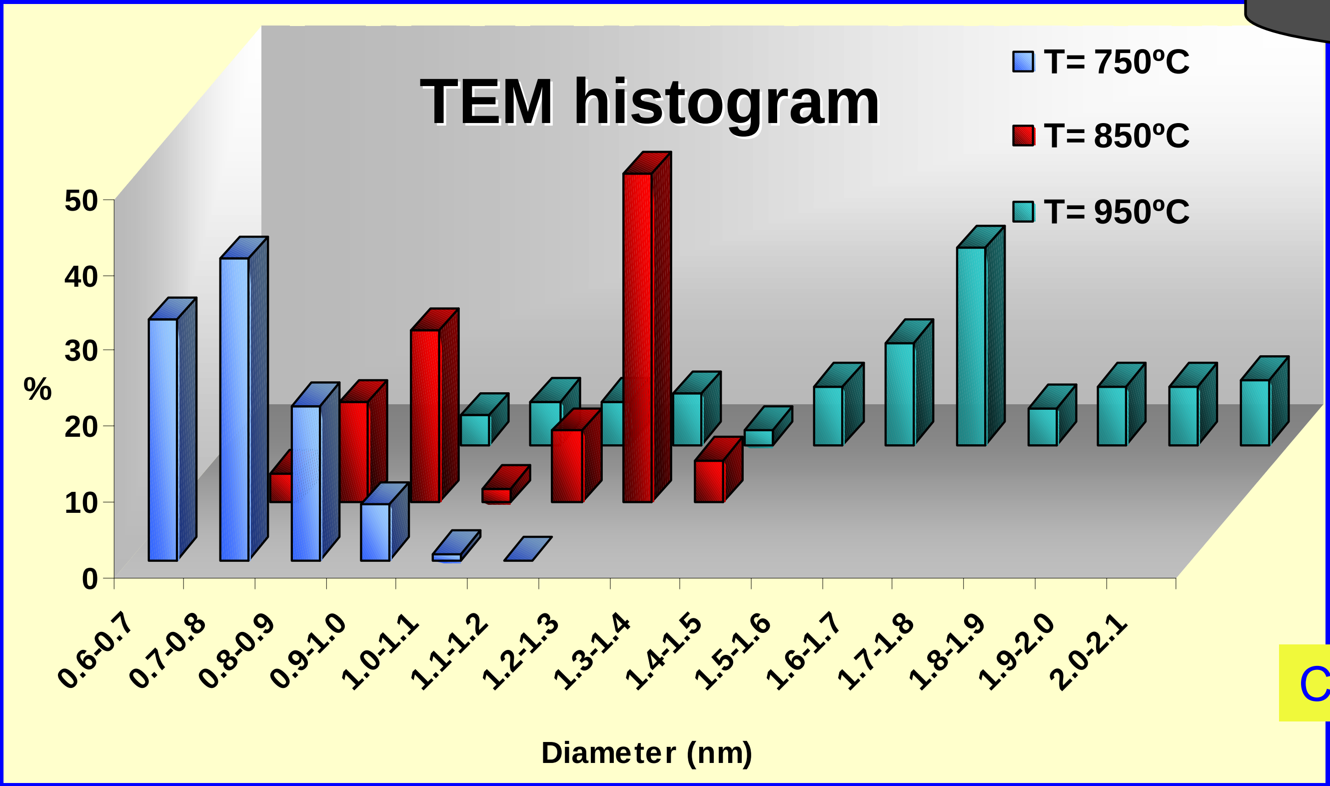
3 nm CNTs from nanoparticles of 3.7 nm and 1.5 nm CNTs from 1.9 nm nanoparticles

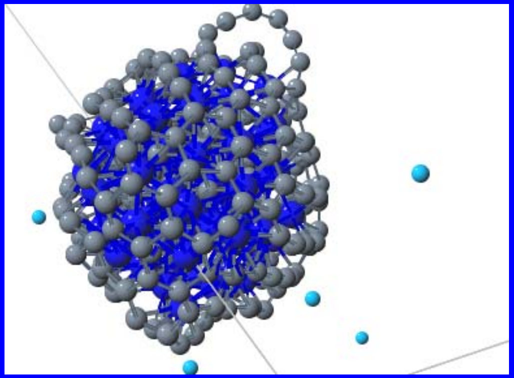
Base-growth model: particle remains anchored on the substrate

CoMoCat- Effect of Reaction Temperature on SWNT Diameter

The nanotube diameter increases as the reaction temperature increases





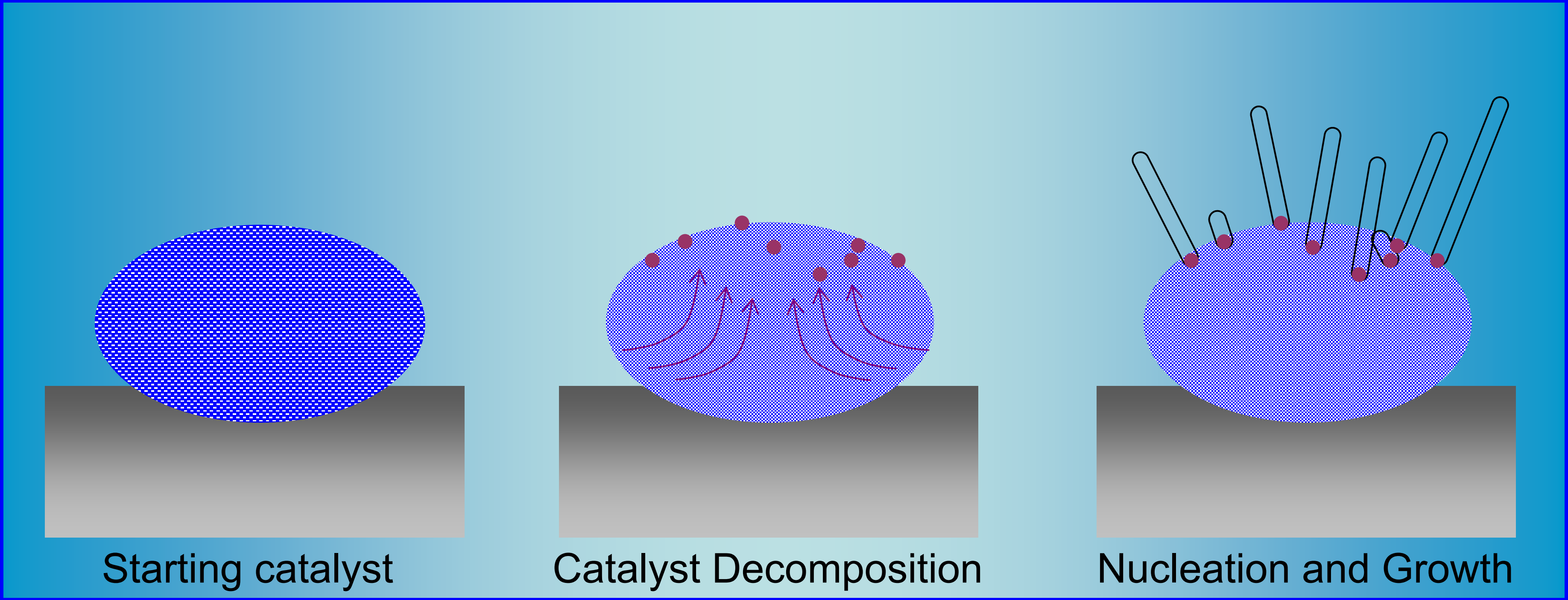


Courtesy –Prof. D. Resasco

Prof. D. Resasco: Common Features of Selective Catalysts:

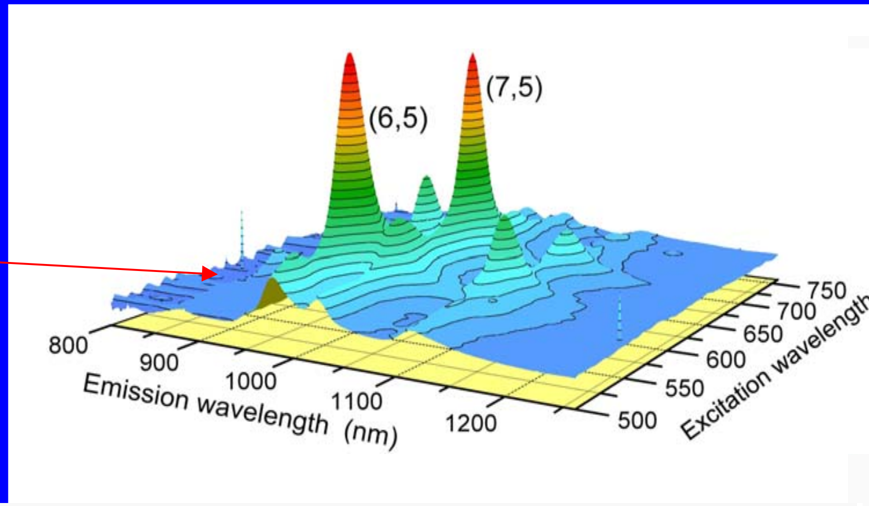
In-situ catalyst Decomposition

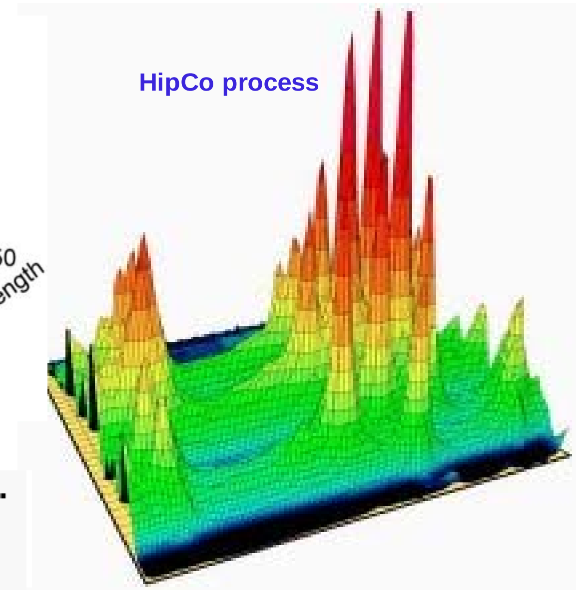
- Co-Mo/supports (SiO_2, MgO, Al_2O_3)
- Co/MCM-41
- Co-Re alloys

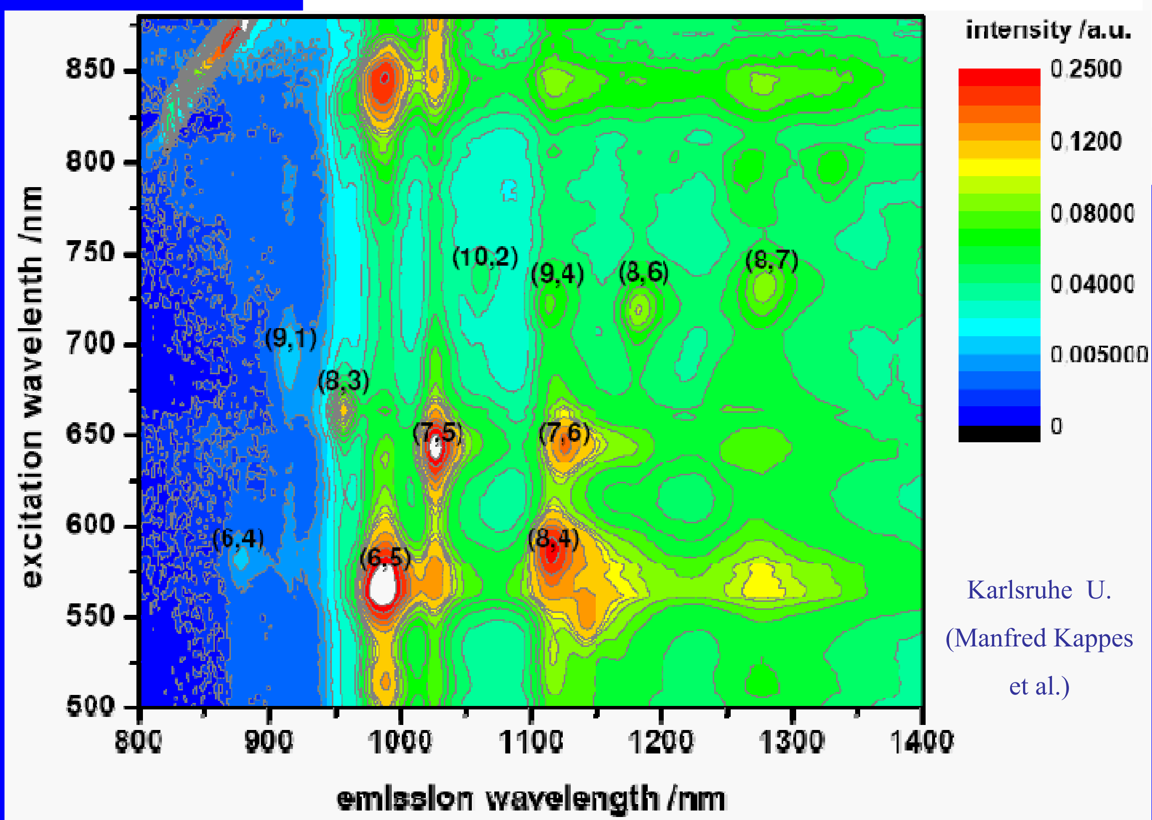


Courtesy –Prof. D. Resasco

CoMoCat





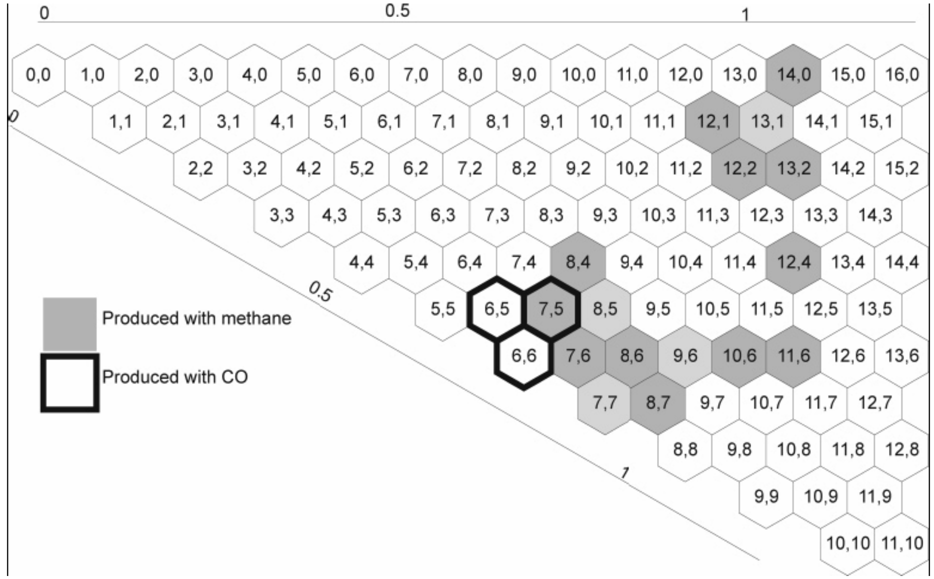


Karlsruhe U.
(Manfred Kappes
et al.)

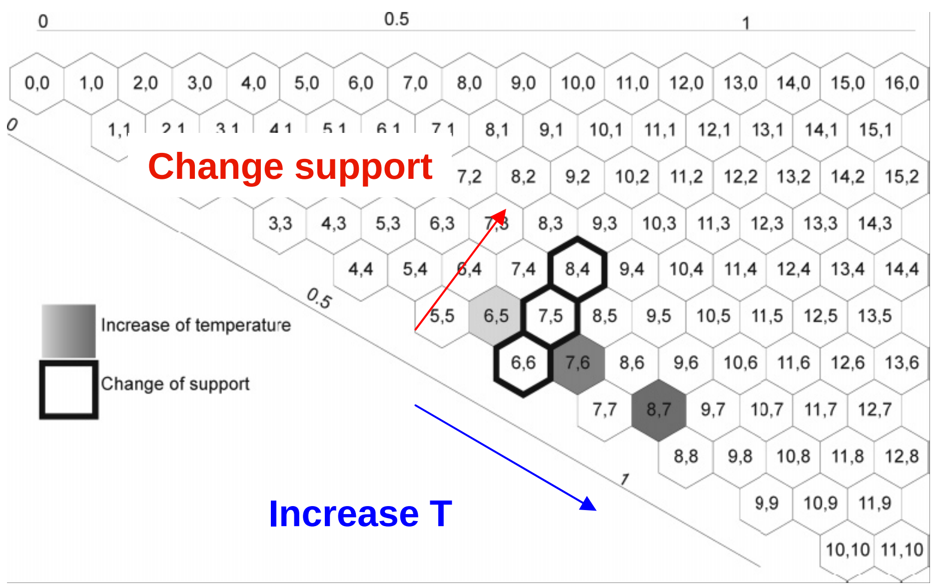
Comparison of Diameter Distribution CoMoCAT Vs. HIPCO Photo-luminescence *SEMICONDUCTING TYBES ONLY*

Courtesy –Prof. D. Resasco

COMoCAt: (*n*,*m*) map, effect of gas feed at 800 °C on the produced SWNT.

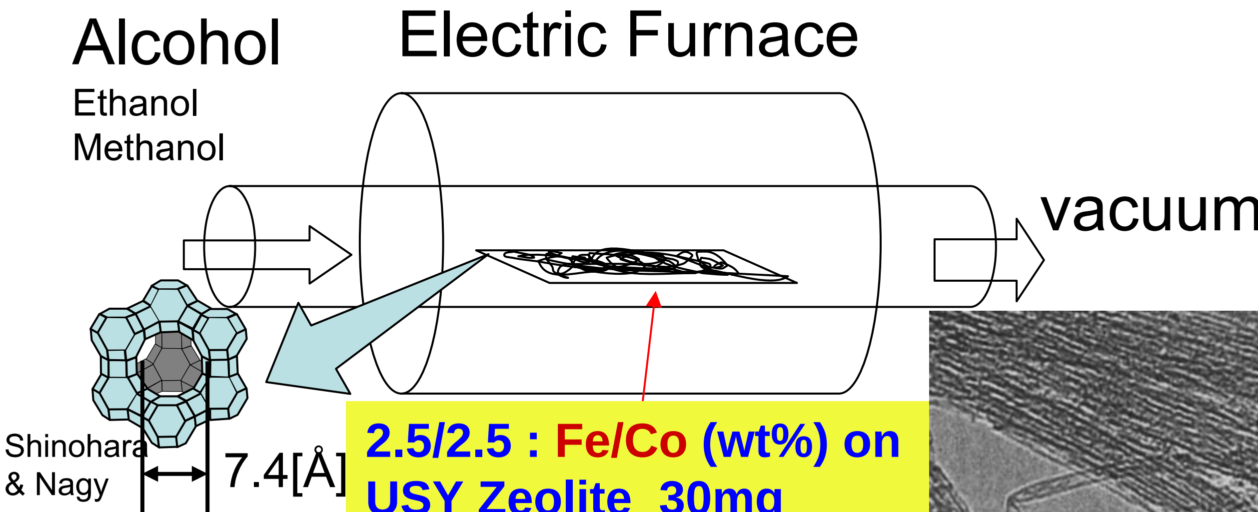


(*n*,*m*) map, effect of temperature and support morphology on the produced SWNT.



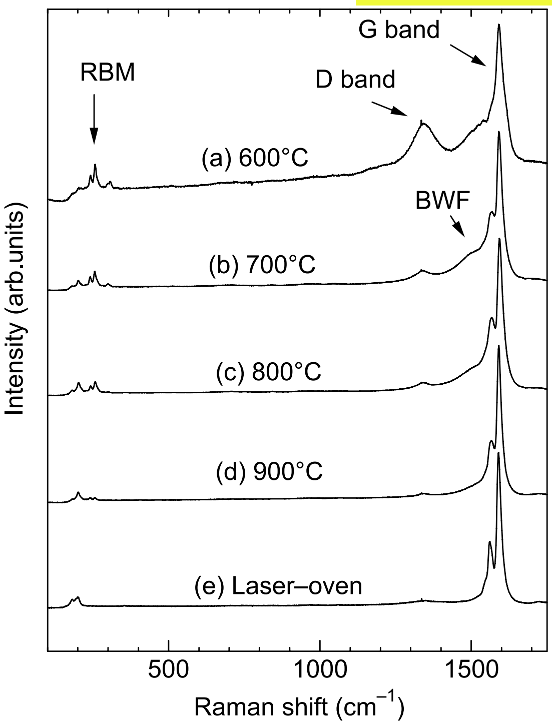
Lolli et al., Phys. Chem. B. 2006

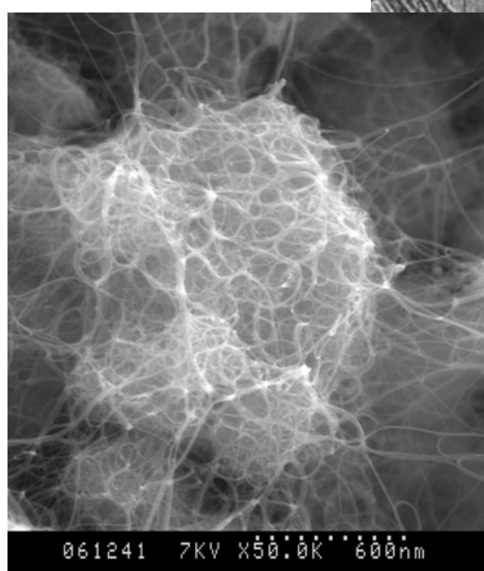
Alcohol CCVD on Catalysts Supported with Zeolite

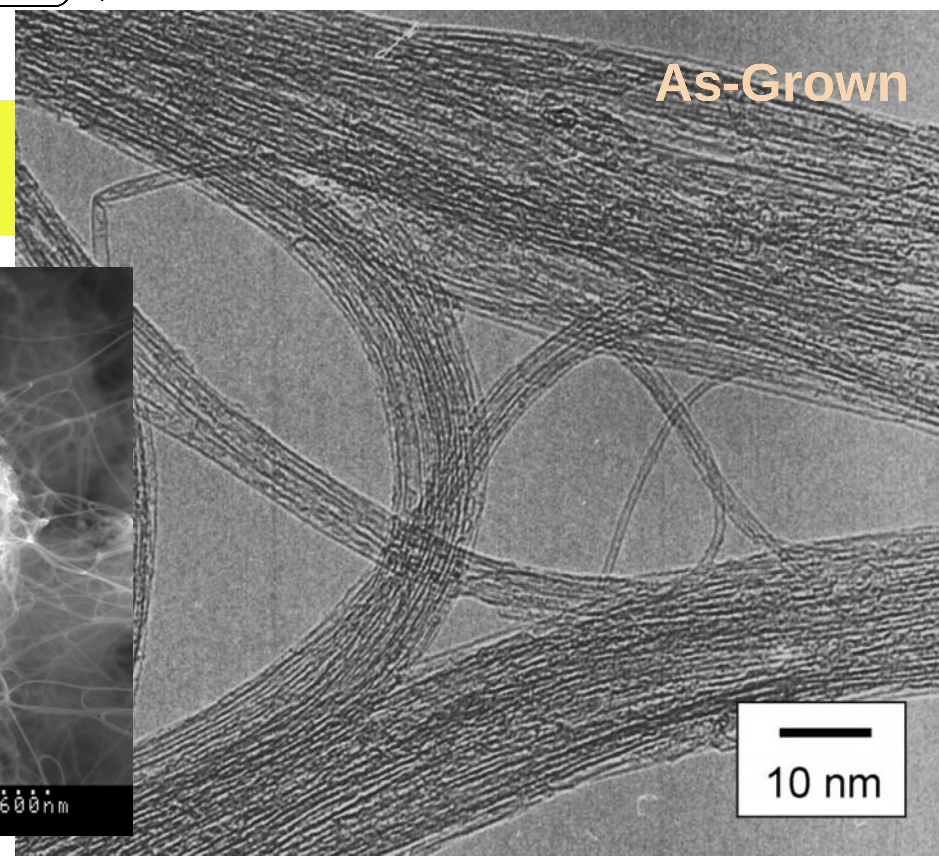


2.5/2.5 : Fe/Co (wt%) on USY Zeolite 30mg

Simple, High-Purity
Low-Temperature
(550-900°C)





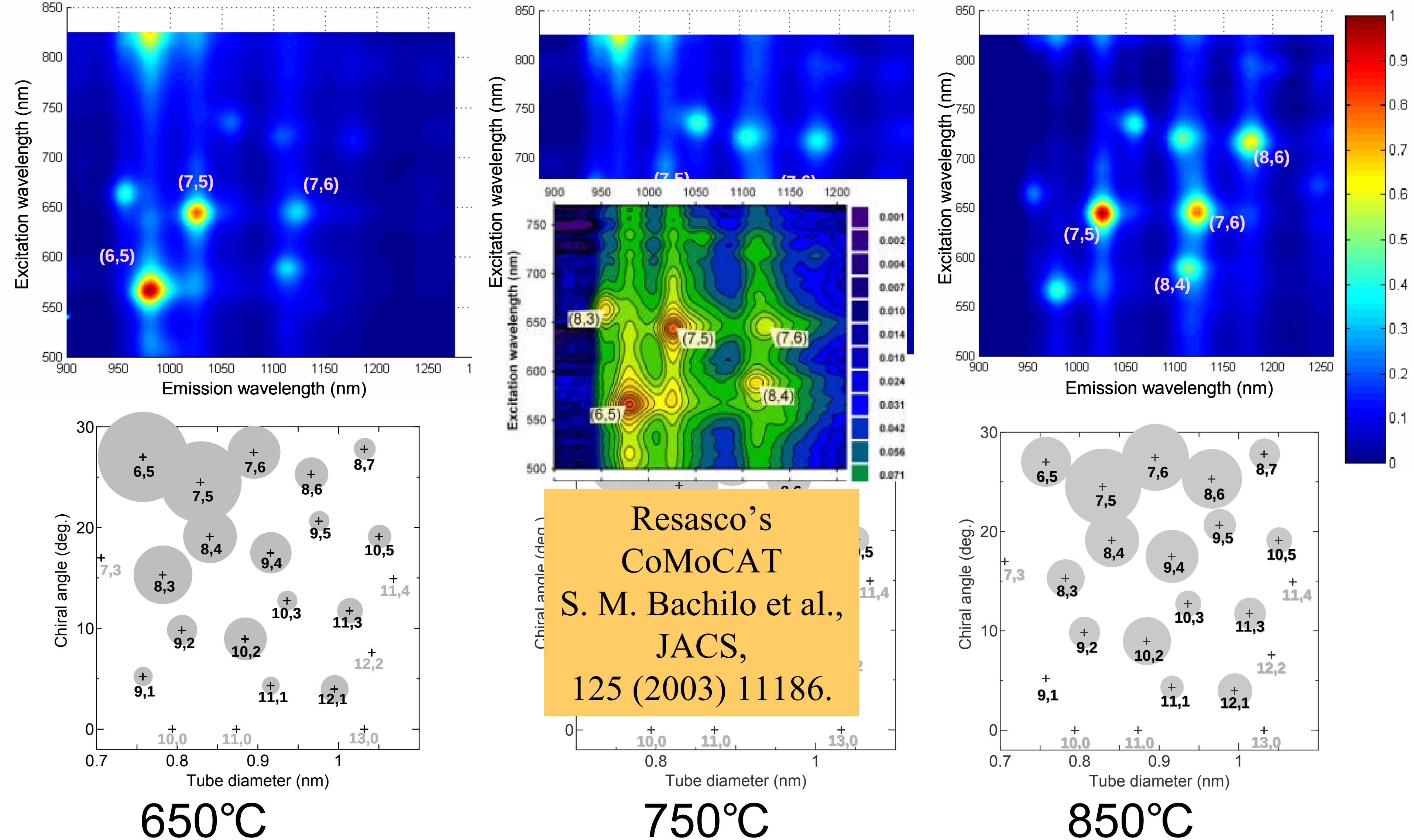


S. Maruyama et al., Chem. Phys. Lett. 360 (2002) 229.

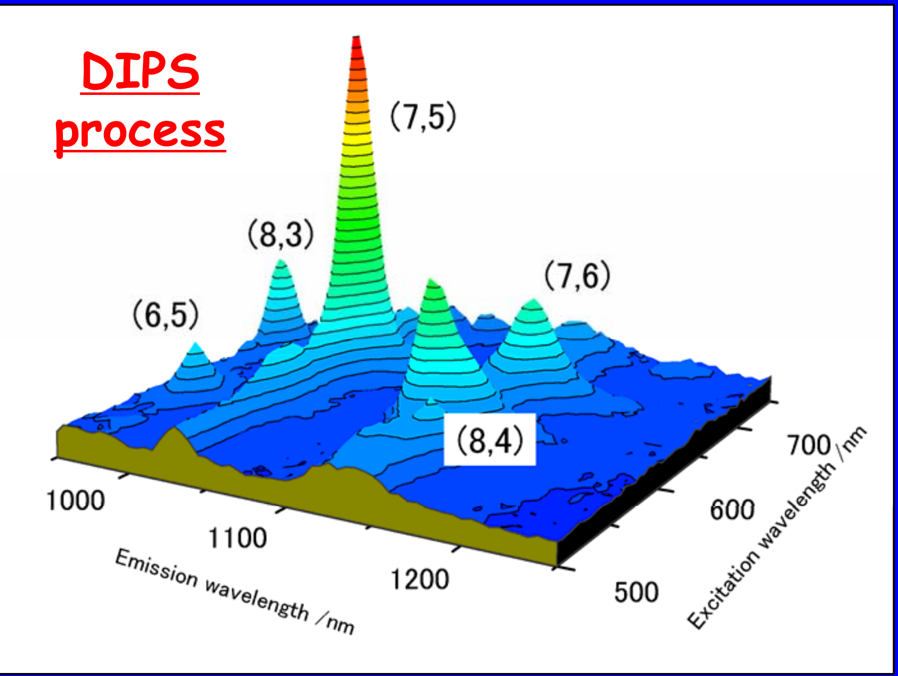
ACCVD Chirality - Semiconducting

Carbon source : Ethanol, CVD time : 10min

S. Maruyama et al.

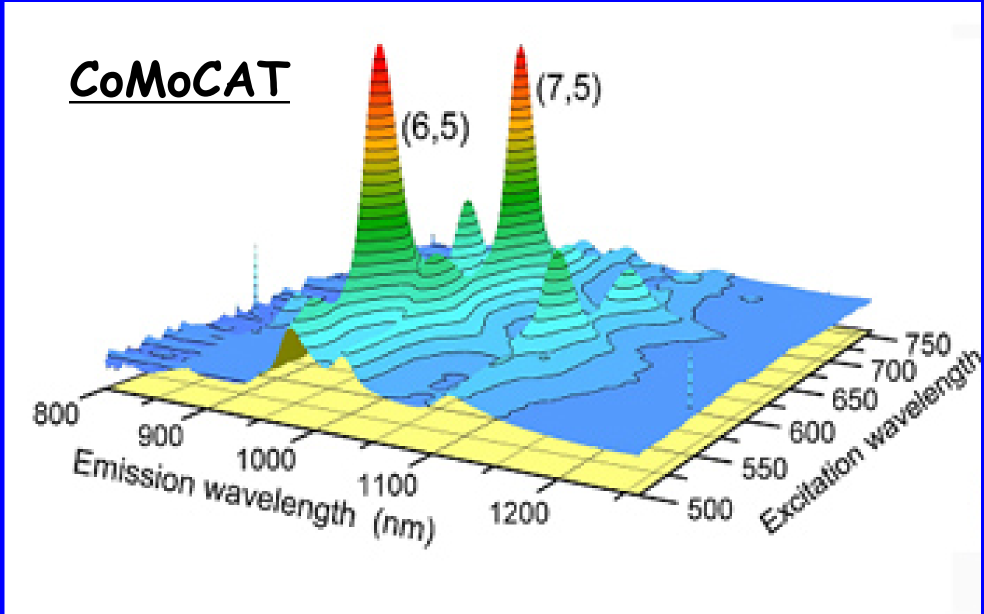


Comparison of DIPS and CoMoCat
Semiconducting



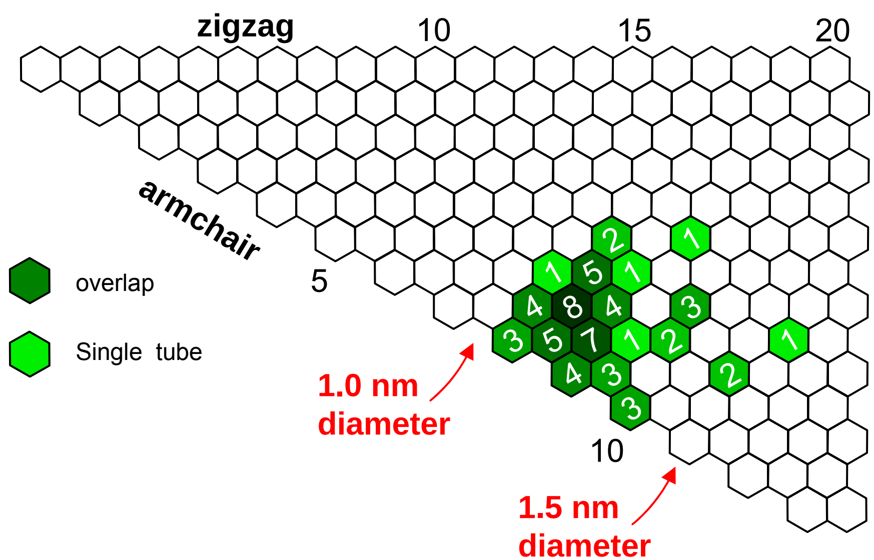
DIPS –Fe catalyst

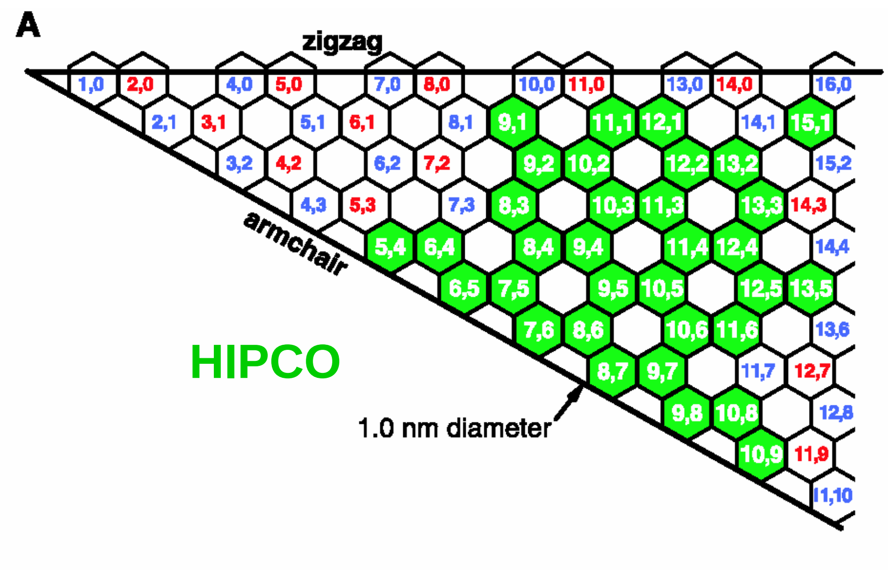
Courtesy Prof. S.Iijima



Spectrofluorimetric analysis (courtesy Prof. Weisman) of SWeNT™ (Left) and HiPCO™ (Right) samples. The comparison reflects the much narrower distribution of diameter and chirality

Floating Catalyst – Fe /Co Chirality

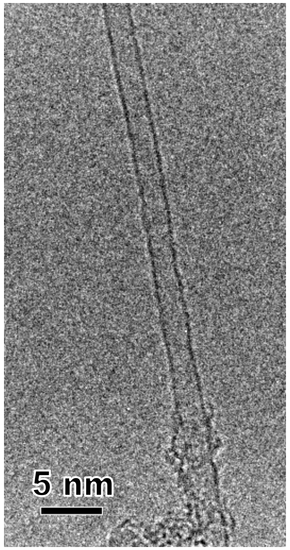


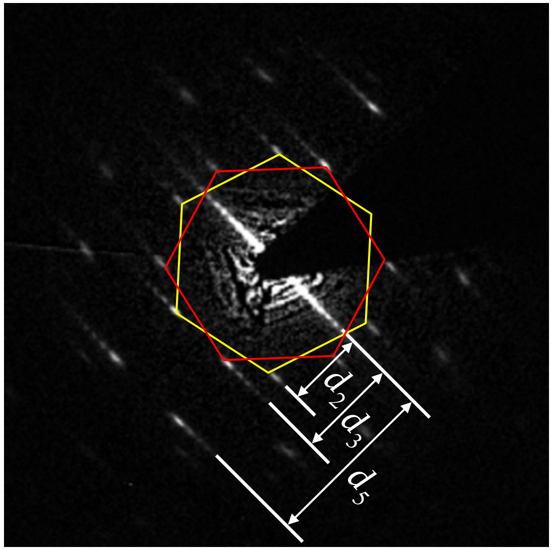


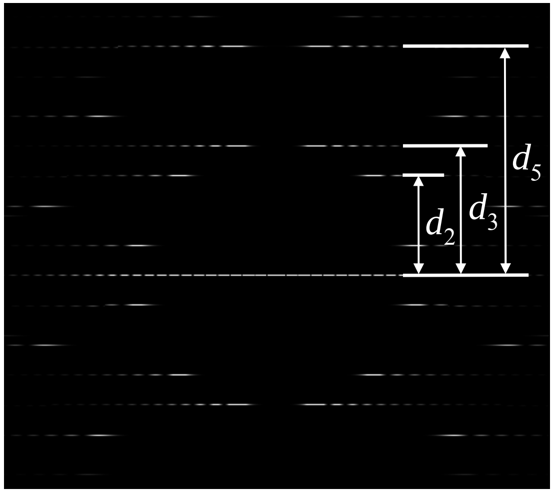
HUT as measured with TEM/ED
BOTH Metallic and Semiconducting

HiPCO semiconducting from fluorescence

(n,m) Determination with Nanoprobre Electron Diffraction - Tilt Angle needs to be considered







Simulation of (23,10) at $\tau = 10°$

	δ (pixels)	d_3 layer-line			d_5 layer-line			n			m		
		$2d_3$ (pixels)	$2\xi_3$	τ(3)	$2d_5$ (pixels)	$2\xi_5$	τ(5)	n^t	n	ε (n)	m^t	m	ε (m)
Experimental	4.67	97.58	20.895	9.92	172.8	37.002	10.46	23.29	**23**	0.29	10.27	**10**	0.27
Simulation	10.44	218	20.881	9.70	386	36.973	10.21	23.28	**23**	0.28	10.25	**10**	0.25

	δ (pixels)	d_3 layer-line			d_2 layer-line			n			m		
		$2d_3$ (pixels)	$2\xi_3$	τ(3)	$2d_2$ (pixels)	$2\xi_2$	τ(2)	n^t	n	ε (n)	m^t	m	ε (m)
Experimental	4.67	97.58	20.895	9.92	74.95	16.049	10.01	23.34	**23**	0.34	10.16	**10**	0.16
Simulation	10.44	218	20.881	9.70	168	16.092	10.84	23.28	**23**	0.28	10.25	**10**	0.25

courtesy Dr. Hua Jiang

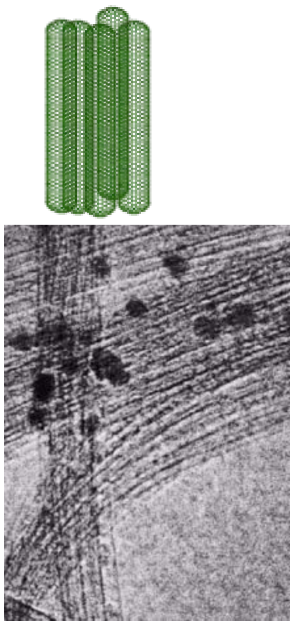
Individual SWCNT*s onto substrates at $T_{ambient}$

Carbon arc-discharge

Laser ablation

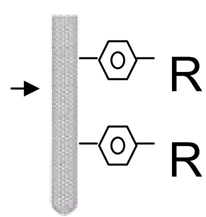
HiPCO process

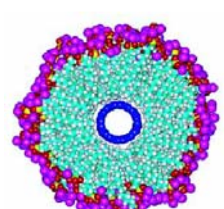
Substrate Chemical Vapour Deposition

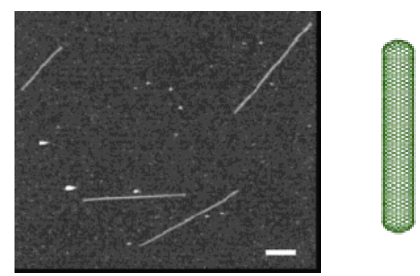


Bundles of CNTs (HiPco)

Surfactants, Polymers, etc
Functionalization







High growth temperature (500 °C)

Difficult integration in devices

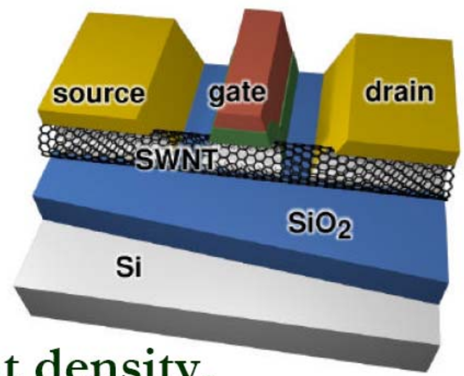
Temperature sensitive substrates can not be used

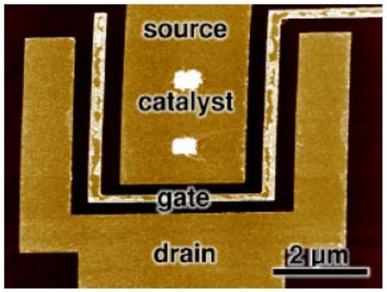
SWCNT's in Future NanoElectronics Applications

World wide economic activity associated with electronics:
(Phaedon Avouris, IBM, 3/2006)
- Semiconductors 215 B$
- Electronics 1 T$
- IT enabled services 5 T$

CNT transistor
-Advantage-

- High speed operation is expected.
  g_m ~10000 μS/μm[1] (p-Si **x** ~20)
- Excellent durability to large current density.
  $10^{9\sim10}$ A/cm^2 (Si **x** ~100)
- Compatible with high-κ gate oxides.
  HfO_2[1], $SrTiO_3$[2]…
- Low cost substrate can be used.
  Polymer[3]





Nihey et al, JJAP 2004

From Ishida et al., NEC, NT05

ISSUES TO BE SOLVED:

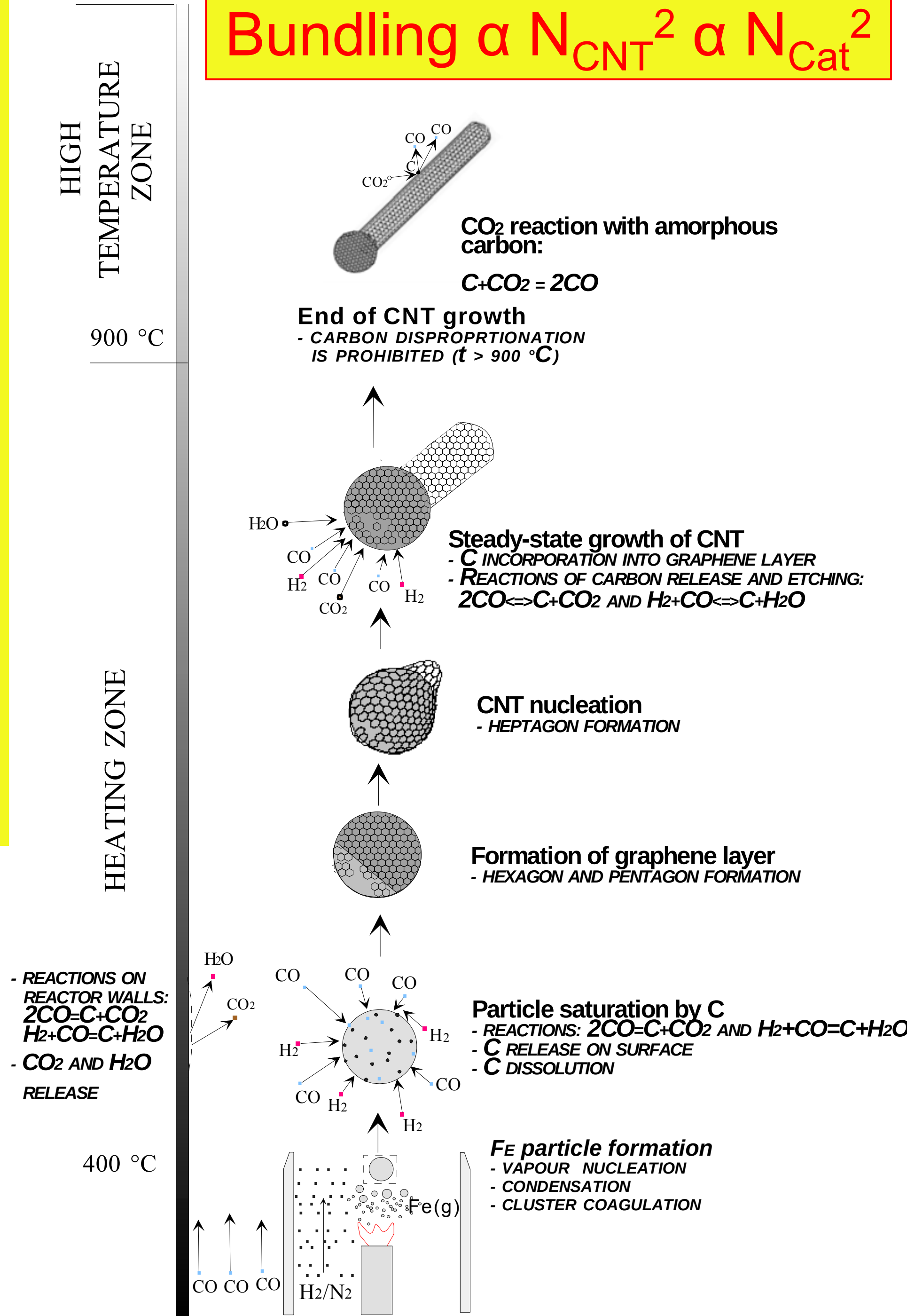
individual SWCNT with given (n,m) at ambient T to exact location at substrate

i.e.

how to integrate SWCNT's into electronics integrated manufacturing processes

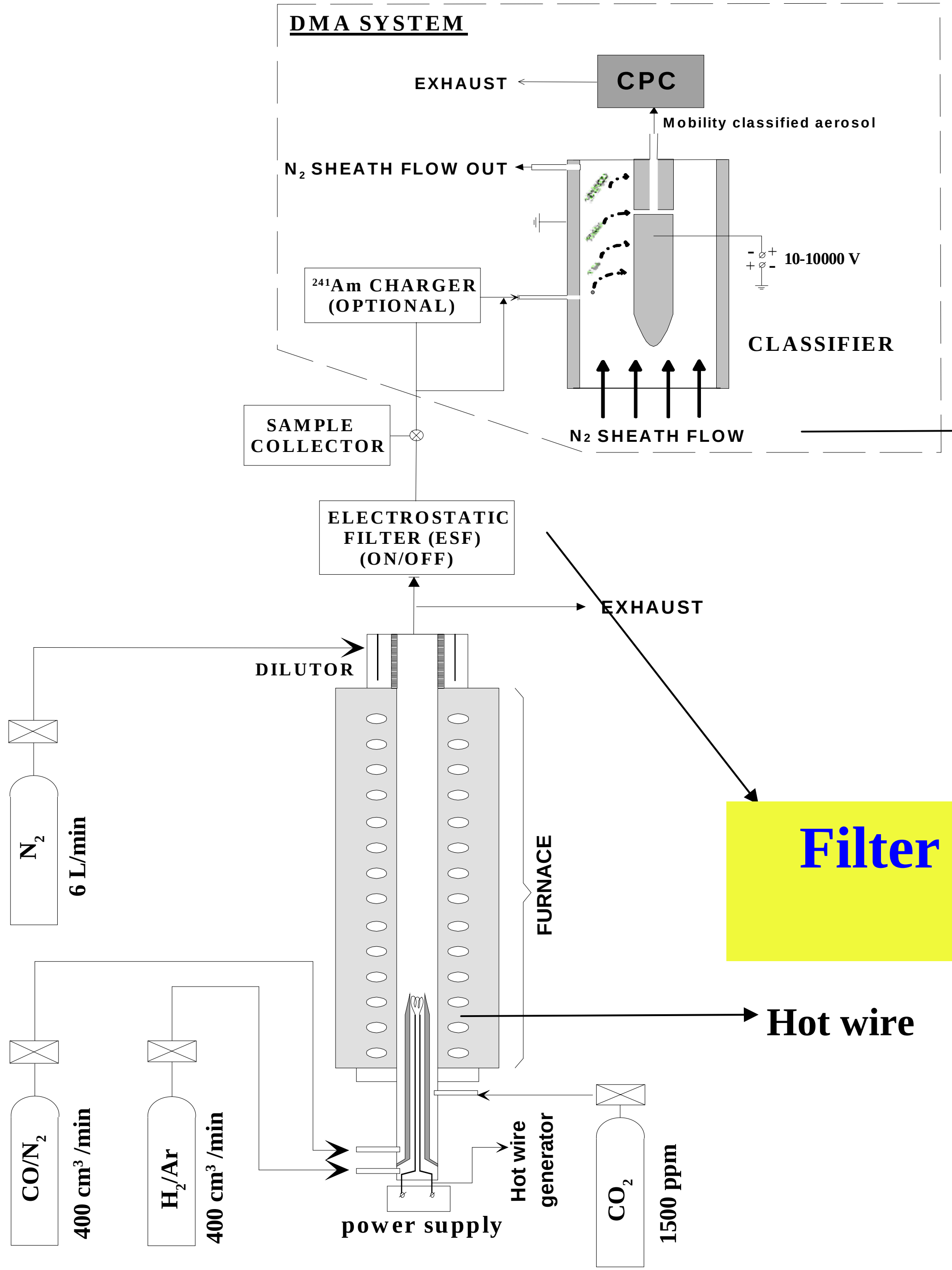
Schematic presentation of mechanism of CNT formation – *control of bundling and charging ?*

Bundling α N_{CNT}^2 α N_{Cat}^2



A. G. Nasibulin, D. P. Brown, P. Queipo, D. Gonzalez , H. Jiang, E. I. Kauppinen (2005) An essential role of CO2 and H2O during single-walled CNT synthesis from carbon monoxide. *Chemical Physics Letters* **417**, 179-184

Experimental set up

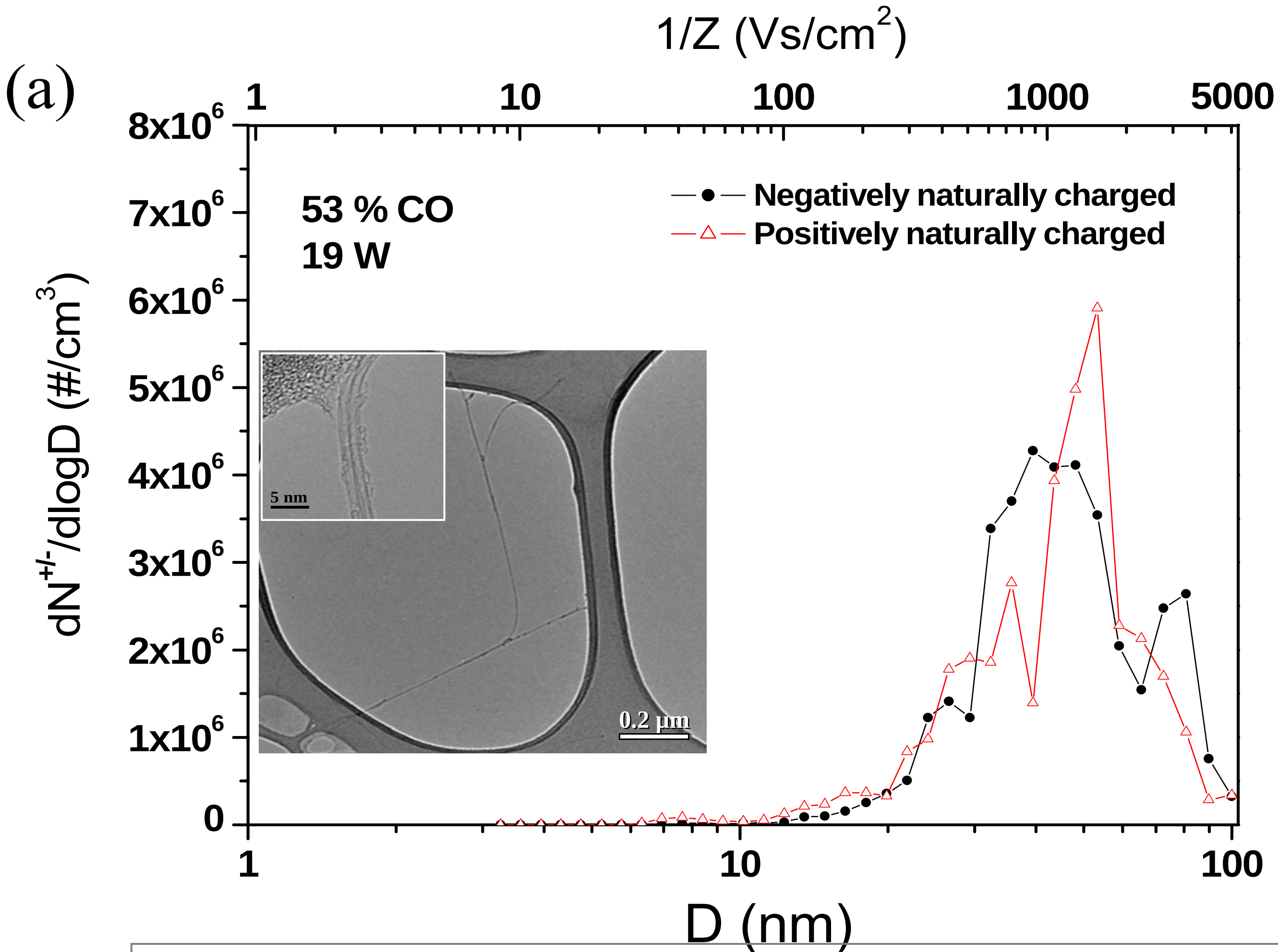


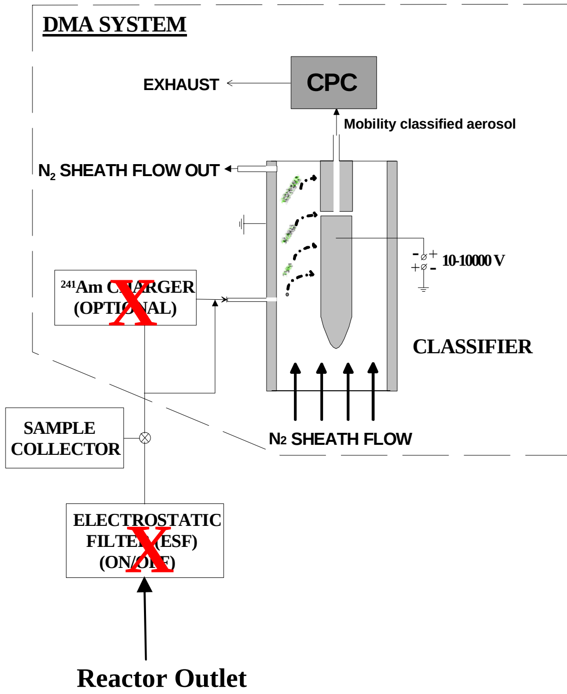
Reminder: DMA can classify only charged aerosol particles

Filter out electrical charged aerosol particles

Hot wire

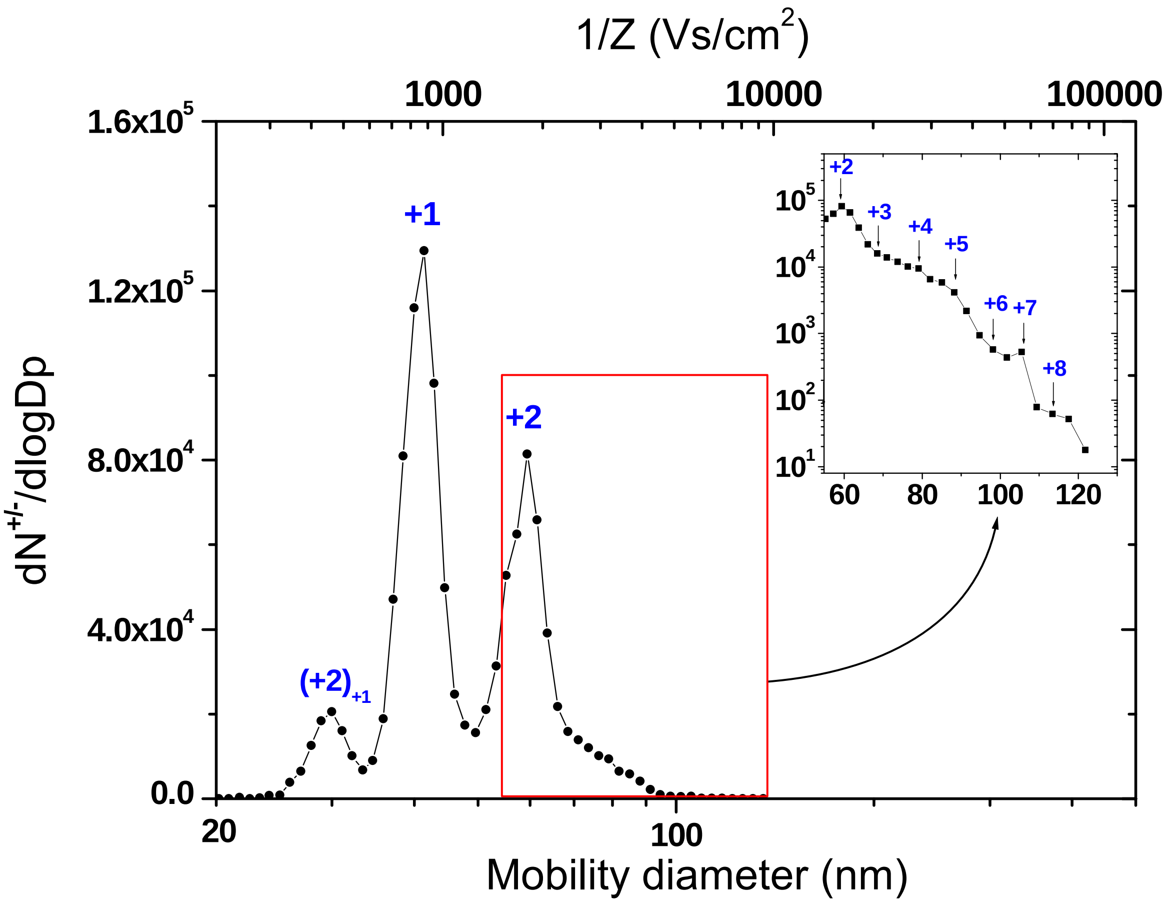
Mobility size distribution of naturally charged CNTs

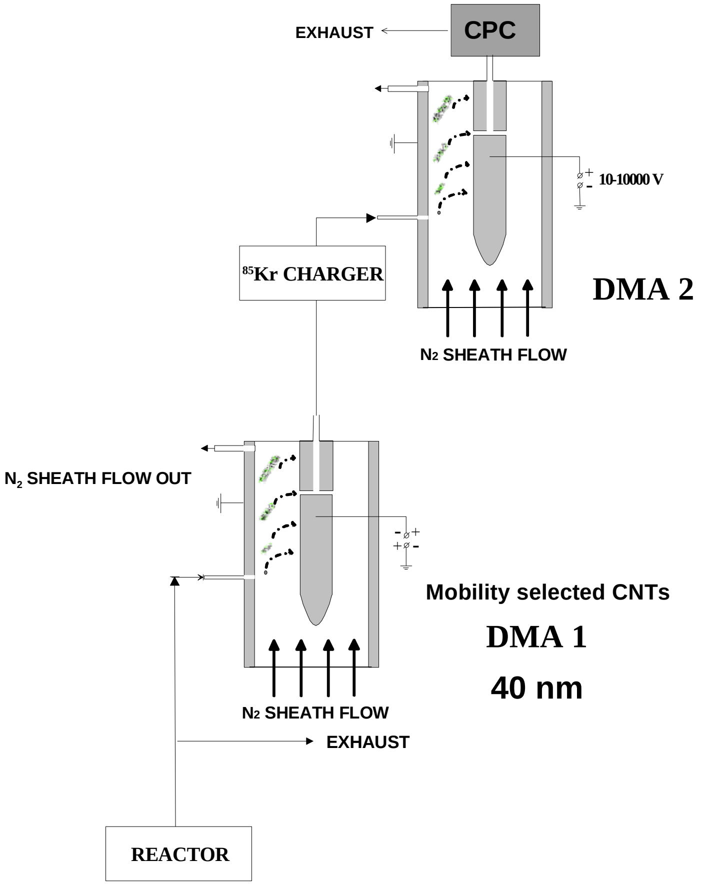




Carbon nanotubes are naturally charged (equally positively and negatively)

Charge distribution of CNTs bundles via Tandem DMA experiment





Bundled carbon nanotubes can host up to 8 elementary charges

Charged fraction ($N^{+/-}$) of CNTs at different reactor temperatures. (N^{+}) and (N^{-}) indicate the polarity distribution of charged CNTs

Temperature (°C)	$N^{+/-}$ (%)	N^{+} (%)	N^{-} (%)
700	99	47	53
800	99	48	52
900	97	41	59

Bundled nanotubes are electrically charged regardless reactor temperature

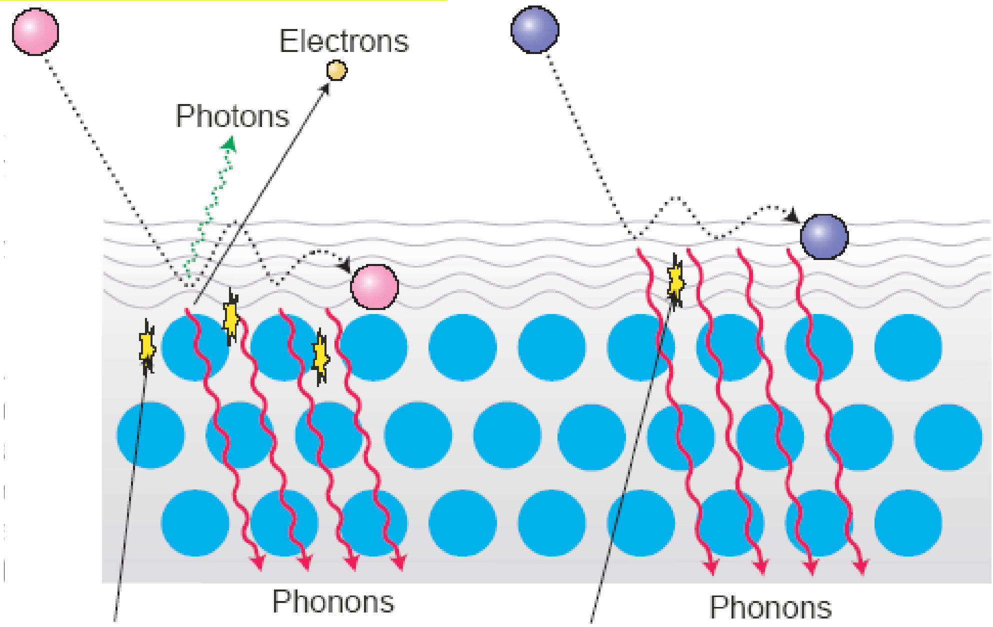
Possible charging mechanisms

Surface reactions ?

Energy dissipation ?

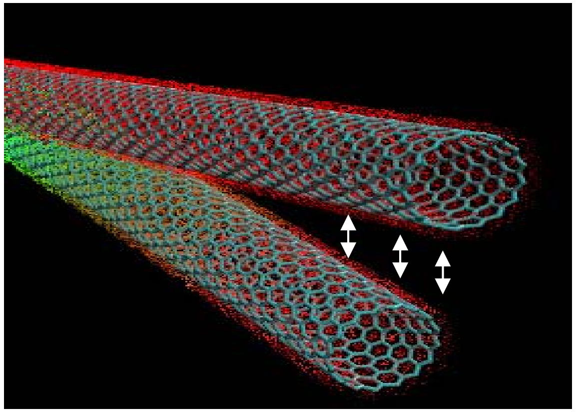
Excitation of lattice vibration (phonons)

Electronic excitations (electrons, photons, ions)



D. J. Auerbach, Science, 21, 294, 2001

Bundling process

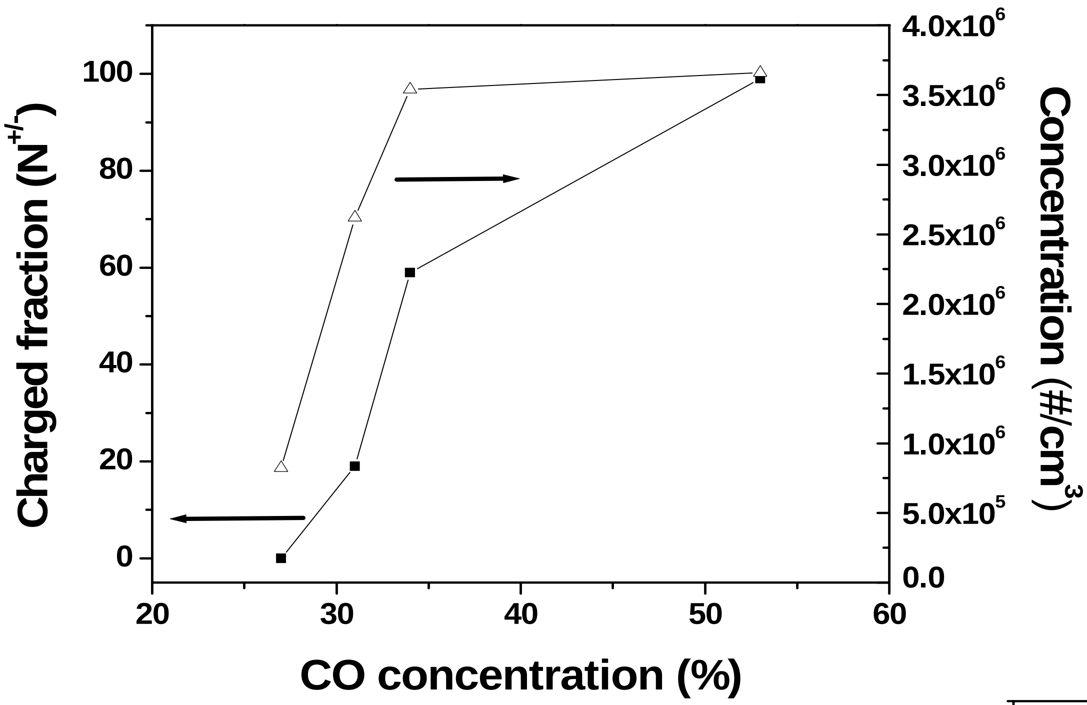


(10,10) Armchair nanotubes

Energy

1 eV/nm

Ion-emission via dissipation of the van der Waals energy released during nanotube bundling ?

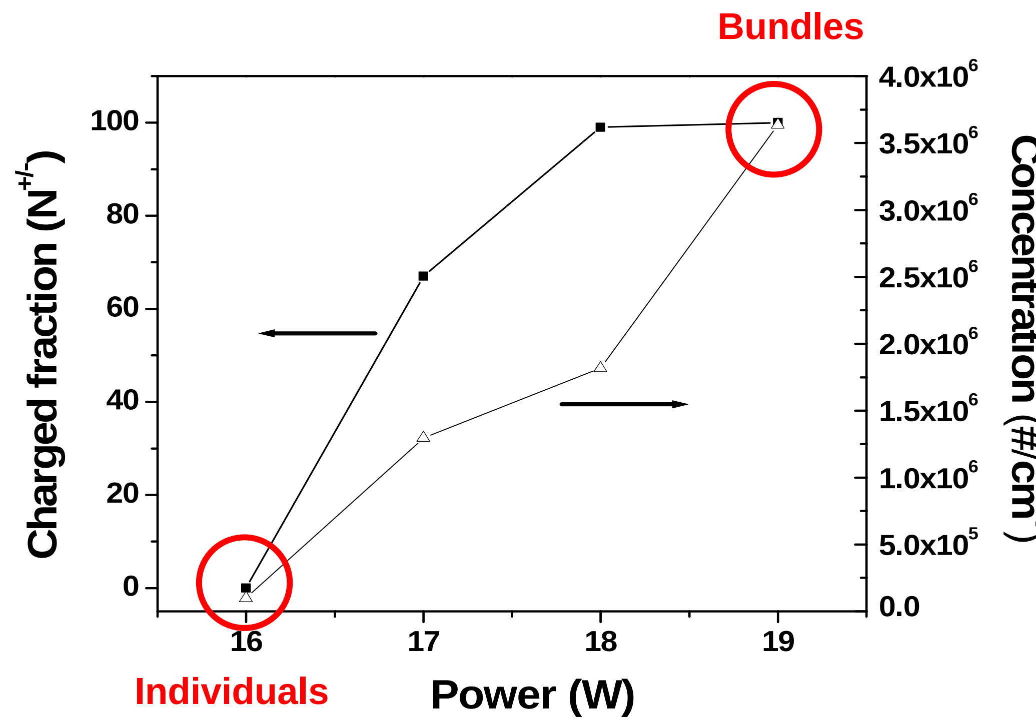


Higher CO – more clusters – higher NT concentration

Higher charged fraction

gher heating power - more clusters – higher NT concentration

Higher charged fraction



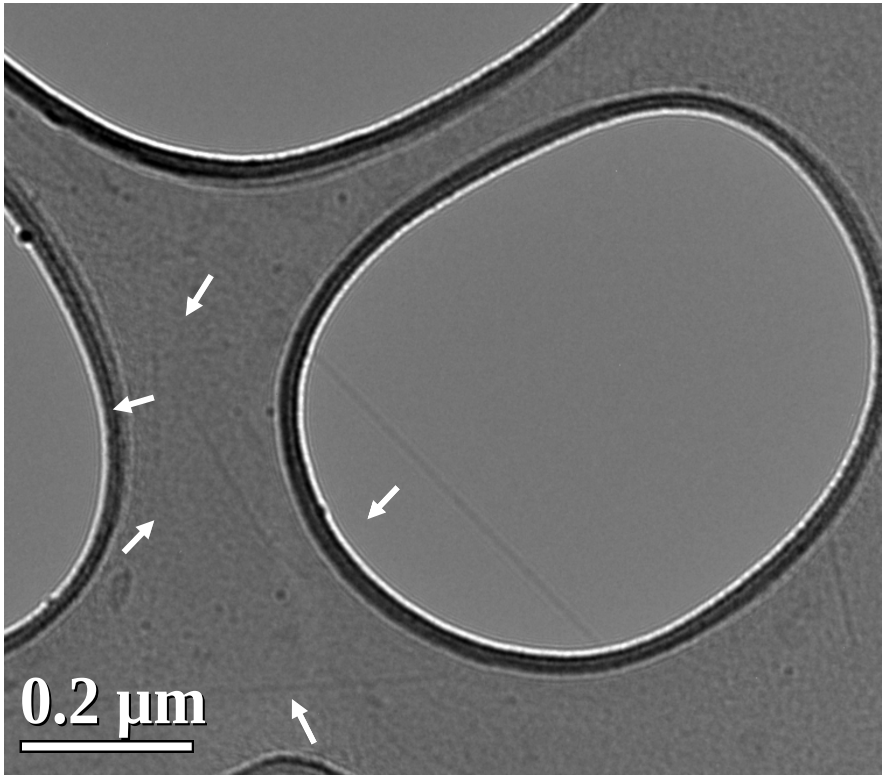
Collection of electrically neutral CNTs (i.e. ESF on)

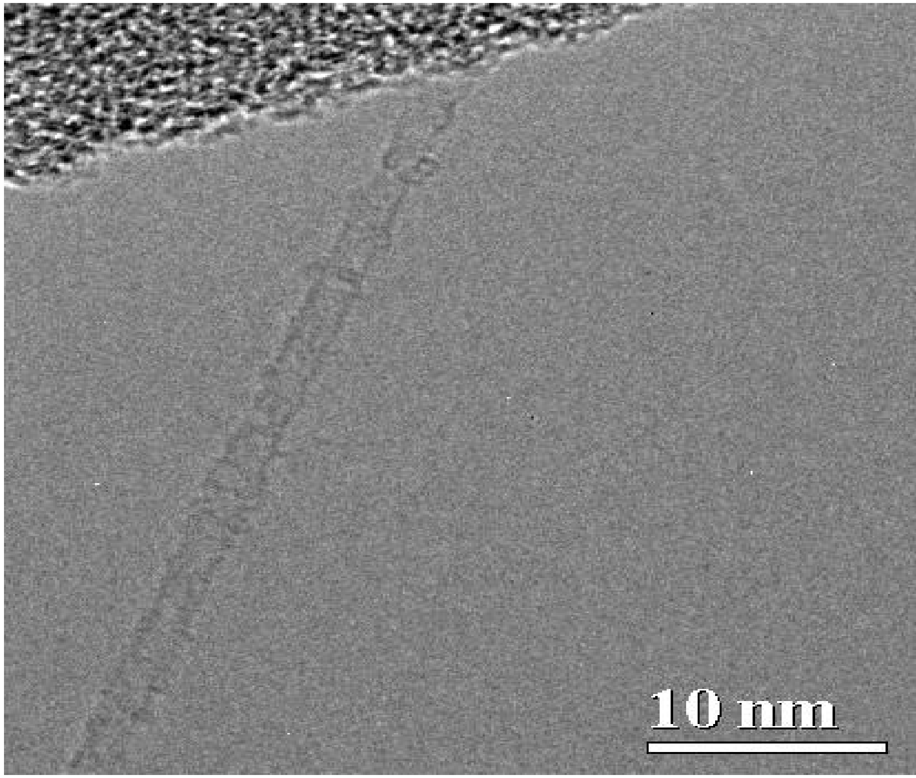
Minimum heating power (16 W)

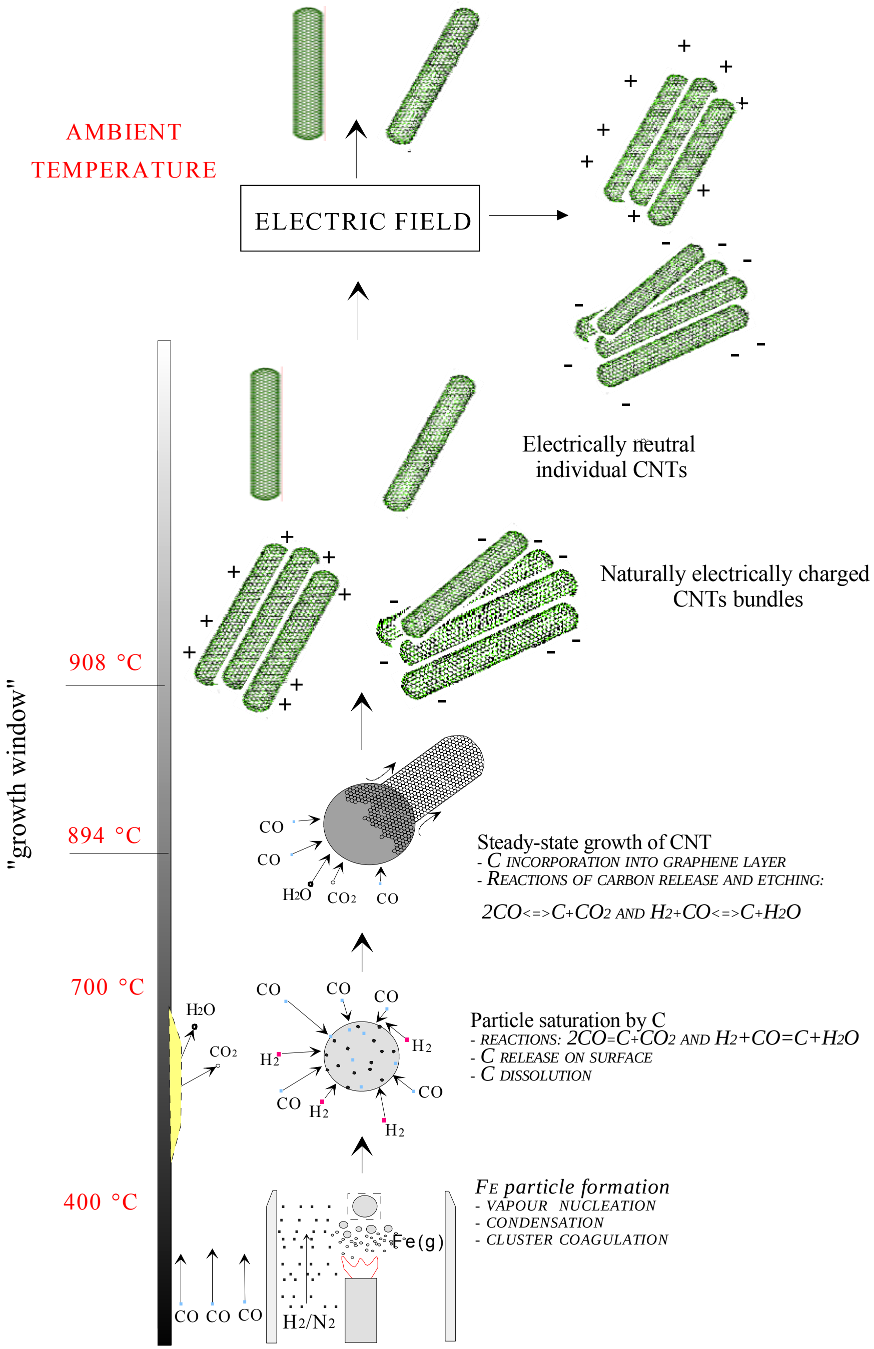
53 % CO concentration

⇨ **Charged fraction $N^{+/-}=0$**

Individual single-walled carbon nanotubes







- **HWG method for the synthesis of single-walled CNTs**

- **Spontaneous electrical charging of bundled CNTs**

- **Individual CNTs remain electrically neutral**

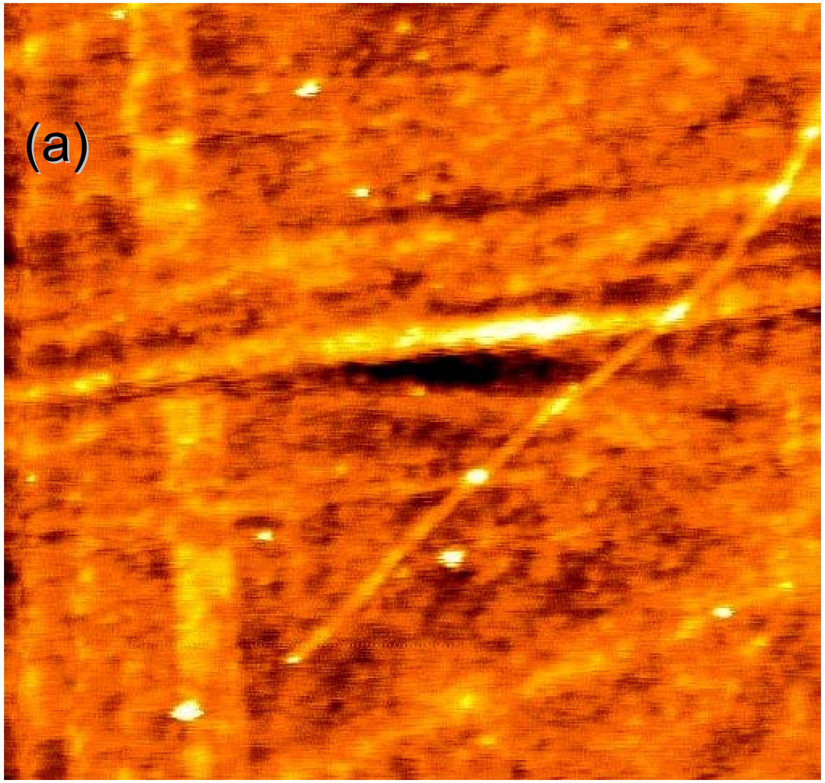
Applicability

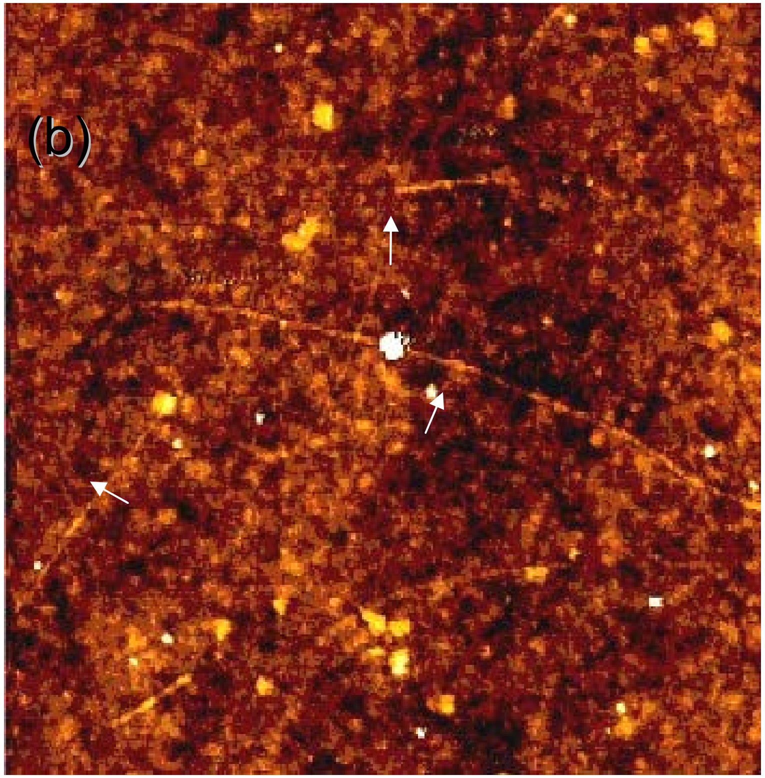
Deposition of individual CNTs at ambient temperature on any solid substrate

Selective deposition of individual CNTs at ambient temperature on substrates by electrophoresis/thermophoresis

Epoxy-based substrate (MT=300 °C)
Temperature sensitive substrate

SiO_2(260 nm)/Si





Collaboration

Dr. Albert G. Nasibulin (aerosol synthesis of CNTs)
Dr. Hua Jiang (HR-TEM, ED/TEM)
Dr. David P. Brown (combined aerosol-CFD modelling)
Dr. David Gonzalez (charging of CNT's)
Dr. Paula Queipo (cluster-catalyzed surface CVD synthesis of CNTs)
Prof. Sergei D. Shandakov (Marie Curie Fellow 2006-07, high yield synthesis)
Andrei Ollikainen, Anton Anissimov (growth and applications in electronics)

Prof. Daniel E. Resasco, Oklahoma U., USA (CVD growth & chirality)
Prof. David Tomanek, Michigan State U., USA (atomic modelling)
Dr. Peter V. Pikhitsa, Odessa Nat. Univ., Ukraine (SWCNT Nucleation)
Prof. Risto Nieminen, Dr. Arkady Kraseninnikov, COMP/HUT Finland (atomic modelling)
Dr. Bernd Freitag, FEI, Netherlands (C_s-TEM imaging)

Funding

* Academy of Finland via TULE program/ELENA Consortium
* EU FP5 RTN NanoCluster
* EU FP6 Marie Curie Fellow
* TEKES FinNano & MASI Programs

Tutorial Material

Dr. A. Loiseau, Prof. S. Maruyama, Prof. M. Endo, Prof. S. Iijima, Prof. K. Bolton, Prof. S. Farhat, Dr. C.D. Scott, Dr. Chris Kingston

Schematic presentation of mechanism of CNT formation

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Simultaneous Synthesis of Fullerenes ?

YES – submitted & to be presented later