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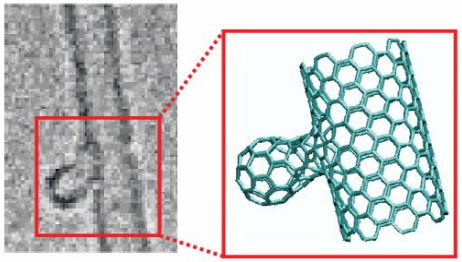

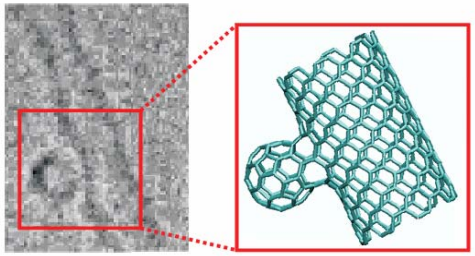

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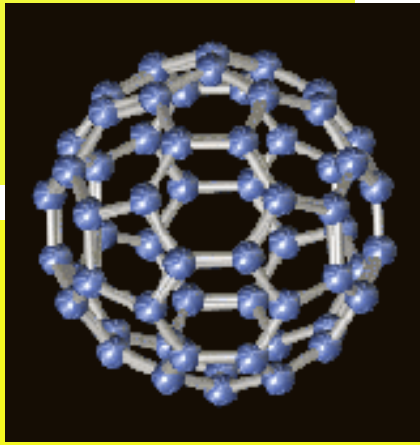
Novel Floating Catalyst Synthesis and Electron Diffraction Characterization of High Purity Individual SWCNTs



Prof. Dr. Esko I. Kauppinen
Helsinki University of Technology (TKK)
Espoo, Finland

3rd NASA-NIST Workshop on Nanotube Measurements
September 26-28, 2007
NIST, Gaithersburg, MD, USA

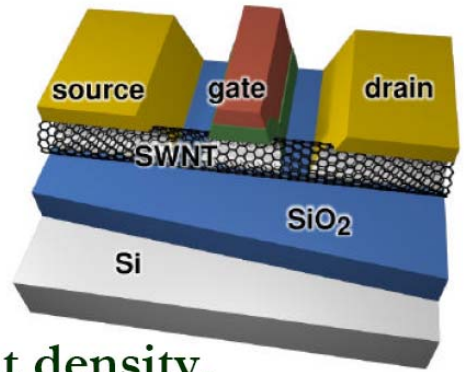
CONTENT

- Individual SWCNT's via floating catalyst PVD/CVD method from Co & Fe catalyst
- CNB's (Carbon NanoBuds = SWCNT+C_{60}) – floating CVD synthesis, structure and properties
- ED/TEM determination of CNT chirality

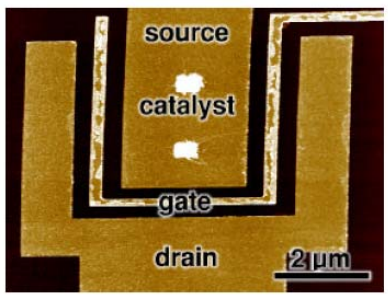
SWCNT's in Future NanoElectronics Applications ???

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:

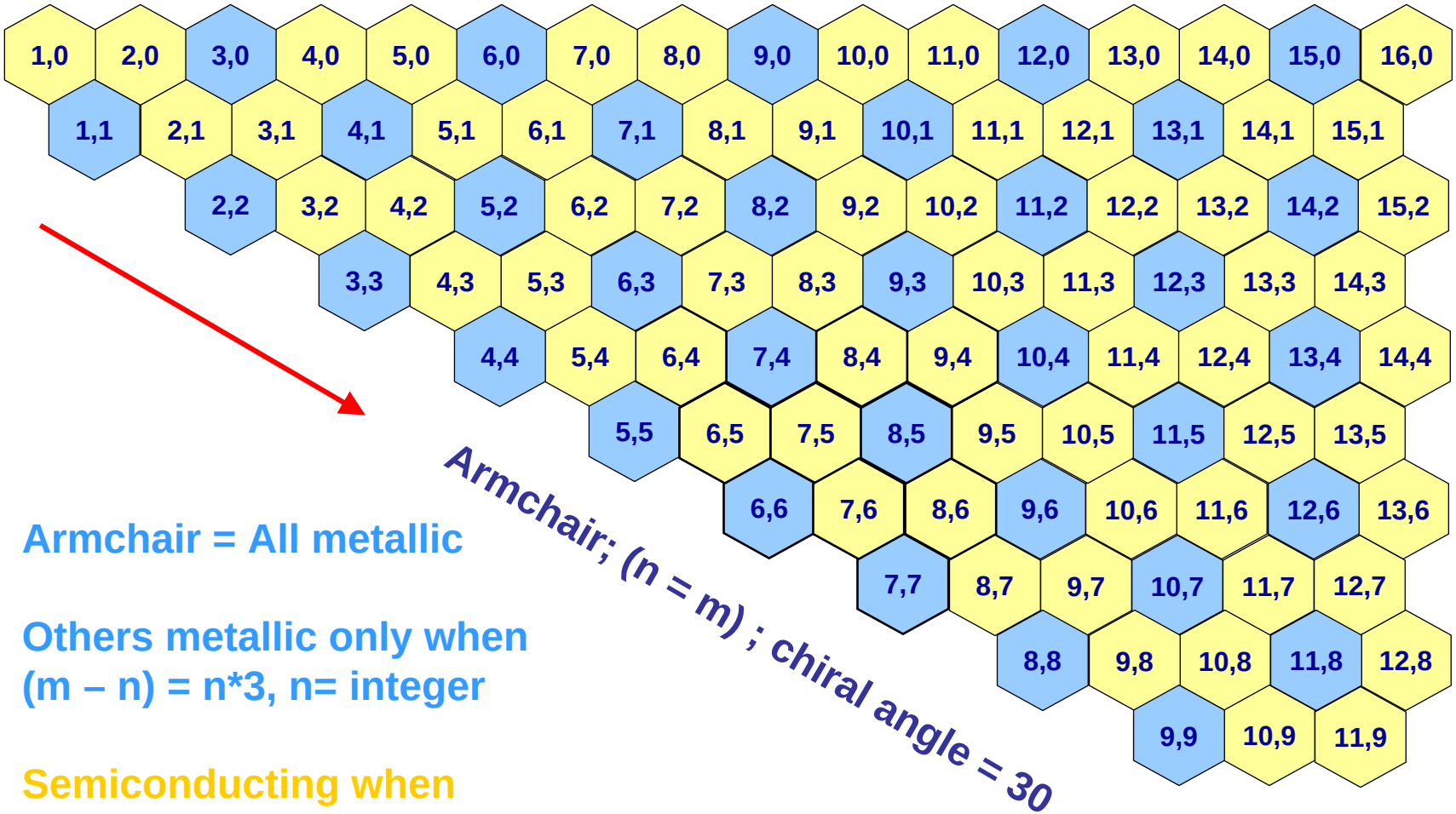
individual SWCNT with given (n,m) Deposited at ambient T to exact location at the substrate

i.e.

how to integrate SWCNT's into electronics integrated manufacturing processes

Chirality Map

Zig-zag; (n,0) ; chiral angle = 0



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

Semiconducting when (m - n) # n *3

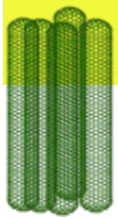
Individual SWCNT*s onto substrates at $T_{ambient}$

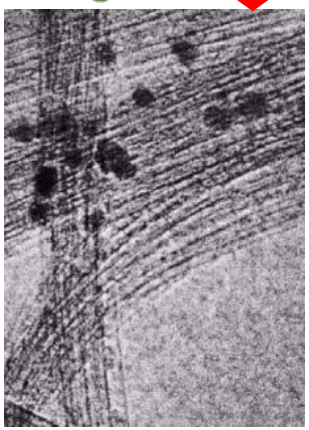
Carbon arc-discharge

Fluidized Bed CVD (CoMoCat)

Laser ablation

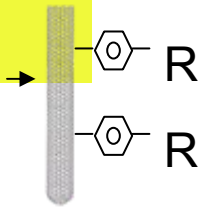
Floating CVDHiPCO process

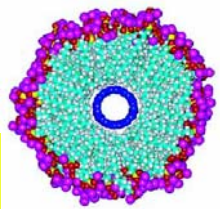




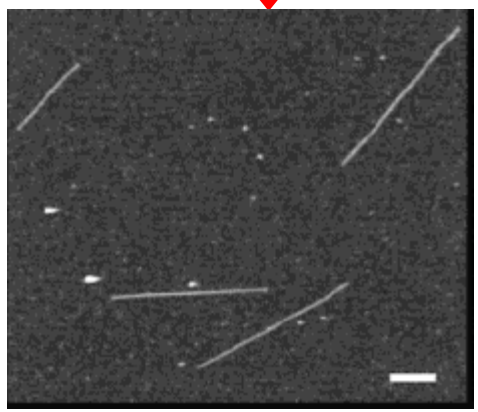
Bundles of CNTs (HiPco)

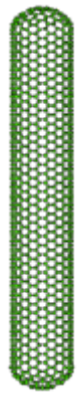
Surfactants/Acids & Sonication to purify & break bundles - Defects introduced ? Chirality controll by tedious separation processes – Purity after deposition ?





Substrate Chemical Vapour Deposition





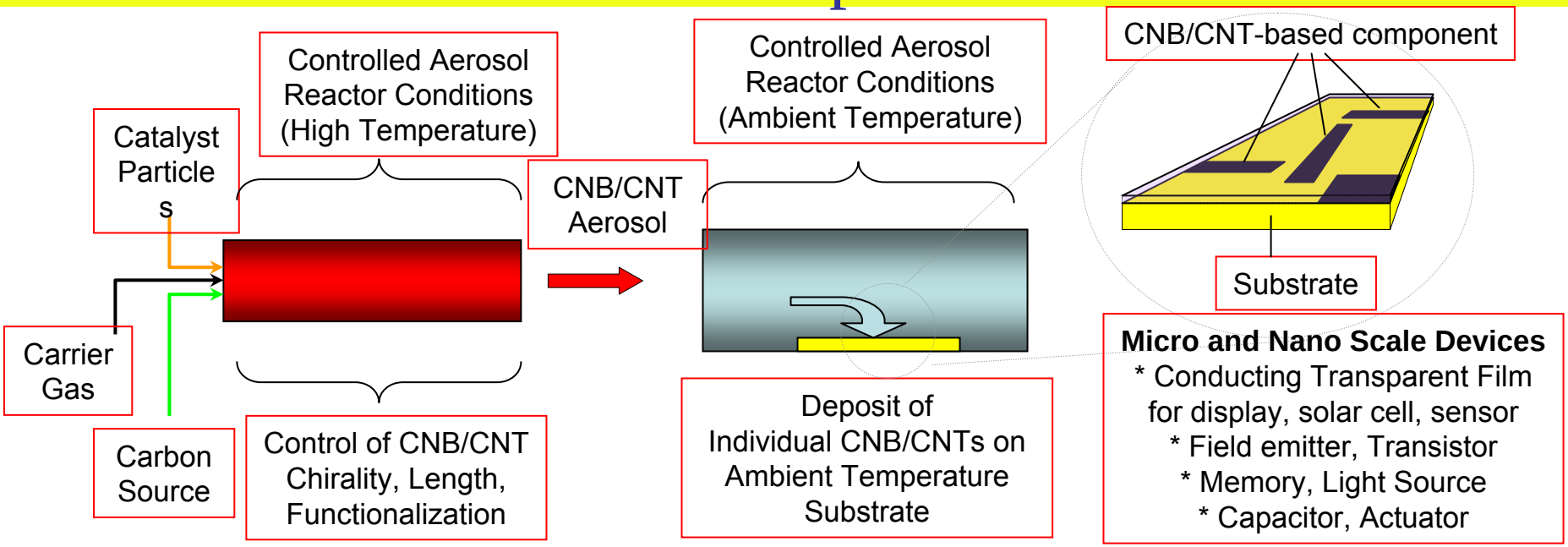
High growth temperature (800 °C)

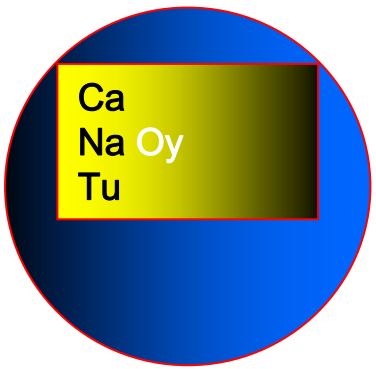
Difficult integration to device structures

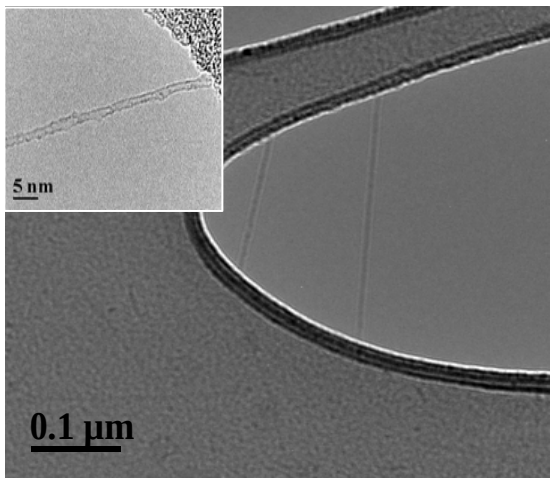
Temperature sensitive substrates can not be used

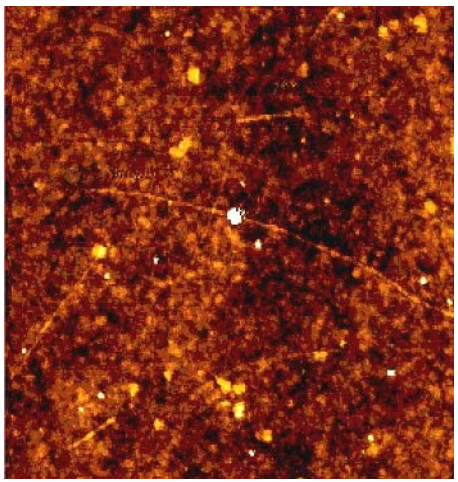
Chirality and positioning controll challenging

Schematics of Novel, Dry CNB/SWCNT Based Integrated Electronics Component Manufacturing Process developed at TKK





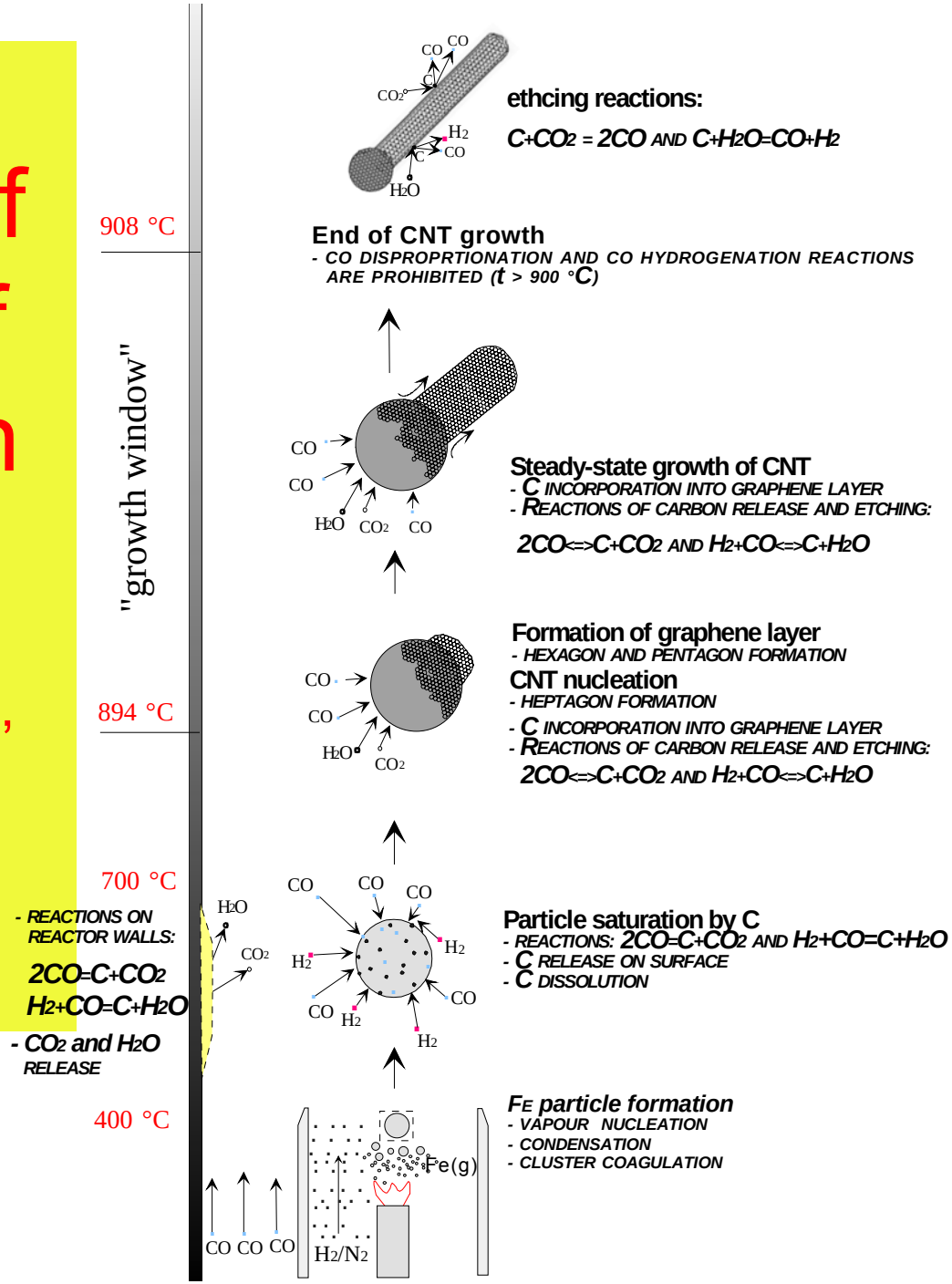




NanoMaterials Group

Schematic presentation of mechanism of CNT formation

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

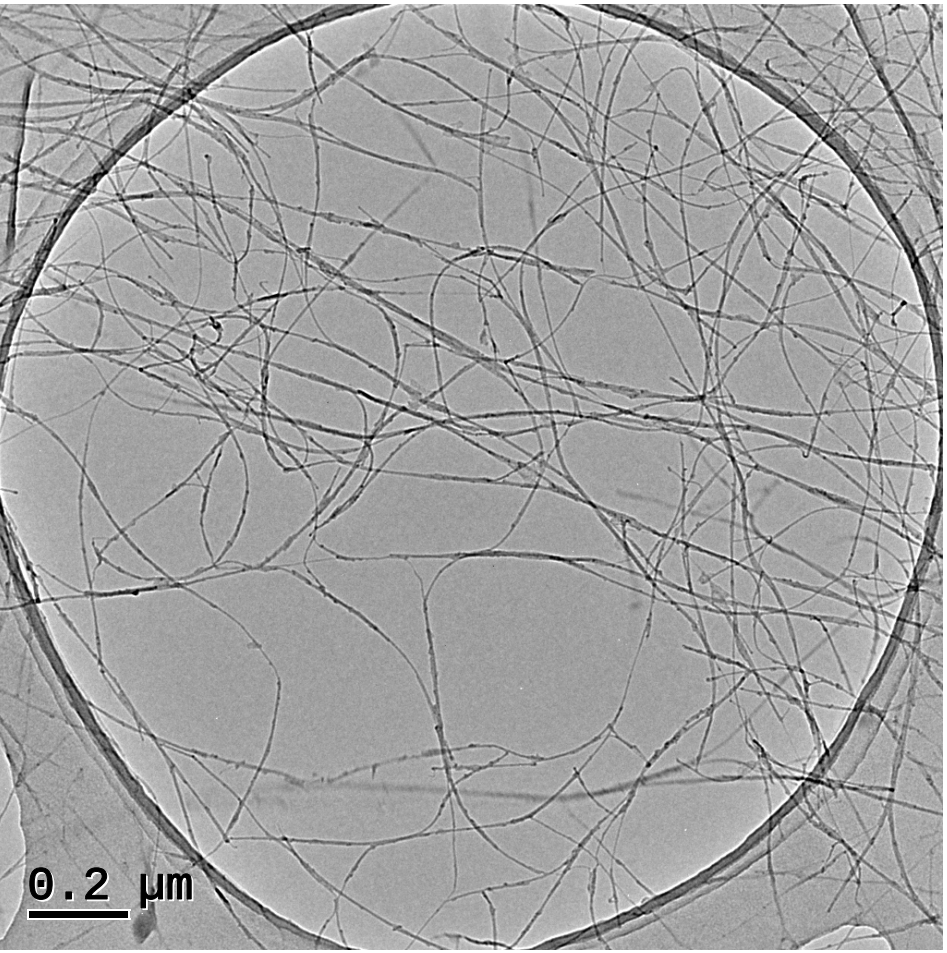


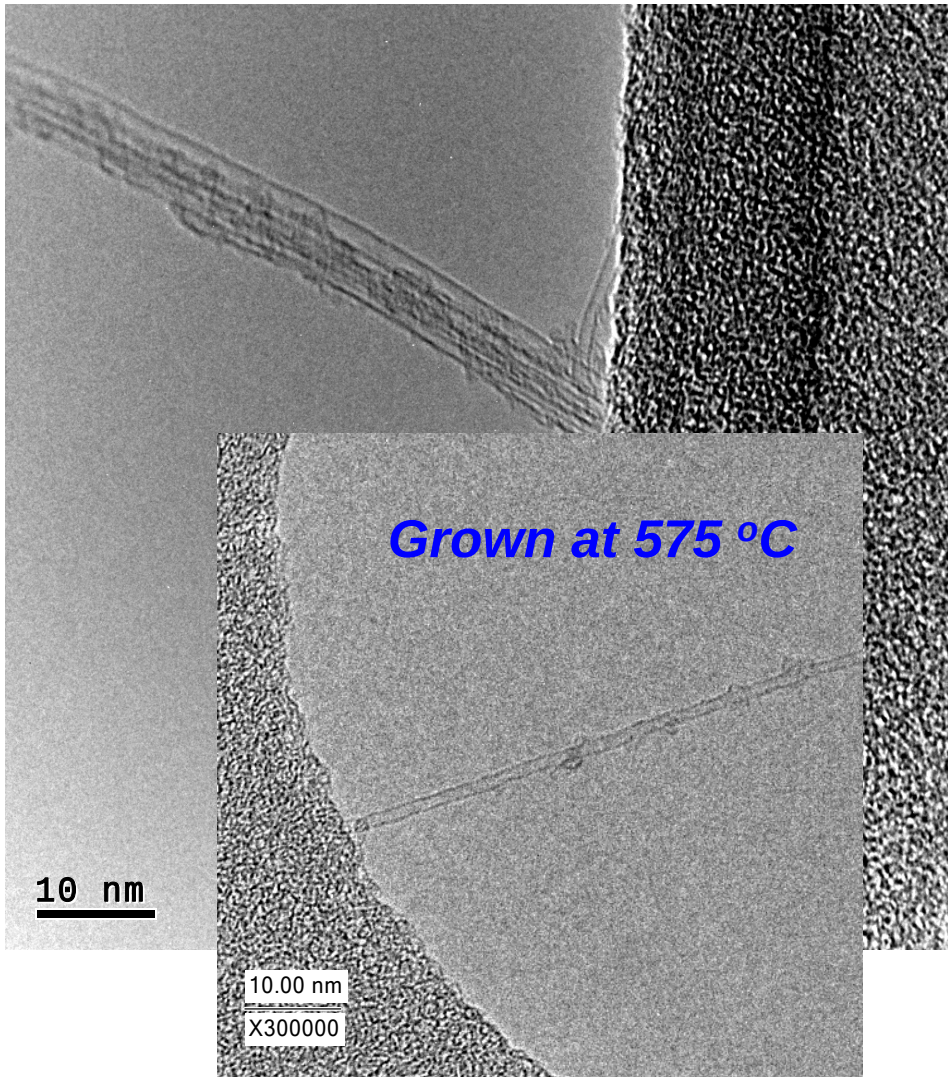
A novel floating catalyst CVD method for synthesis of Carbon NanoBuds*TM*

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.

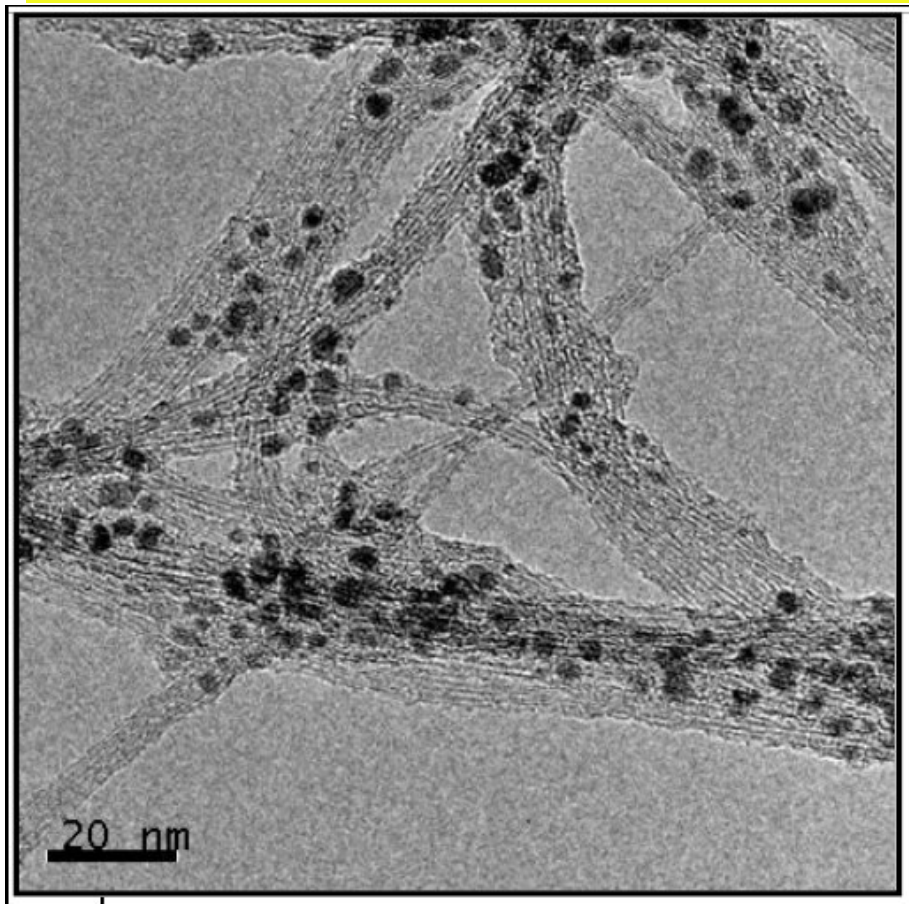
Pre-made catalyst (Fe, Ni, Co) **particles** produced by evaporation-nucleation of metal i.e. PVD from HWG (hot wire generator). **Carbon sources**: CO, alcohols, hydrocarbons.

TEM images of SWCNT's grown at 924 ºC using CO as carbon source and H_2/N_2 mixture through the Fe catalysts cluster source.

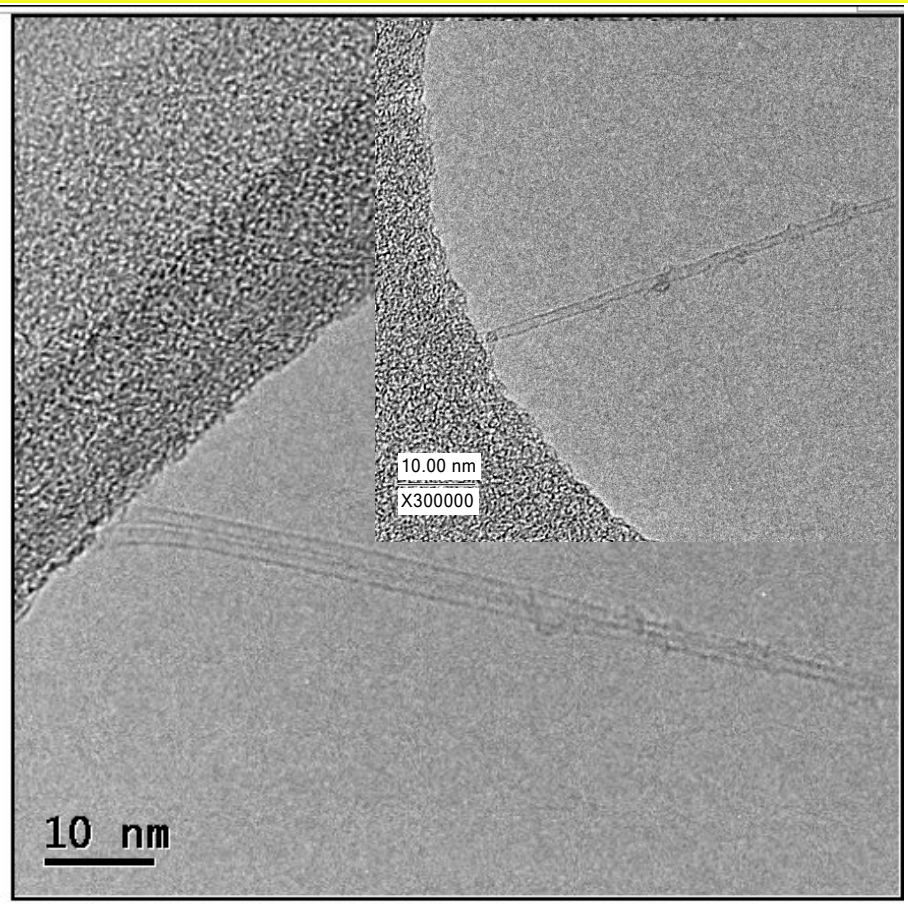




TEM - Comparison to HiPCO

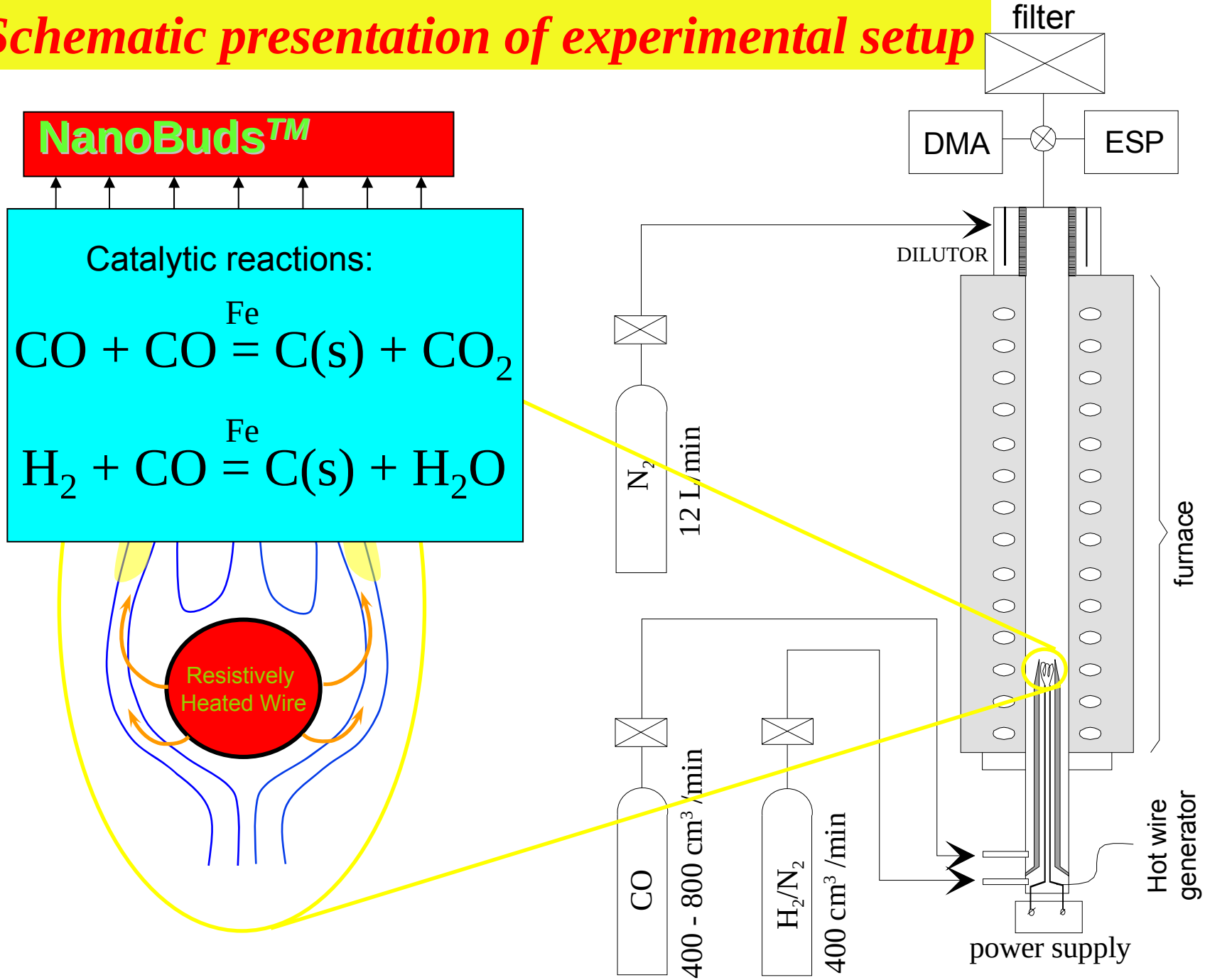


HiPCO

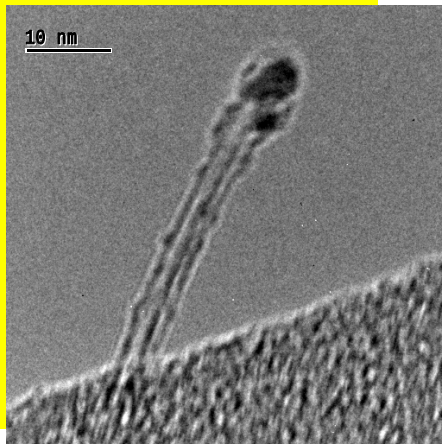


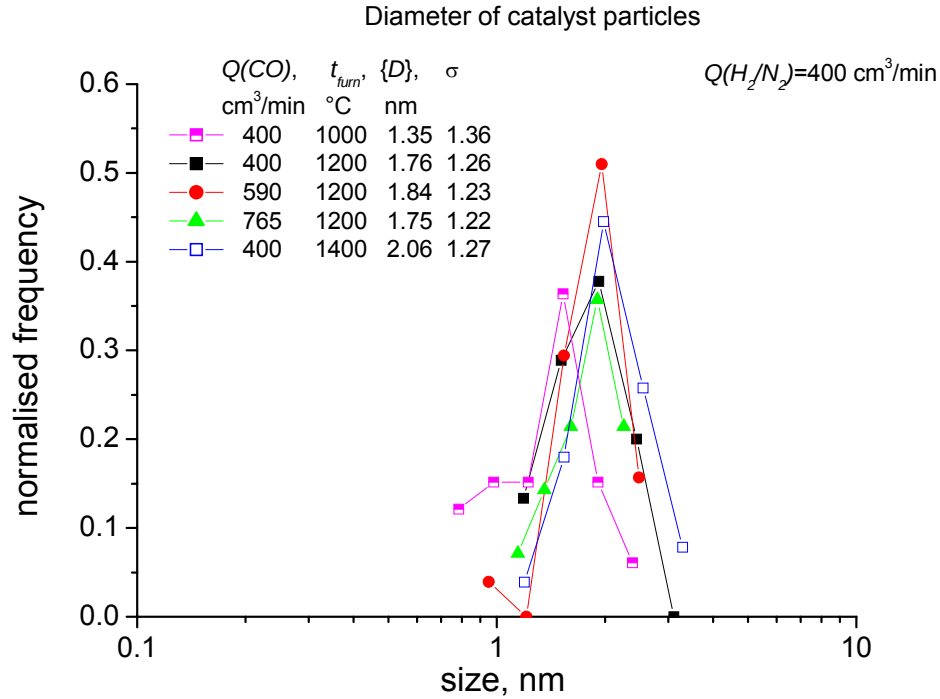
TKK

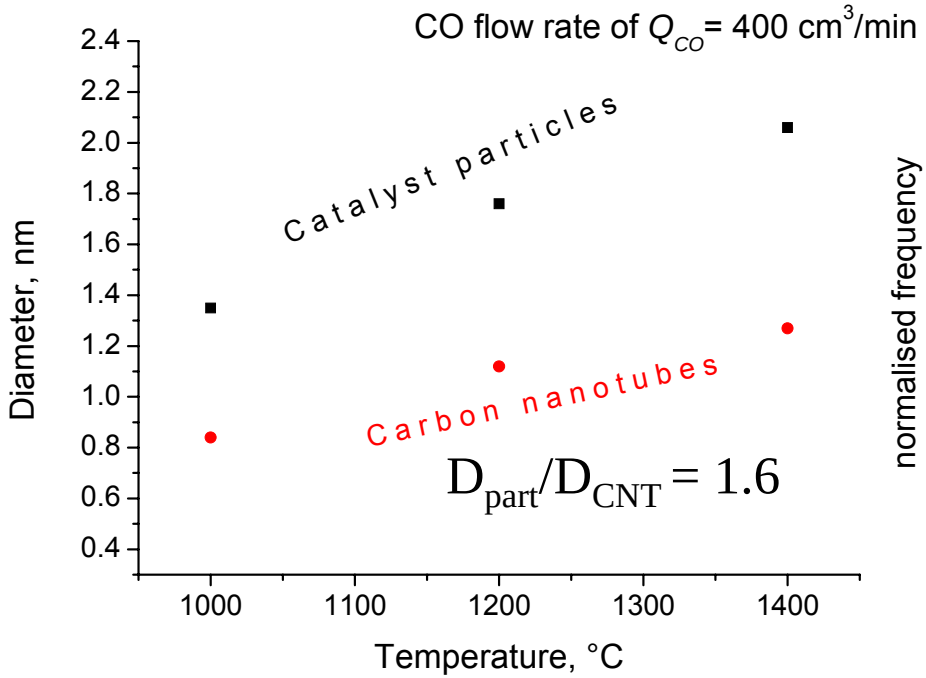
Schematic presentation of experimental setup

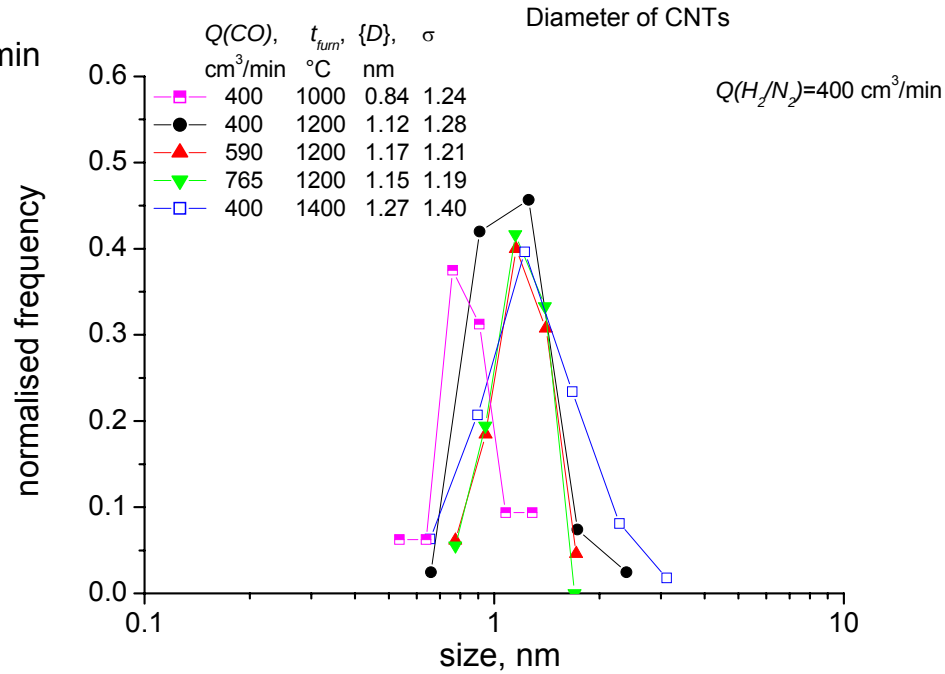


Correlation between diameter of Fe particles and SWCNTs – controll of catalyst size

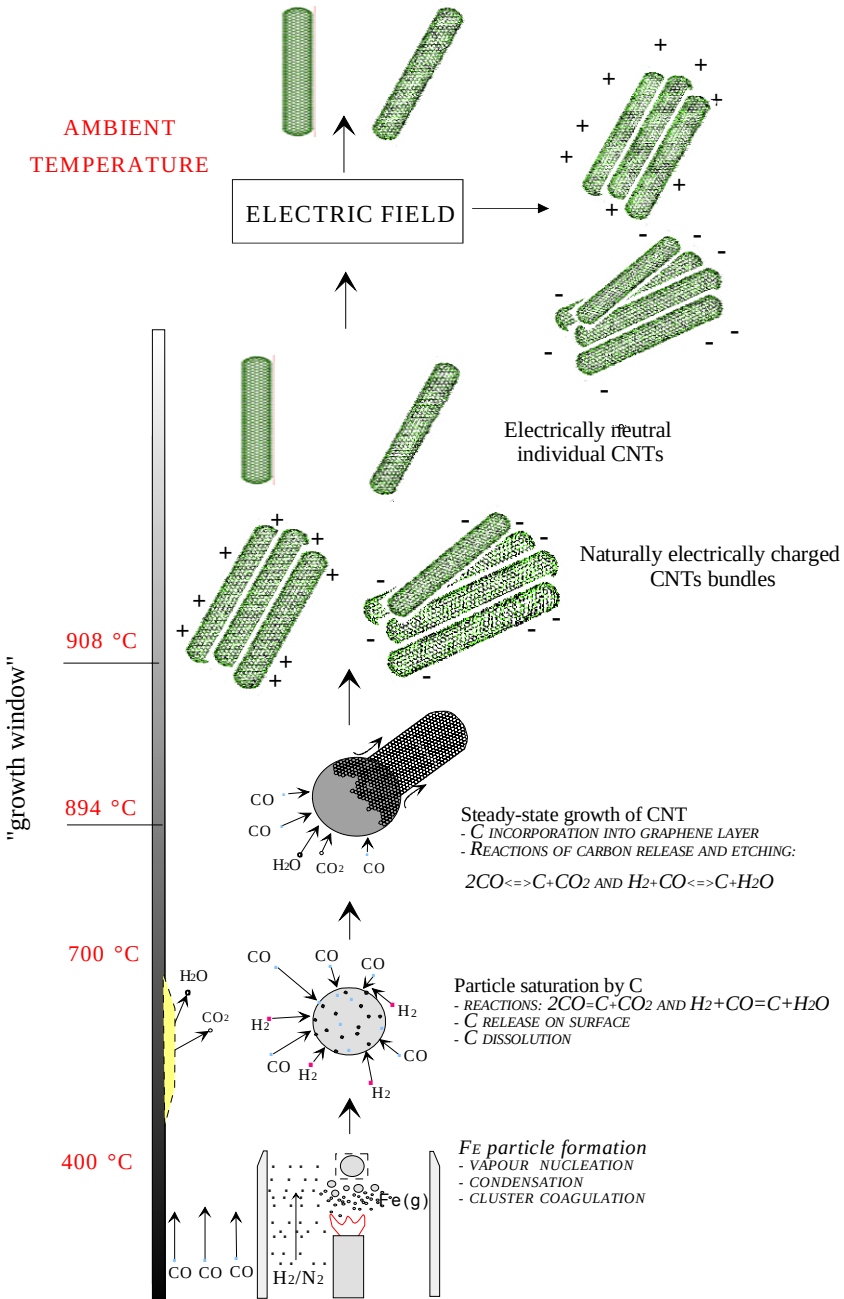








Bundling α N_{CNT}^2 α N_{Cat}^2



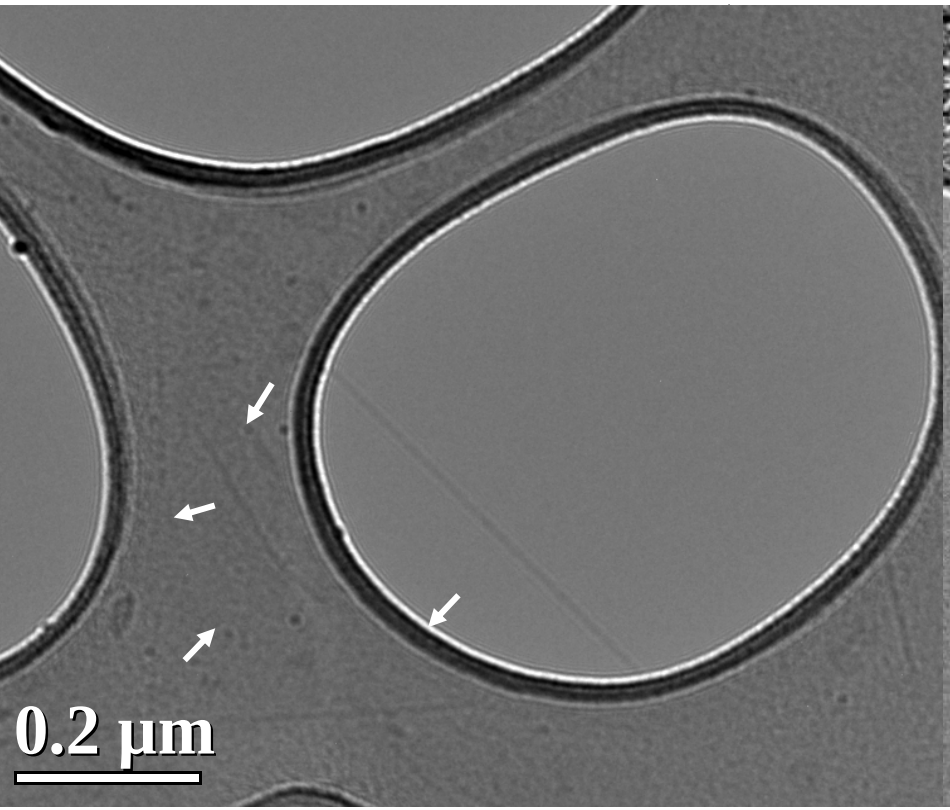
Controlling Bundling

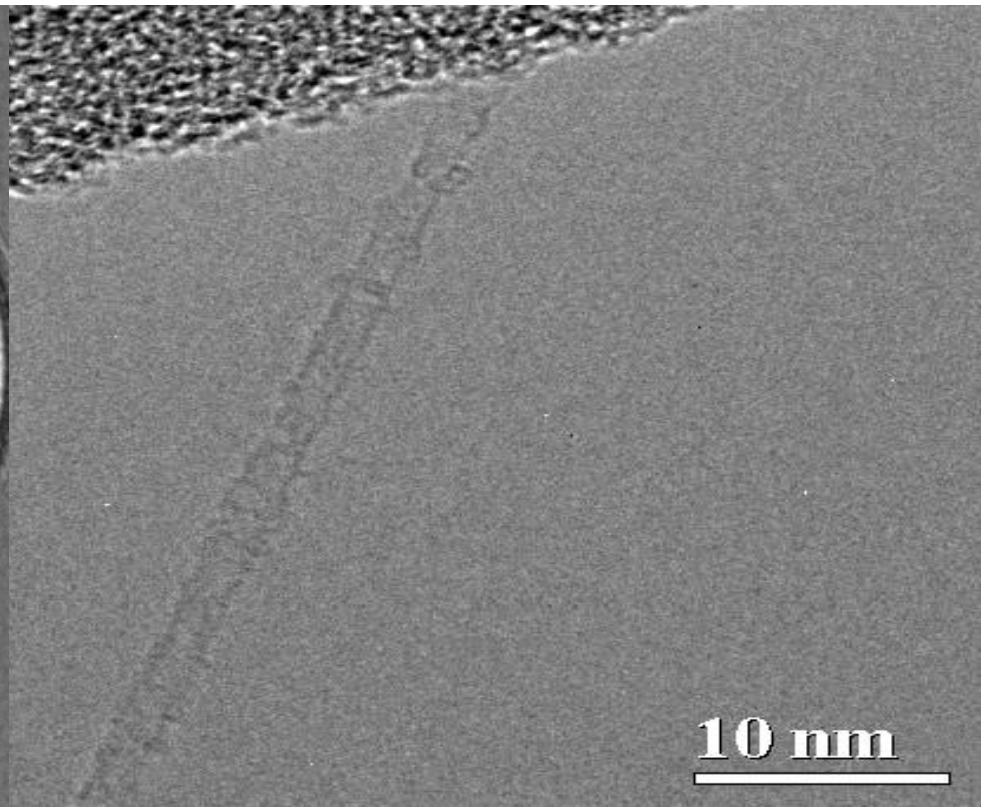
- **HWG method for the synthesis of single-walled CNTs**
- **Spontaneous electrical charging of bundled CNTs**
- **Individual CNTs remain electrically neutral**

Applicability

Deposition of individual CNTs at ambient temperature on any solid substrate

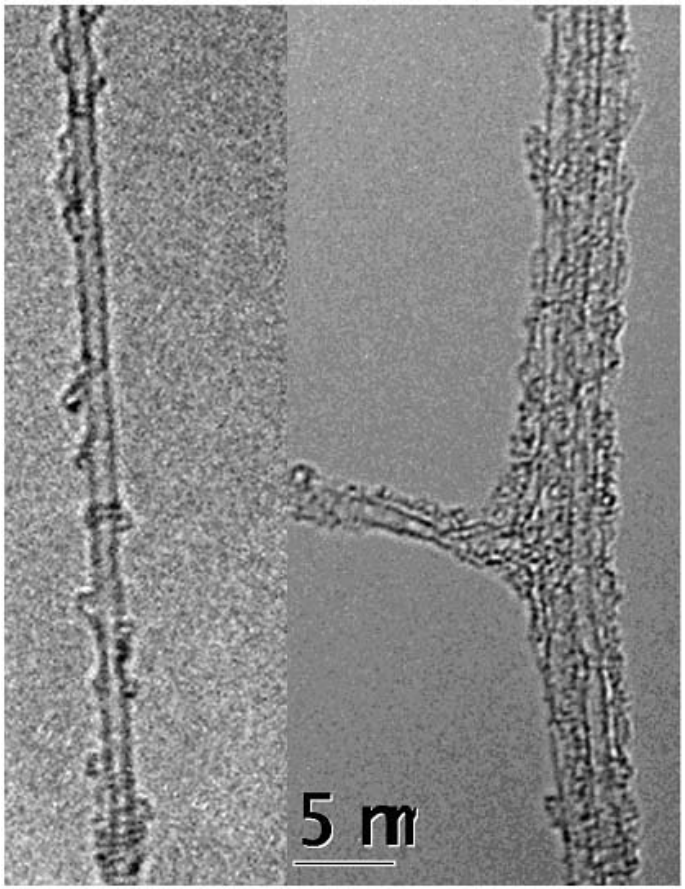
Individual single-walled carbon nanotubes Deposited at ambient Temperature

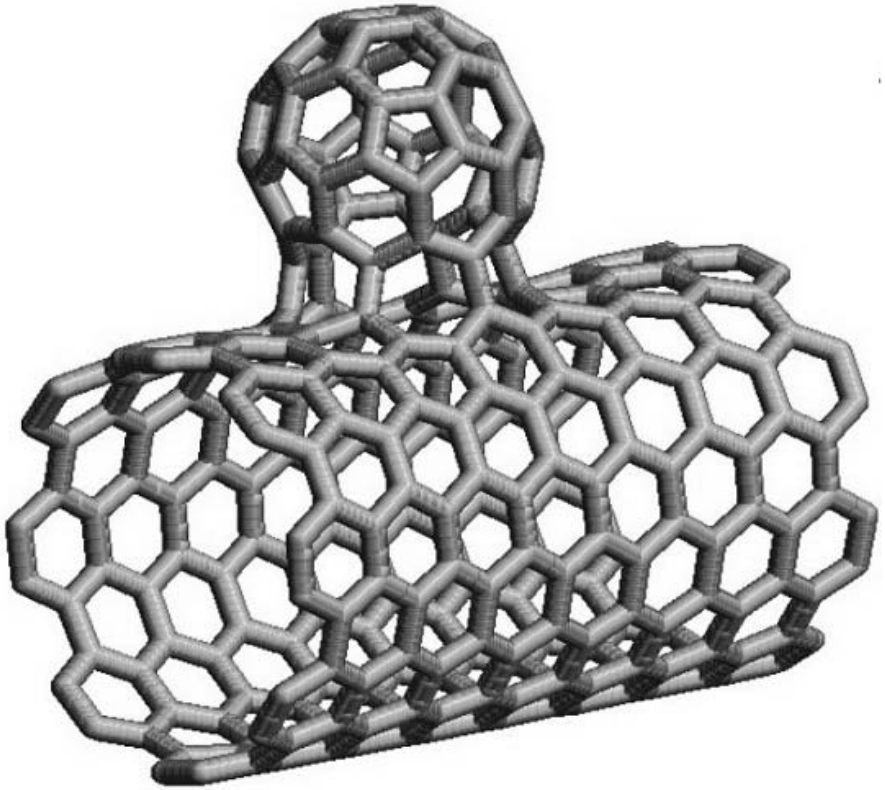




CNB-NanoBud™

New Carbon NanoMaterial





Nanobud™ combines Carbon Nanotubes and Fullerenes in Single Structure with Covalent Bonding

Nasibulin & Kauppinen et al. Nature Nanotechnology, 2(3) 156 March 2007

Mechanism of *CNB* Formation

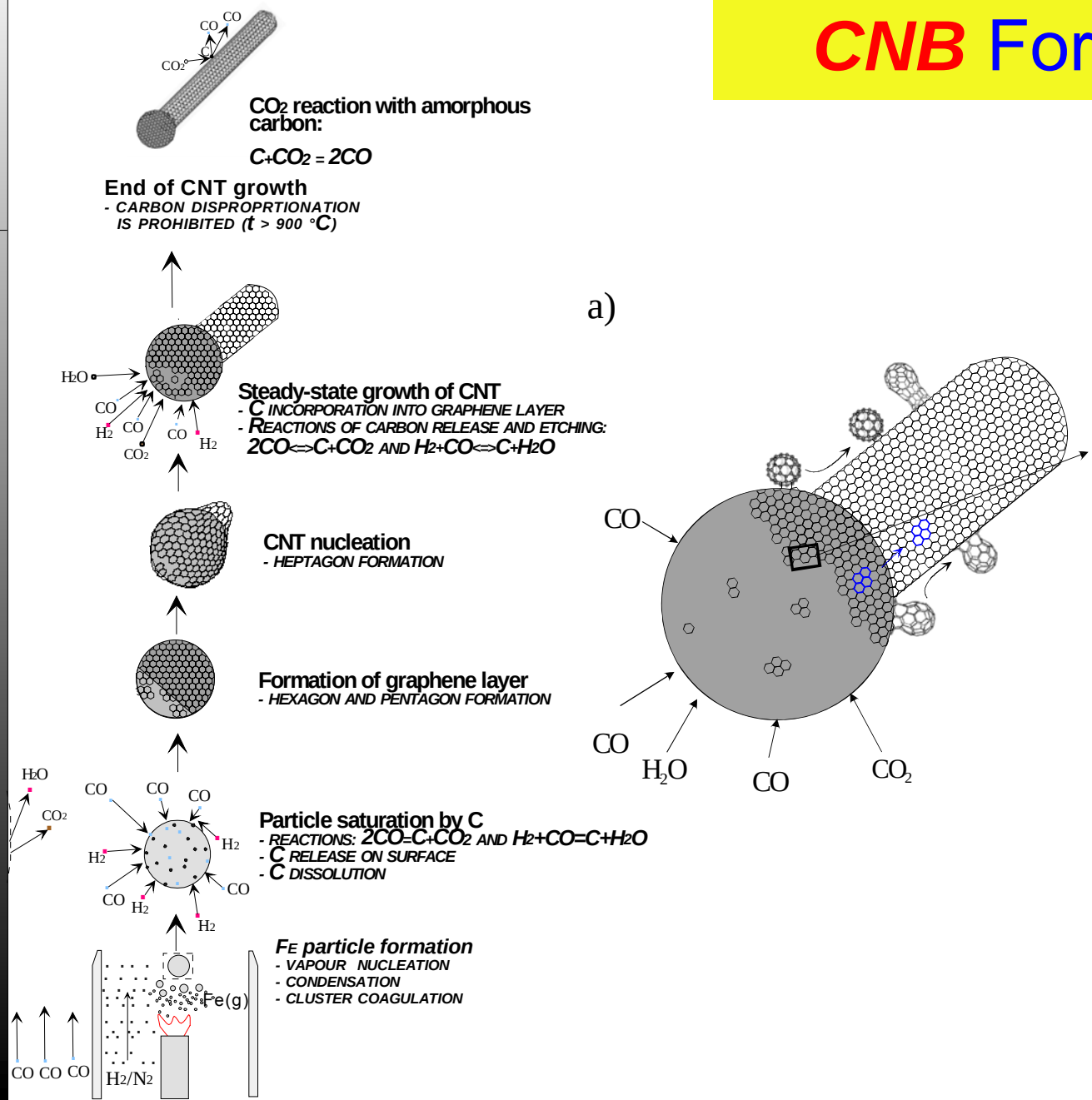
$$\text{Bundling} \propto N_{CNT}^2 \propto N_{Cat}^2$$

HIGH TEMPERATURE ZONE

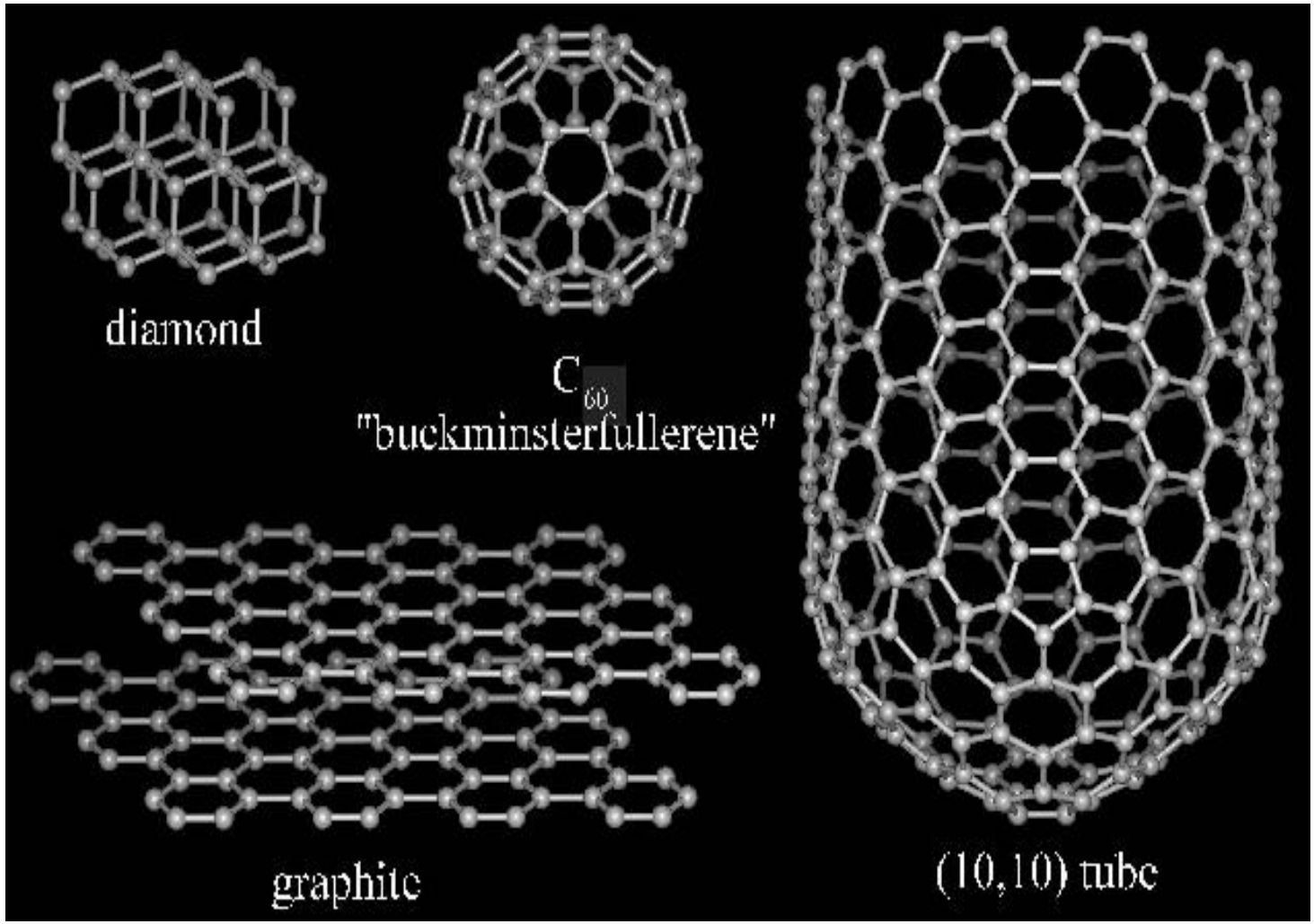
900 °C

HEATING ZONE

400 °C



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



NanoBuds™ on FEI Titan TEM at 80kV with image C_s-corrector - Movie

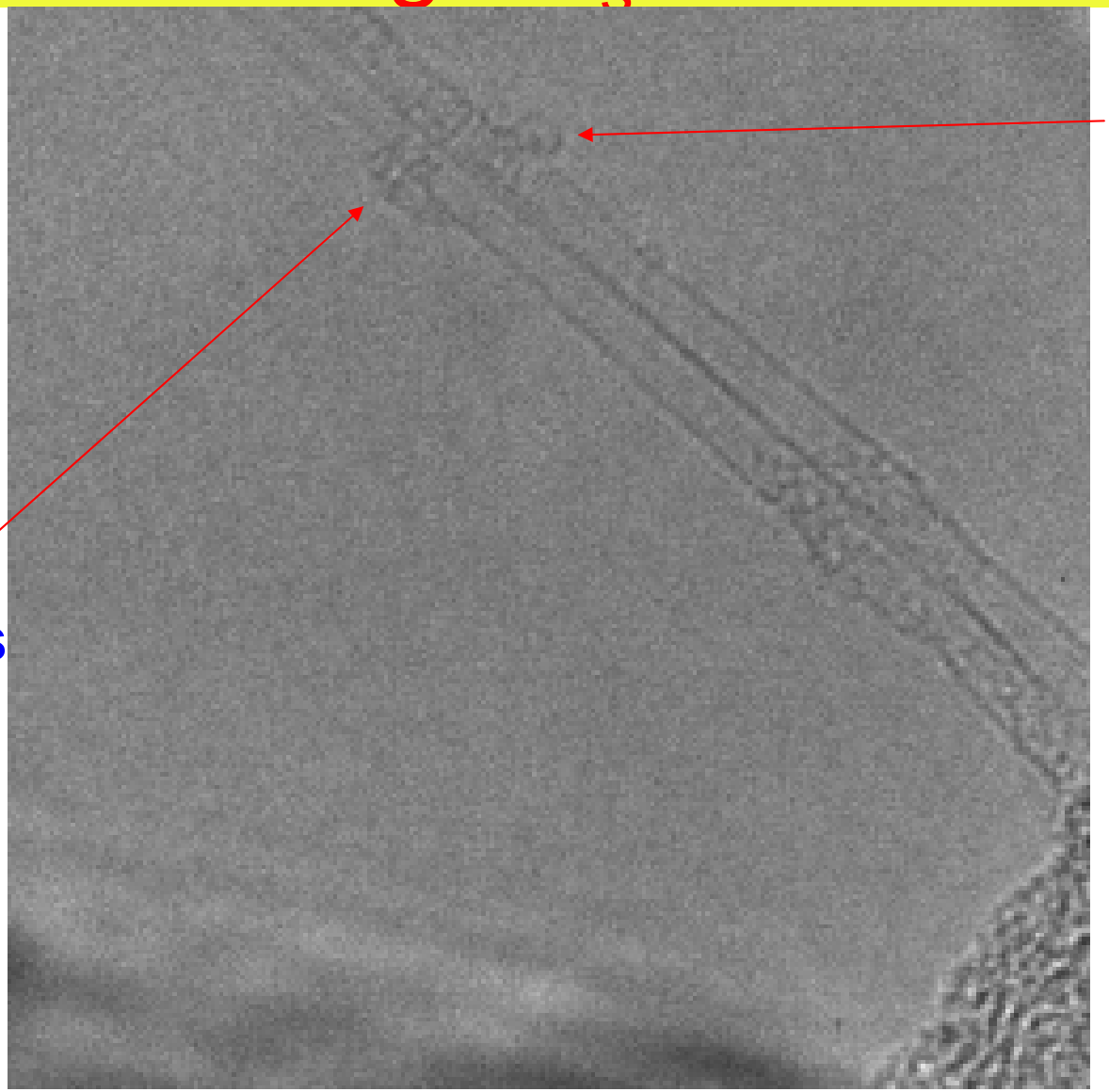
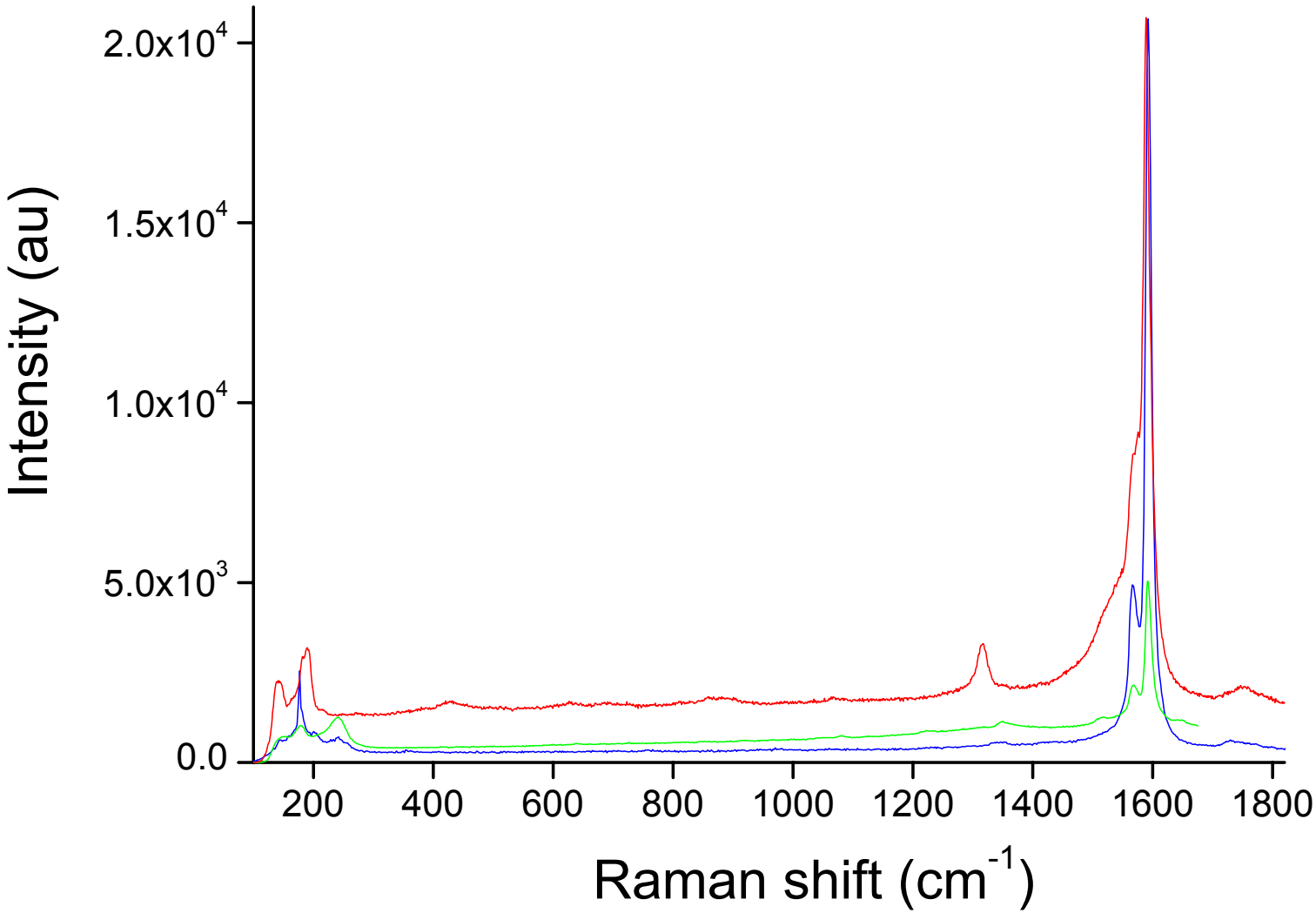
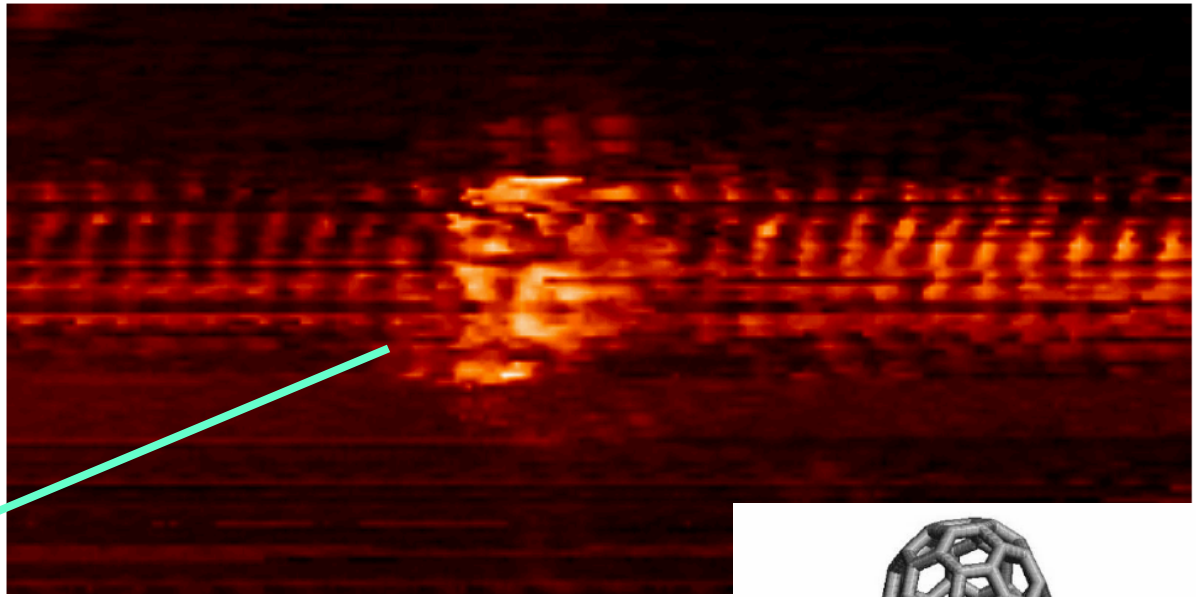


Image :B.Freitag FEI; samples : Prof. Kauppinen Helsinki, Finnland

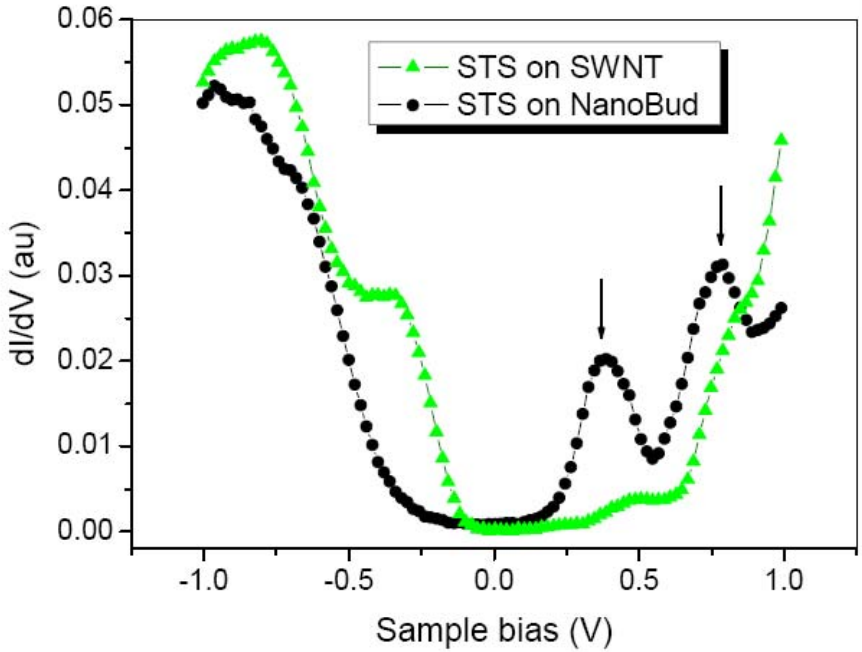
Raman spectra of NanoBuds carried out by using red (633 nm), green (514 nm), and blue (488 nm) lasers.

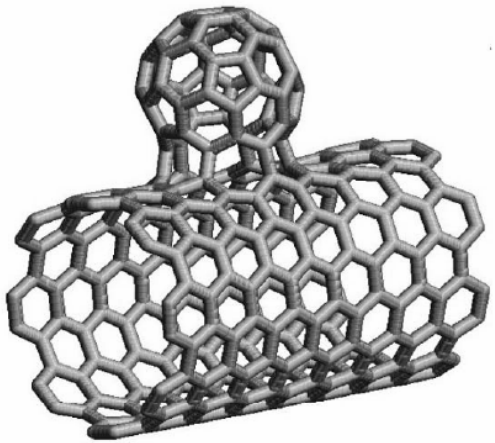


LT UHV STM: Chemisorbed Fullerene on Nanotube Lattice



Fullerene





Peaks in the LDOS are due to nanobuds, cannot be assigned to physisorbed fullerenes

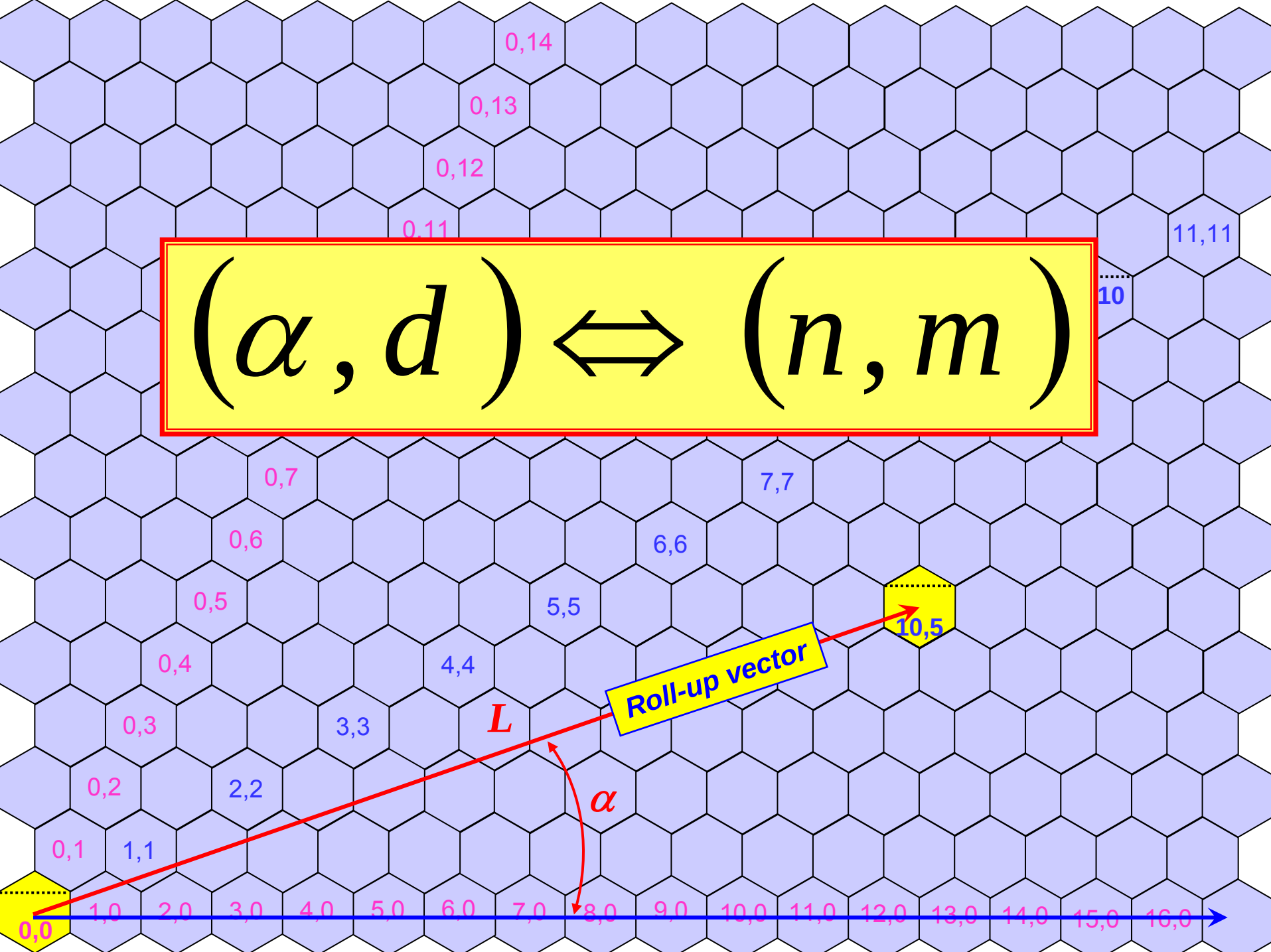
Nanometer Range Controll for DOS !

Nasibulin & Kauppinen et al. Nature Nanotechnology, 2(3) 156 March 2007

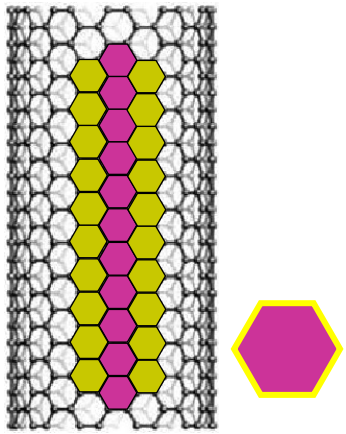
Chirality
of
SWCNTs
by
Electron Diffraction

We are targeting for an easy solution for a simple and fast structure determination of SWCNTs.

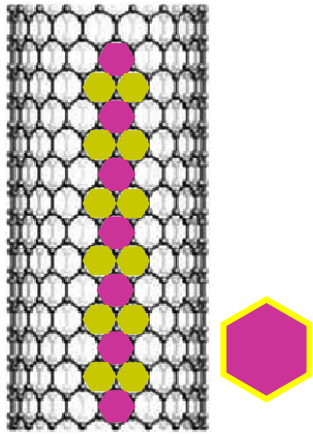
$$(\alpha, d) \Leftrightarrow (n, m)$$



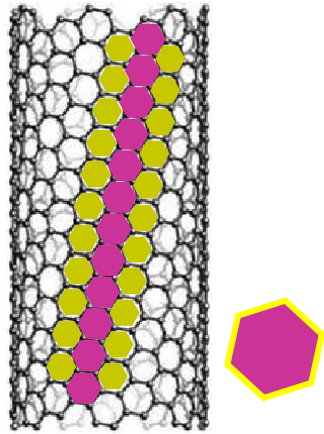
Electron Microscopy for SWCNTs



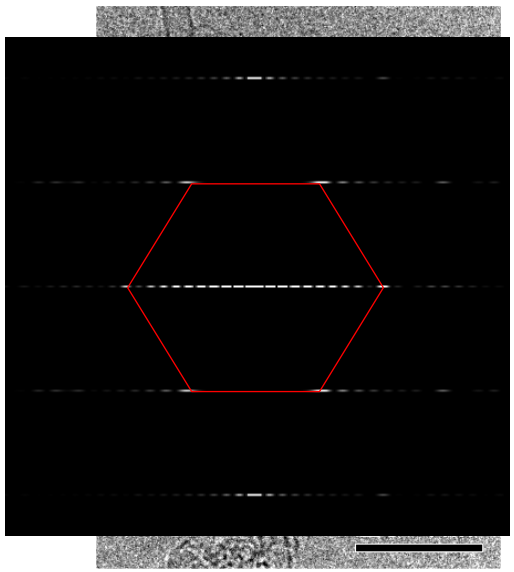
Arm-chair

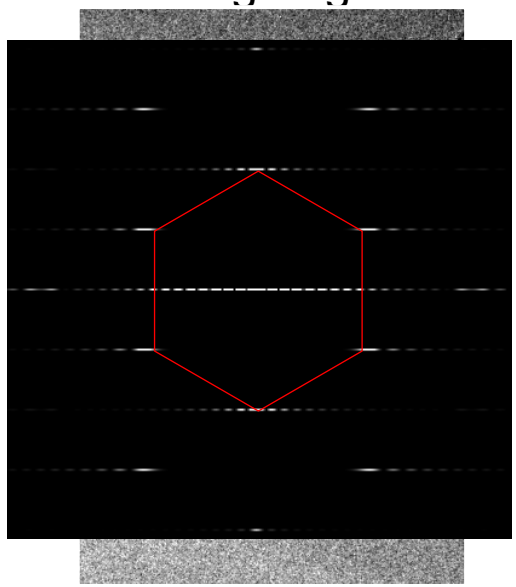


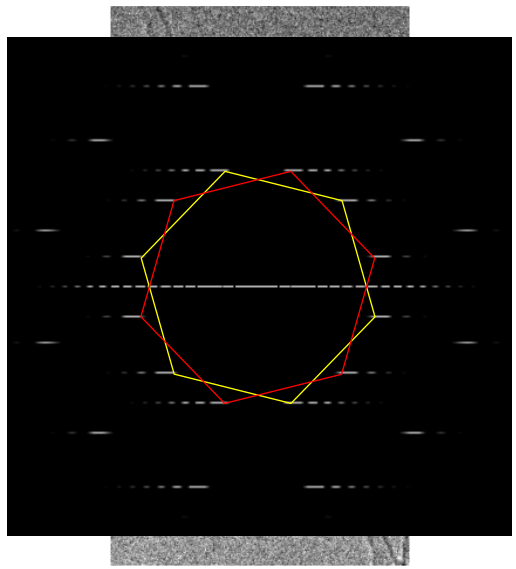
Zig-zag



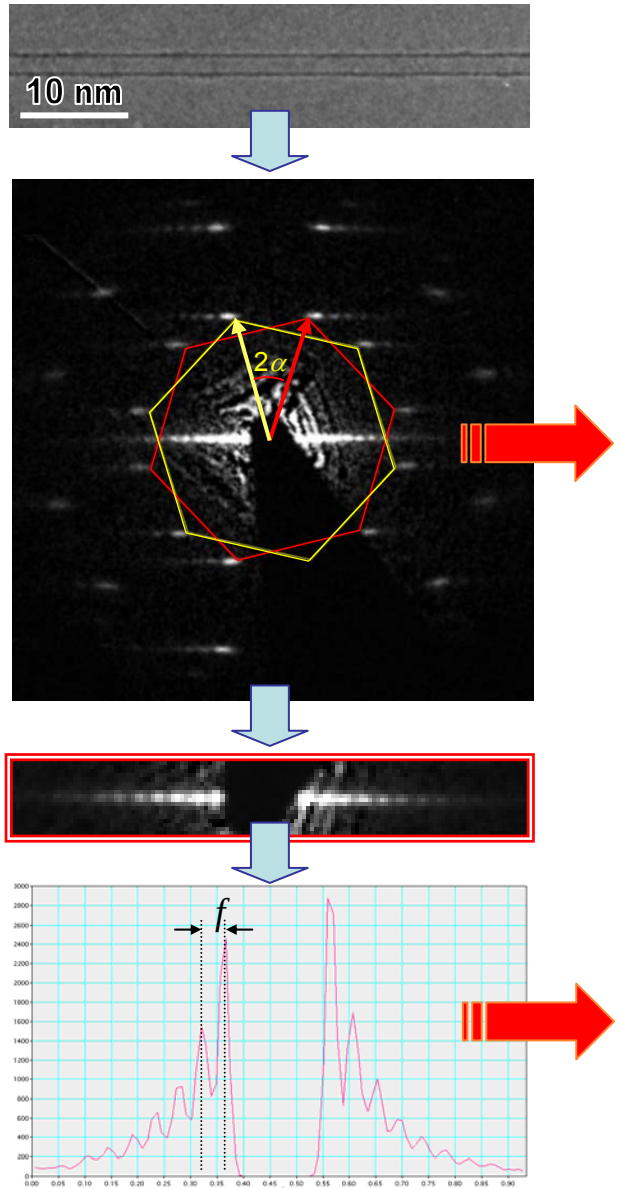
Chiral

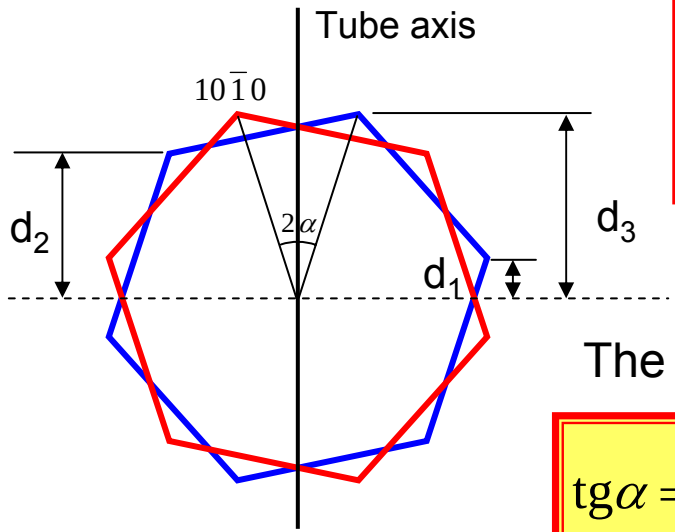






From (α, d) to (n, m) --- conventional method





The chiral indices:

$$(m,n)=(21,9)$$

The chiral angle:

$$\mathrm{tg}\alpha=\frac{d_2-d_1}{\sqrt{3}d_3}=17^\circ$$

The equatorial modulation is described as a 0-order Bessel function:

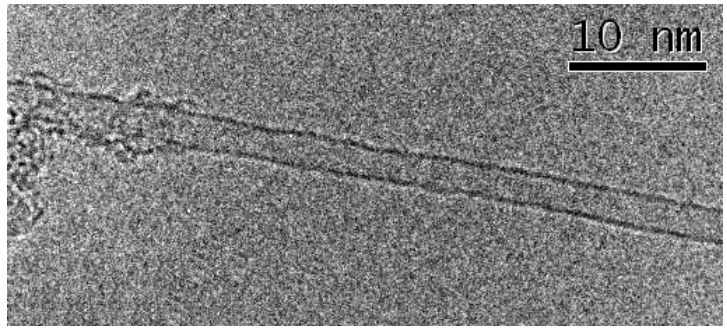
$$I_0(\pi R D_0)\propto J_0^{\,2}(\pi R D_0)$$

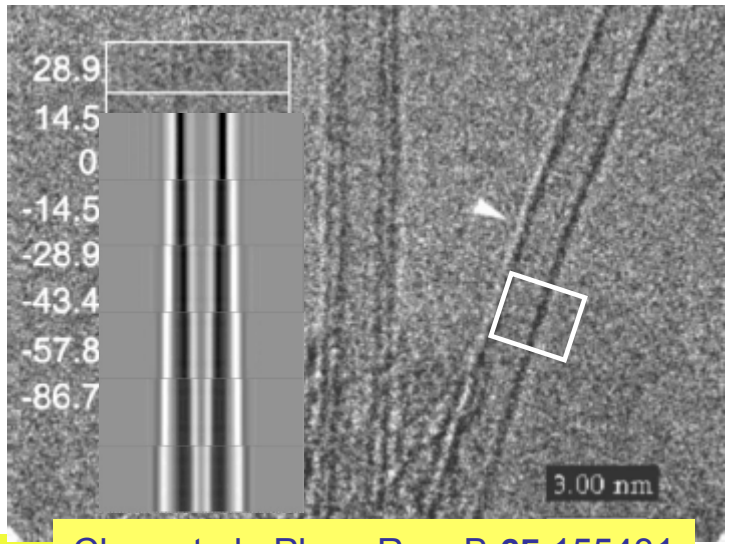
The tube diameter:

$$d\propto\frac{1}{f}=2.09\ nm$$

From (α, d) to (n, m) --- Why not HREM?

- **Why not measure the nanotube diameter directly from HREM images?**





Chen et al., Phys. Rev. B **65** 155431

In general the image contrast depends
sensitively on the imaging conditions and in particular the defocus value used in imaging and the relative orientation of the tube with respect to the incident electron beam.

Typical 10 % error:
Image is not reliable for *d* measurement.

From (α, d) to (n, m) --- accuracy

- **The measurement accuracy needed for chirality determination is high –** ***examples***

Semi-conductive tube

Metallic tube

m	n	α	D_0
(11 ,	3)	11.74	1.0
(12 ,	3)	10.89	1.08
Relative difference		7.8%	8.0%

m	n	α	d
(20 ,	9)	17.65	2.01
(21 ,	9)	17.00	2.09
Relative difference		3.7%	3.8%

m	n	α	d
(29 ,	16)	20.53	3.09
(30 ,	16)	20.03	3.17
Relative difference		2.5%	2.6%

d (nm)	Relative difference
~1.0	8%
~ 2.0	3.8%
~ 3.0	2.5%
~ 4.0	1.9%

- *The larger the tube diameter is, the higher the accuracy is needed for identification*

From (α, d) to (n, m) --- problems

$$(d, \alpha) \Longrightarrow (n, m)$$

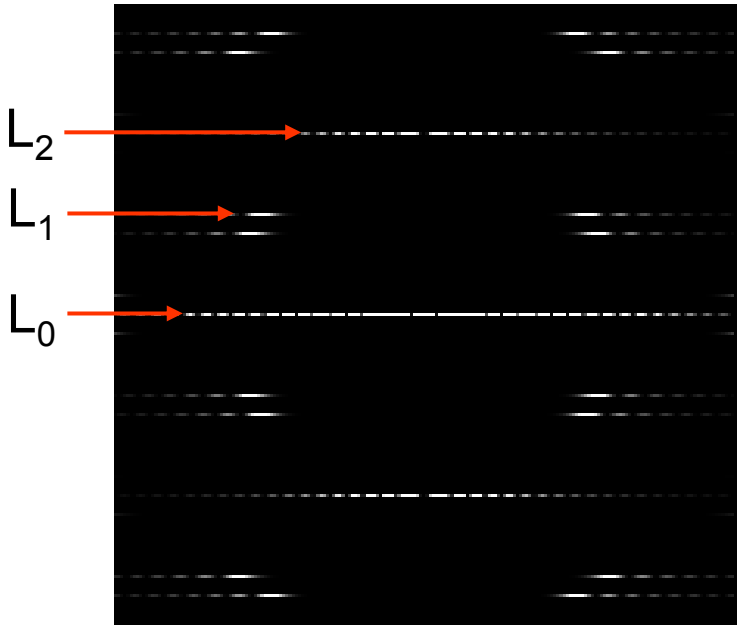
- **Calibration:**

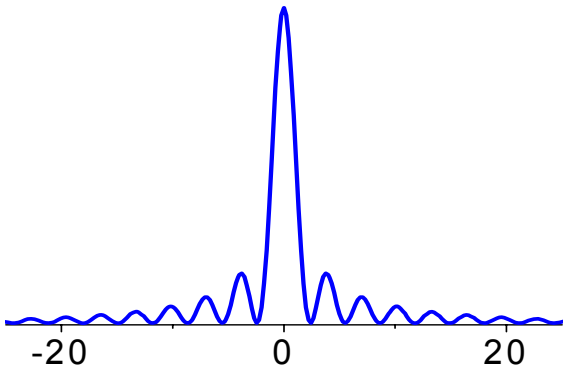
  Absolute calibration **of the electron diffraction pattern is needed to accurately measure the tube diameter.**

  The calibration is sensitively *tilt dependent*, so a tilt-compensation procedure is necessary for the determination.

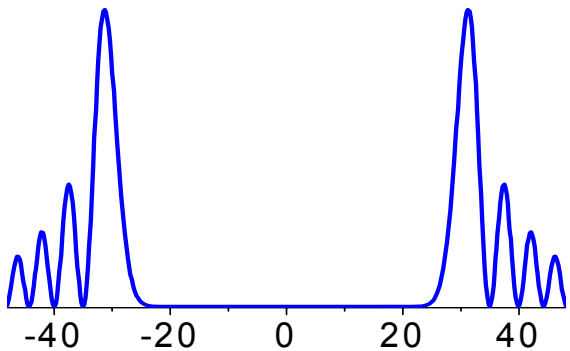
- **Insufficient accuracy**

Bessel function analysis --- H Jiang et al, Phys Rev B 74 (2006), 035427

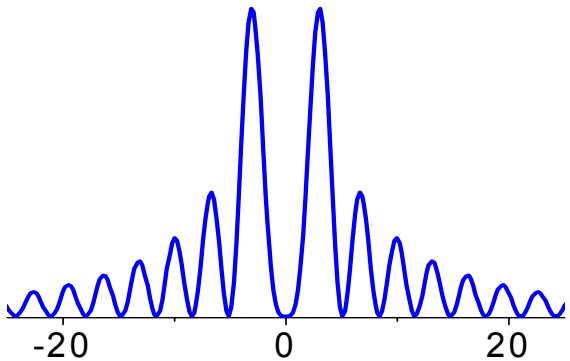




L_0 Profile



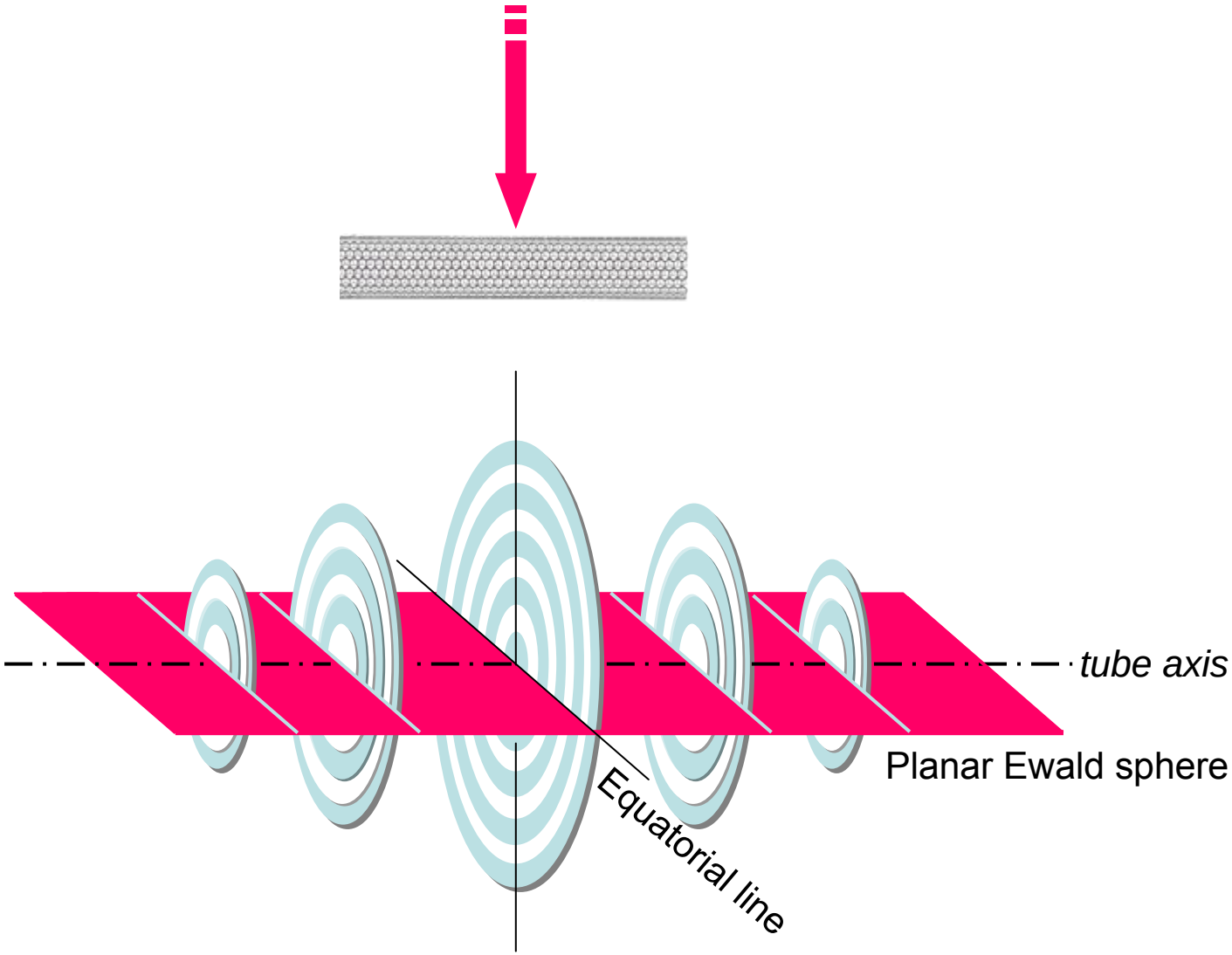
L_1 Profile



L_2 Profile

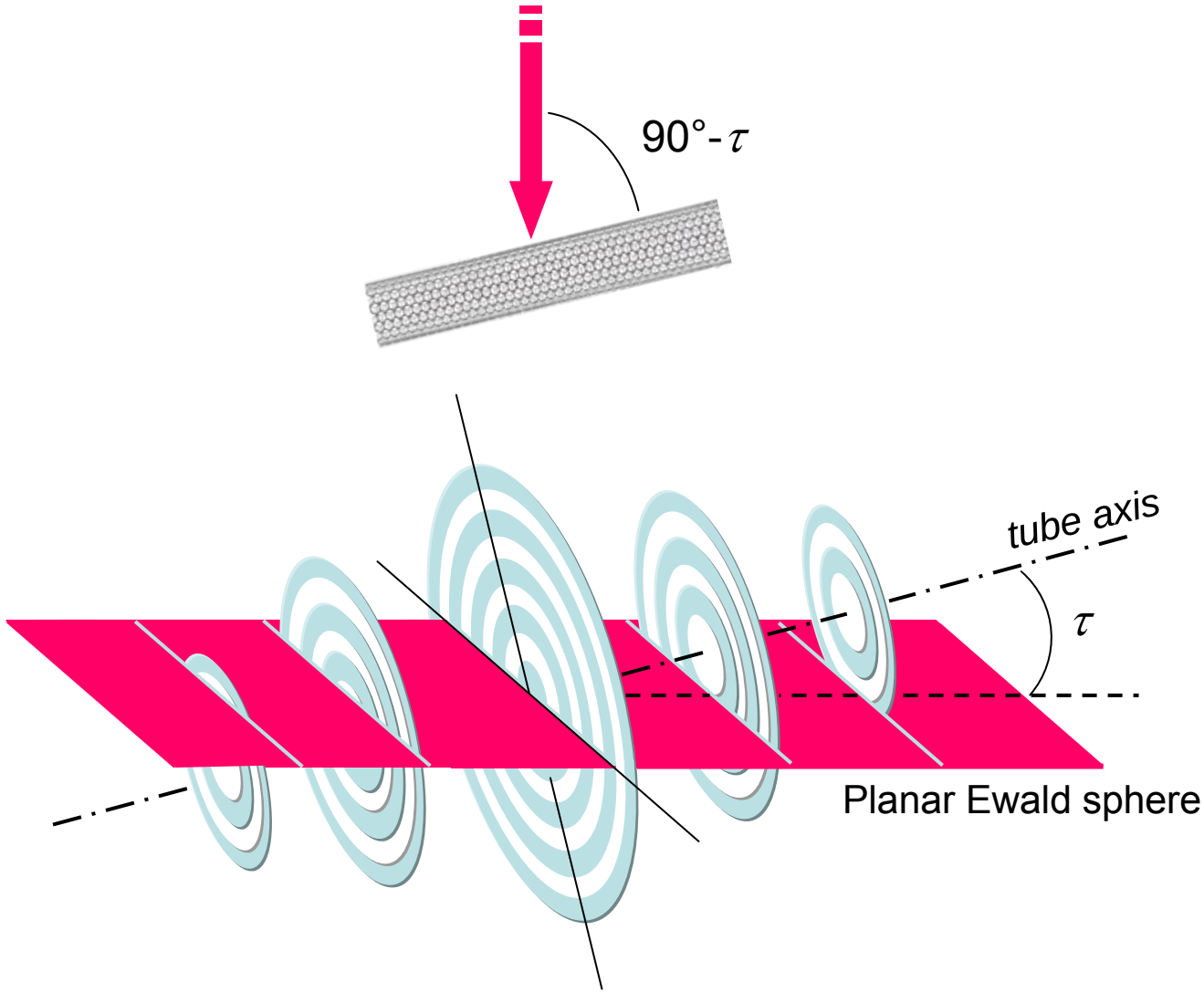
Tube Tilt: How does it affect the validity?

Normal incidence



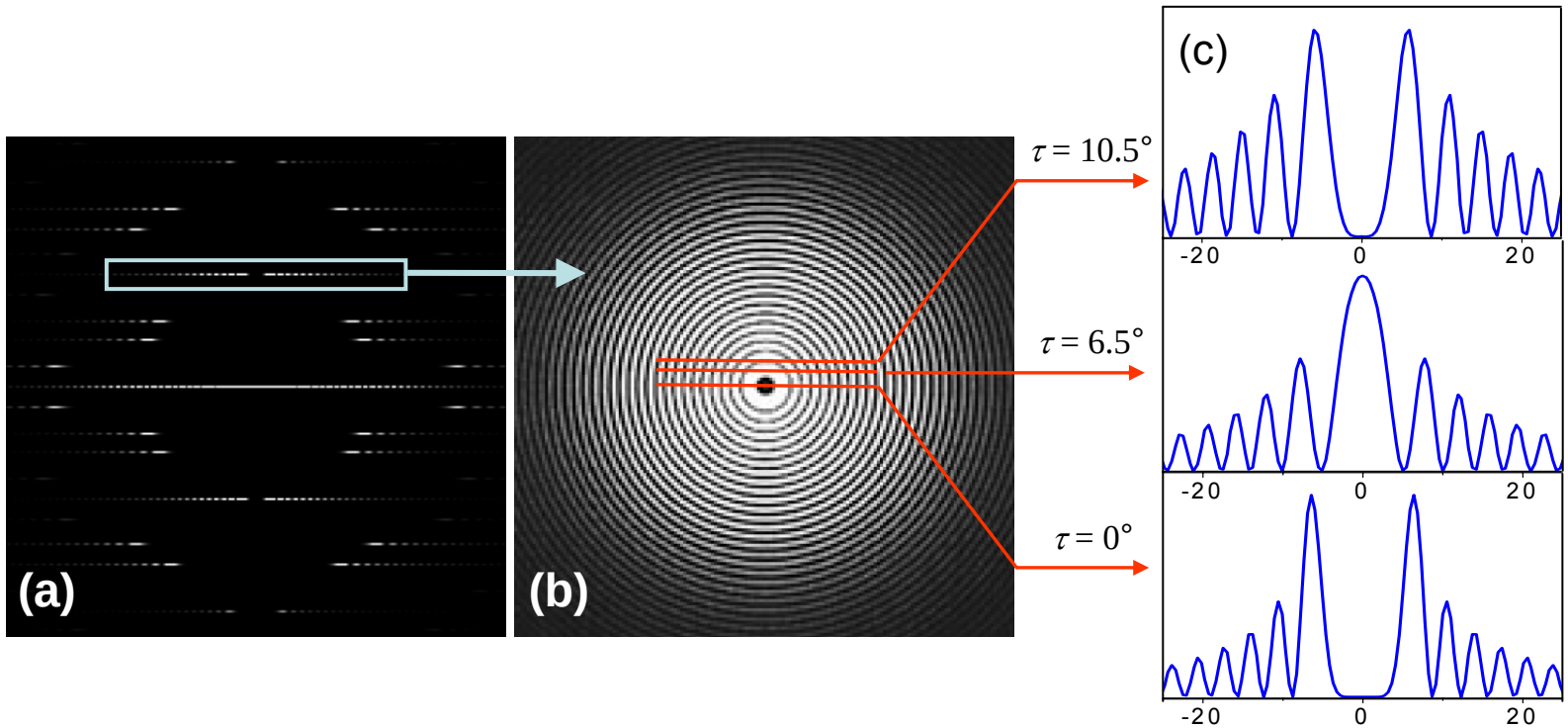
Tube Tilt: How does it affect the validity?

Inclined incidence



Tube Tilt: How does it affect the validity?

Examples



Intensity profile is highly tilt-sensitive !!

Bessel function analysis *--- Problems*

- **Intensity profiles along diffraction layer-lines are dominated by Bessel functions of certain orders; The orders of the Bessel functions are directly correlated with the chiral indices (n, m).**

- **The diffraction layer-lines having wider intensity-gaps suffer less from the tilting effect and tolerate higher tilt angles, thus are favored for (n, m) evaluation.**

- **<u>Problems:</u>**

  Results are tilt sensitive. No effective method is available to compensate the tilt.

- **Prospect:**

  This method should be suitable for (n, m) analysis of DWCNTs since it does not rely on the equatorial line.

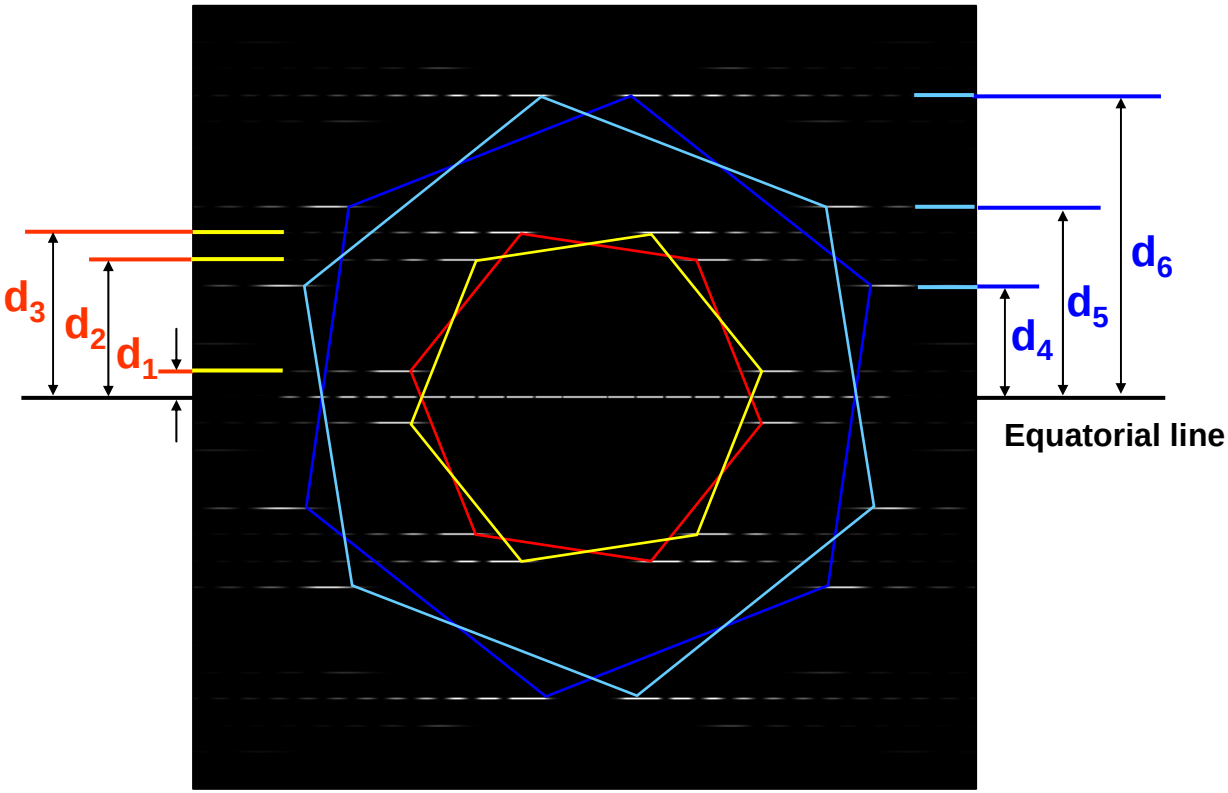
Way out ?

- ☞ **Conventional method:** ***From (α, d) to (n, m)***

- ☞ **New method 1:** ***Bessel function analysis***

- ☞ **New method 2:** ***Intrinsic layer-line distances***

Take a look at "Layer-line distances"



Simple ideas --- "intrinsic" layer-line distance"

Let's bring up a new concept: "intrinsic" layer-line distance ξ_i, which is defined by:

$$\boxed{\xi_i = D_0 \cdot d_i}$$

$$\propto \frac{d_i}{\delta}$$

δ is the pseudo-periodicity along the equatorial line
D_0 is the tube diameter
d_i is the apparent layer line distance

An example: *what are intrinsic layer-line spacings related to?*

Take the 3rd layer-line for example:

$$D_0 = \frac{\sqrt{n^2 + m^2 + nm}}{\pi} \cdot a$$

$$d_3 = \frac{2}{\sqrt{3}a} \cdot \cos\alpha$$

$$\cos\alpha = \frac{2n + m}{2\sqrt{n^2 + m^2 + nm}}$$

Then, we have

$$\boxed{\xi_3 = \frac{2n + m}{\sqrt{3}\pi}.}$$

Expressions of intrinsic layer-line spacings

Layer-line number i	ξ_i^0
1	$\xi_1^0 = \dfrac{n-m}{\sqrt{3}\pi}$
2	$\xi_2^0 = \dfrac{n+2m}{\sqrt{3}\pi}$
3	$\xi_3^0 = \dfrac{2n+m}{\sqrt{3}\pi}$
4	$\xi_4^0 = \dfrac{\sqrt{3}m}{\pi}$
5	$\xi_5^0 = \dfrac{\sqrt{3}n}{\pi}$
6	$\xi_6^0 = \dfrac{\sqrt{3}(n+m)}{\pi}$

Non-dimensional !
Uniquely defined by (n, m) !!

Easy solutions --- to chiral indices (n, m) ☺

Any combination of two ξ_i measurements gives (n, m) values

(ξ_2, ξ_3):

$$n = \frac{\sqrt{3}\pi}{6} \cdot (2\xi_3 - \xi_2) \qquad m = \frac{\sqrt{3}\pi}{6} \cdot (2\xi_2 - \xi_3)$$

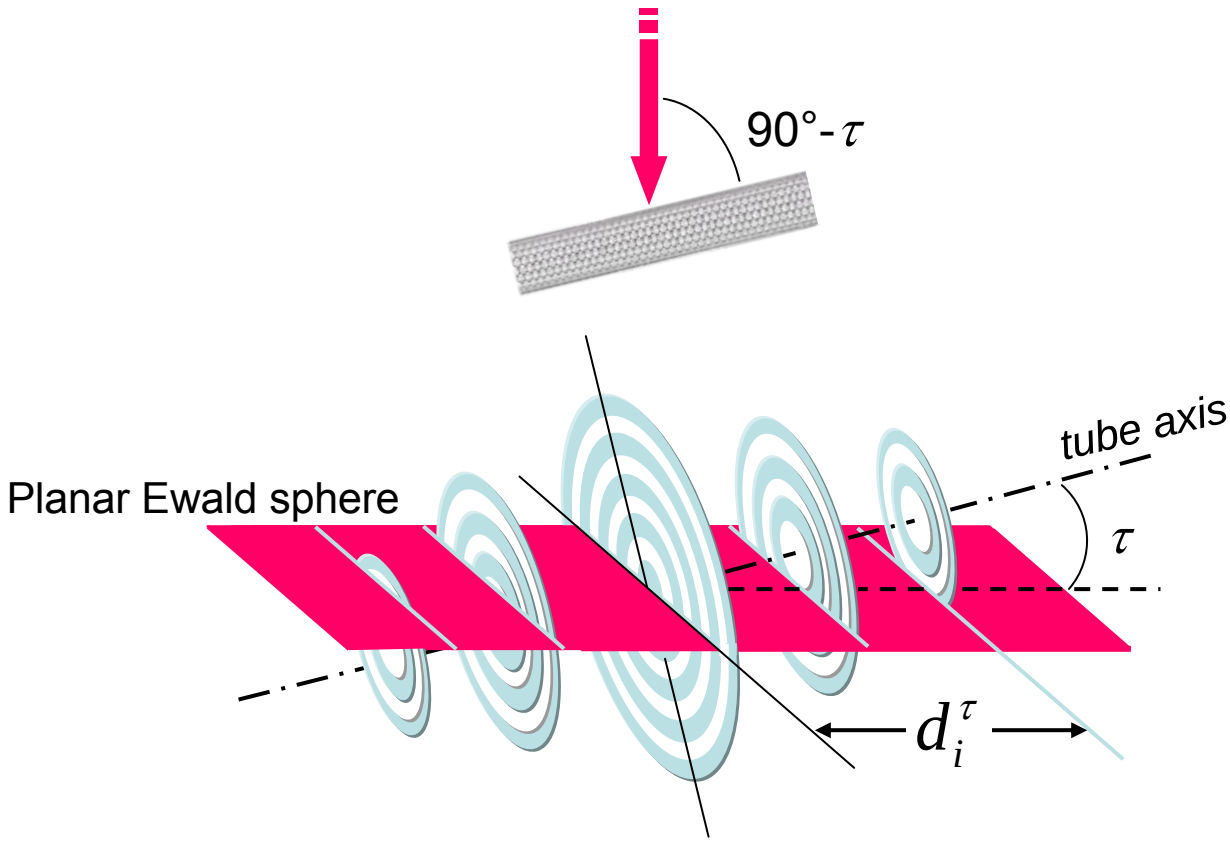
or

(ξ_3, ξ_6):

$$n = \frac{(3\xi_3 - \xi_6)}{2\sqrt{3}}\pi \qquad m = \frac{(2\xi_6 - 3\xi_3)}{2\sqrt{3}}\pi$$

Totally calibration free!!

Tube Tilt --- life is complicated again ☹



$$d_i^\tau = d_i^0 \cdot \frac{1}{\cos\tau}$$

"Positive" Errors

Since: $$\xi_i^{\tau} = \xi_i^{0} \cdot \frac{1}{\cos\tau}$$

Then: $$n^{\tau} = n \cdot \frac{1}{\cos\tau} = n + \varepsilon_n$$

$$m^{\tau} = m \cdot \frac{1}{\cos\tau} = m + \varepsilon_m$$

Obviously: $$\boxed{\varepsilon_{n \text{ or } m} > 0}$$

The error due to the tilt is just a "plus" to us:

1) It is not only a positive number;
2) It is also an advantage for analysis.

Case I

(up to 20° tilt)

If: $\varepsilon_n < 1$

Then: $n = \mathrm{TRUNC}\left(n^{\tau}\right)$

This is the typical case

Case II

(higher tilt)

If: $1 \leq \varepsilon_n < 2$

Then: $n = \mathrm{TRUNC}\left(n^{\tau}\right) - 1$

Even worse Case

(even higher tilt)

If: $\varepsilon_n \geq 2$

Then: On the same consideration as Case II

Cross-checking procedures:

(I) *Intrinsic m / n ratio A*

$$\left(\xi_3^0,\ \xi_6^0\right): \qquad n = \frac{\left(3\xi_3^0 - \xi_6^0\right)}{2\sqrt{3}}\pi \qquad m = \frac{\left(2\xi_6^0 - 3\xi_3^0\right)}{2\sqrt{3}}\pi$$

$$\left(\xi_3^\tau,\ \xi_6^\tau\right): \qquad n^\tau = \frac{\left(3\xi_3^\tau - \xi_6^\tau\right)}{2\sqrt{3}}\pi \qquad m^\tau = \frac{\left(2\xi_6^\tau - 3\xi_3^\tau\right)}{2\sqrt{3}}\pi$$

$$A = \frac{m}{n} = \frac{m^\tau}{n^\tau} = \frac{2\xi_6^\tau - 3\xi_3^\tau}{3\xi_3^\tau - \xi_6^\tau}$$

Totally independent of tubes inclination!!!!

Solutions to tilt angles

When (n, m) are determined, the tilt angle τ can be simply calculated by:

$$\xi_i^{\tau} = \xi_i^{0} \cdot \frac{1}{\cos\tau}$$

As examples:

$$\cos\tau = \frac{\xi_3}{\xi_3^{\tau}} = \frac{2n+m}{\sqrt{3}\pi \cdot \xi_3^{\tau}}$$

$$\text{or} \qquad = \frac{\xi_6}{\xi_6^{\tau}} = \frac{\sqrt{3}(n+m)}{\pi \cdot \xi_3^{\tau}}$$

What else? *--- we need high-quality EDPs*

- **Weak s**

A SWCNT rs in the beam direction e

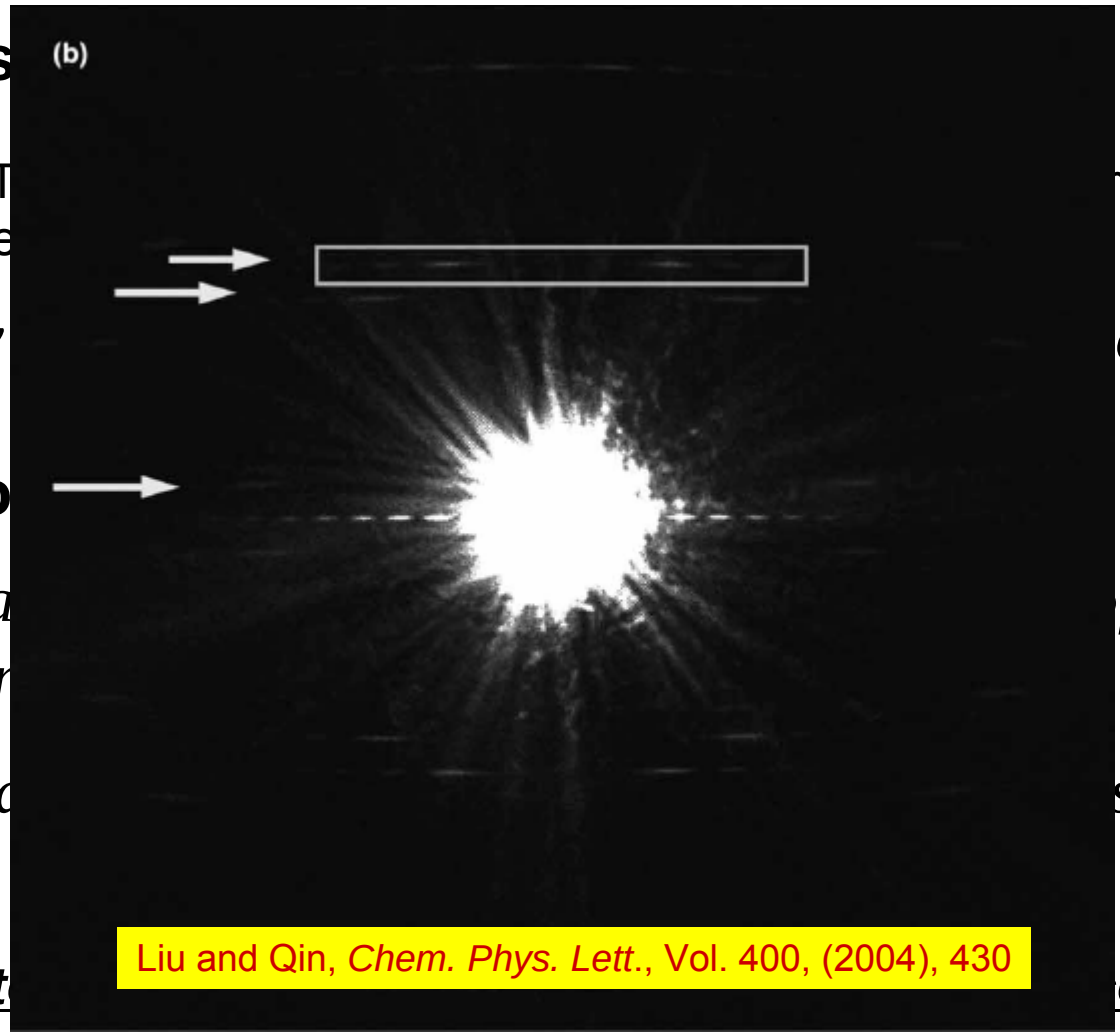
Usually d blurred.

- **Electro**

To increa f CNTs, we need r

To decrea st be limited!

We have t onditions !!!



Liu and Qin, *Chem. Phys. Lett.*, Vol. 400, (2004), 430

How to make a good diffraction pattern?

- **TEM instrument -- *a conventional microscope***

  Philips CM-200 FEG 80 kV , (early version of FEI TEM)

  Gatan 1k x 1k multi-scan CCD camera

- **Parallel-beam Micro-diffraction mode**

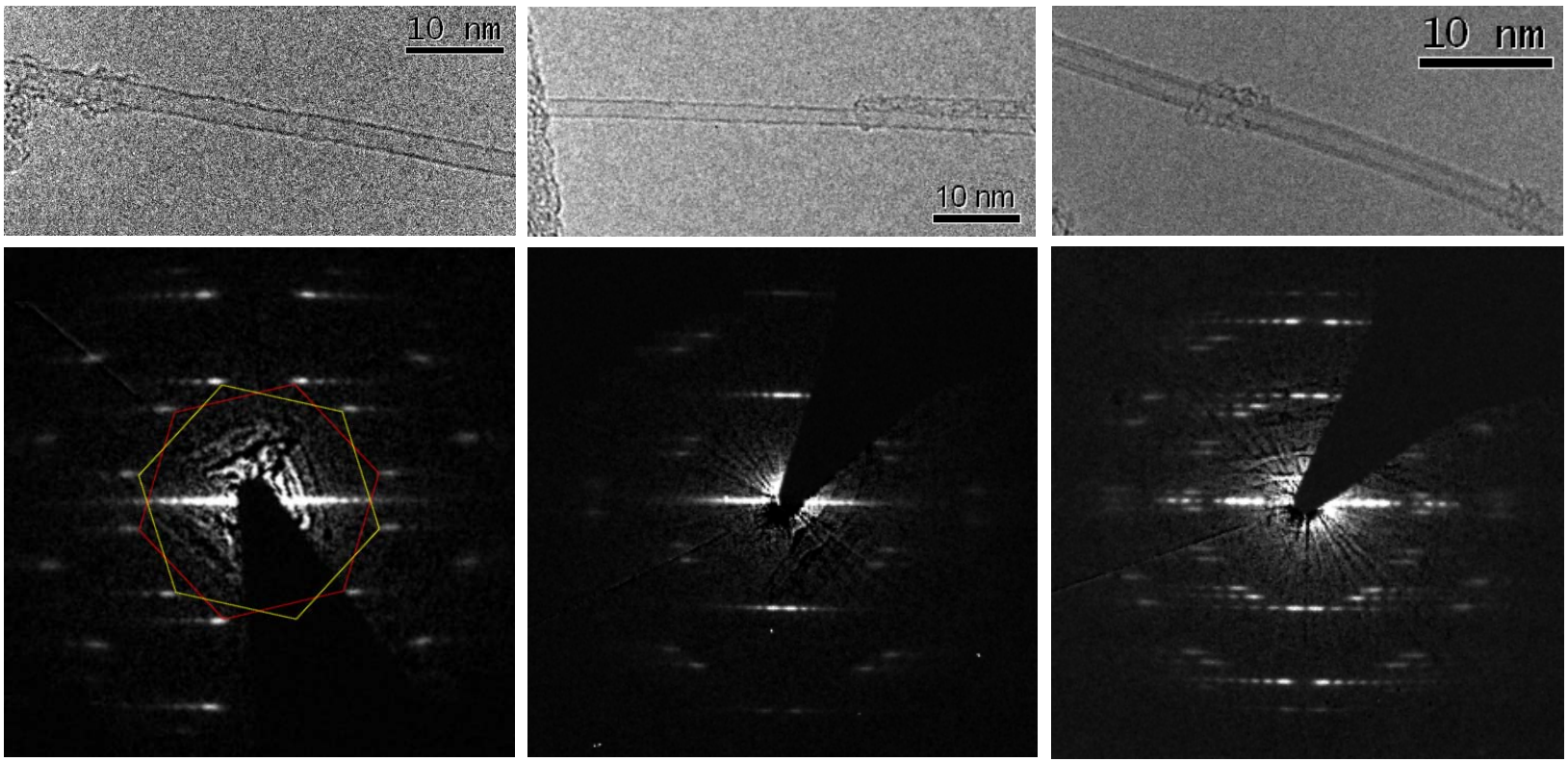
  Beam size ~50 nm
  Electron dose ~ 10^4 /s nm^2
  Exposure time 3.0 sec

- **Data processing**

  An additional pattern that was recorded in the vacuum without tube was subtracted from the original pattern so as to reduce the effect of the strong central peak and the background.

Image gallery:

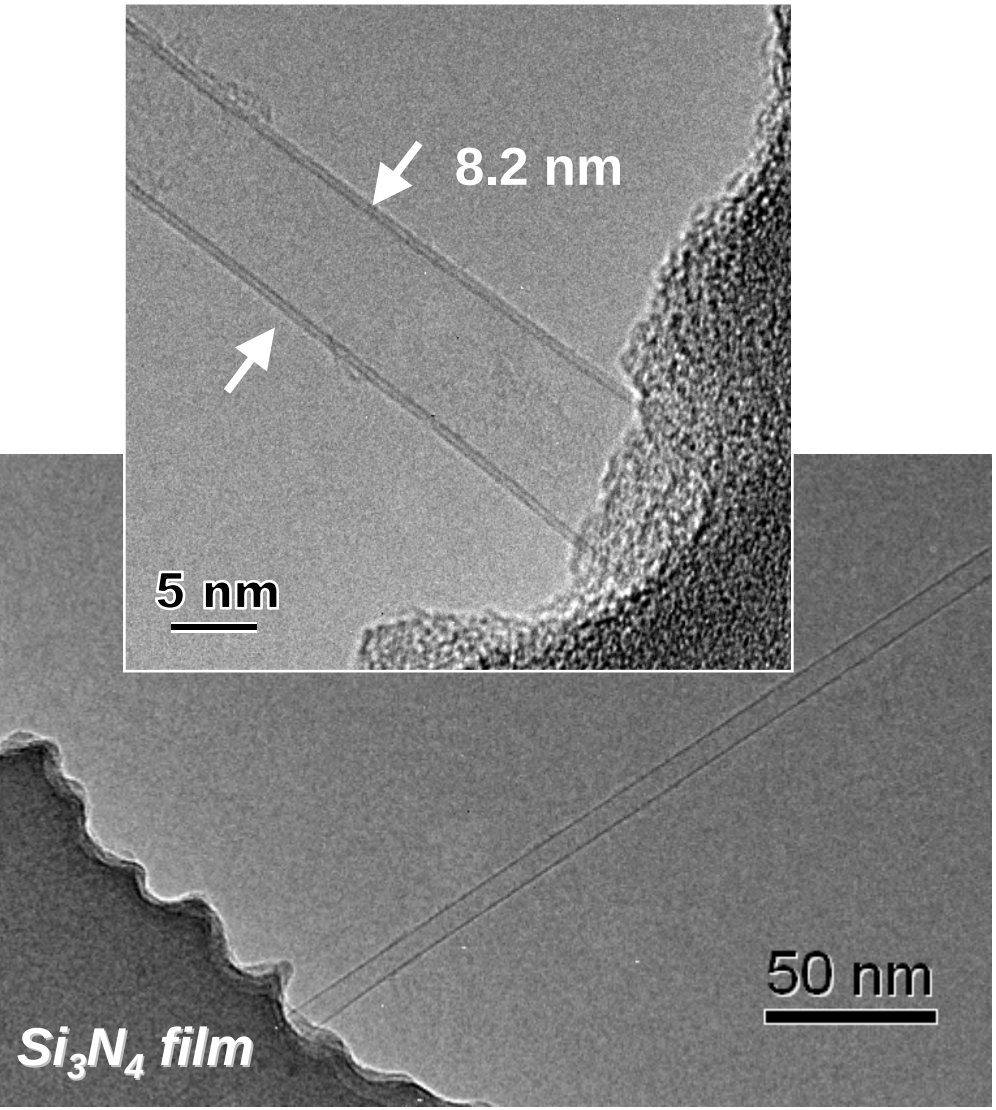
Individual CNTs

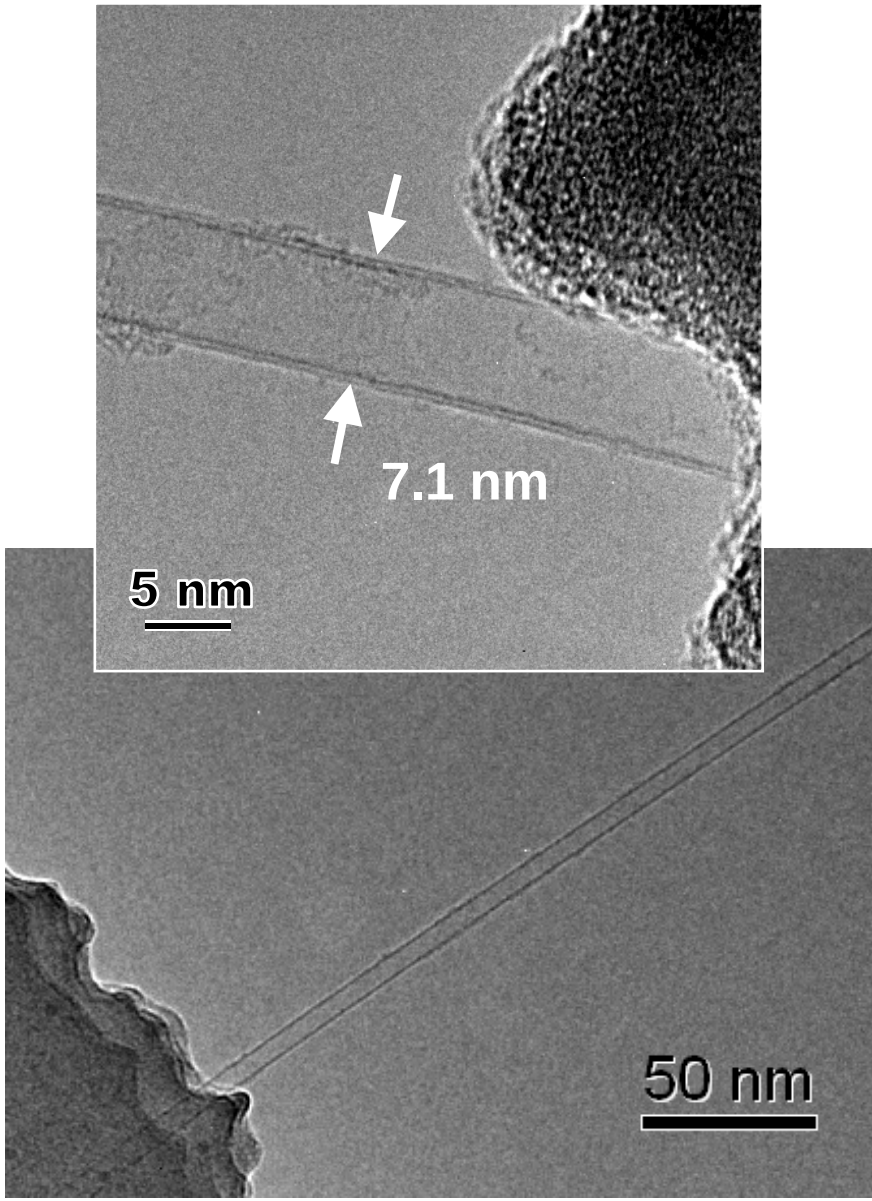


Single-walled | Single-walled | Double-walled

Image gallery:

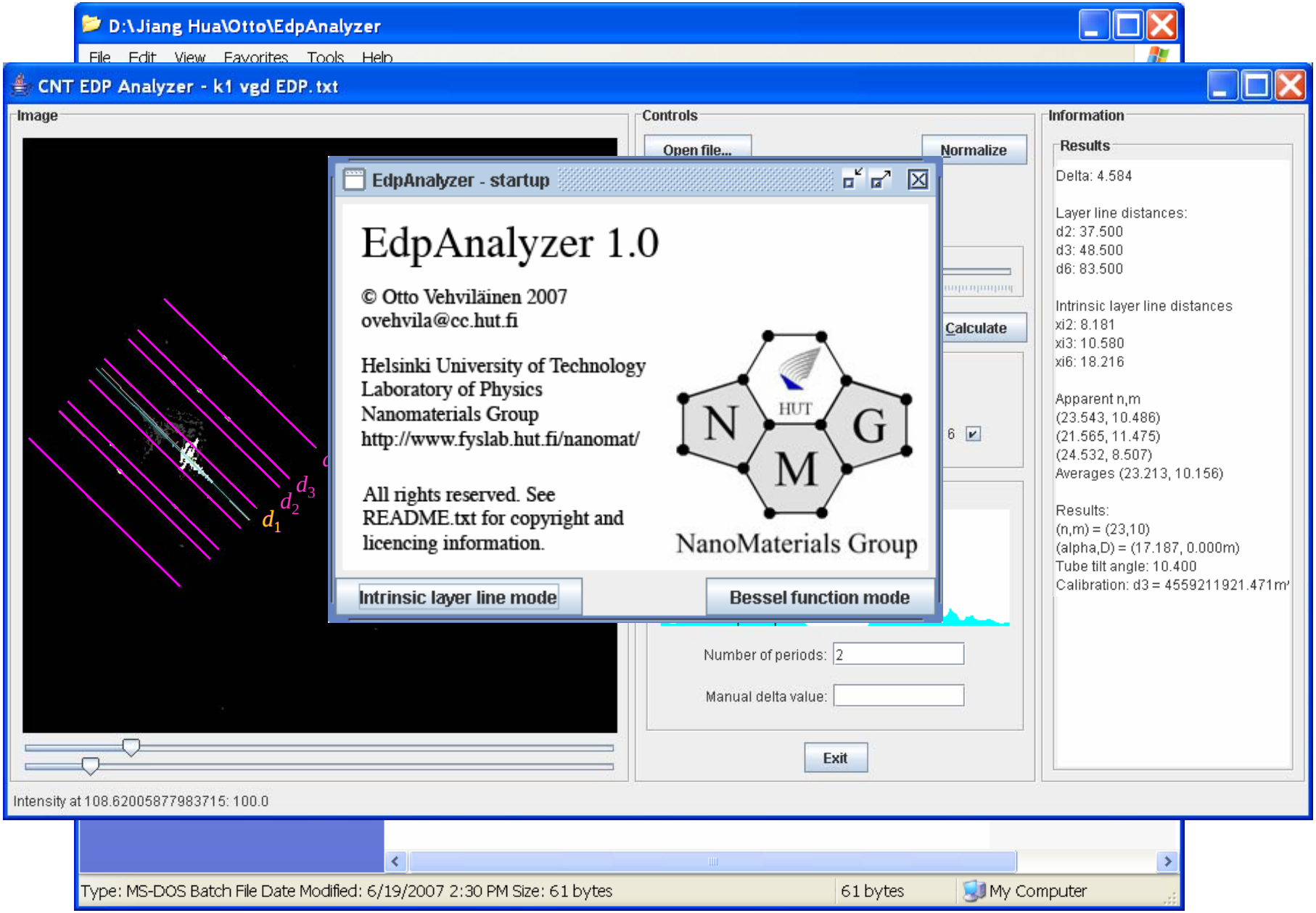
Ultra-thick DWCNTs



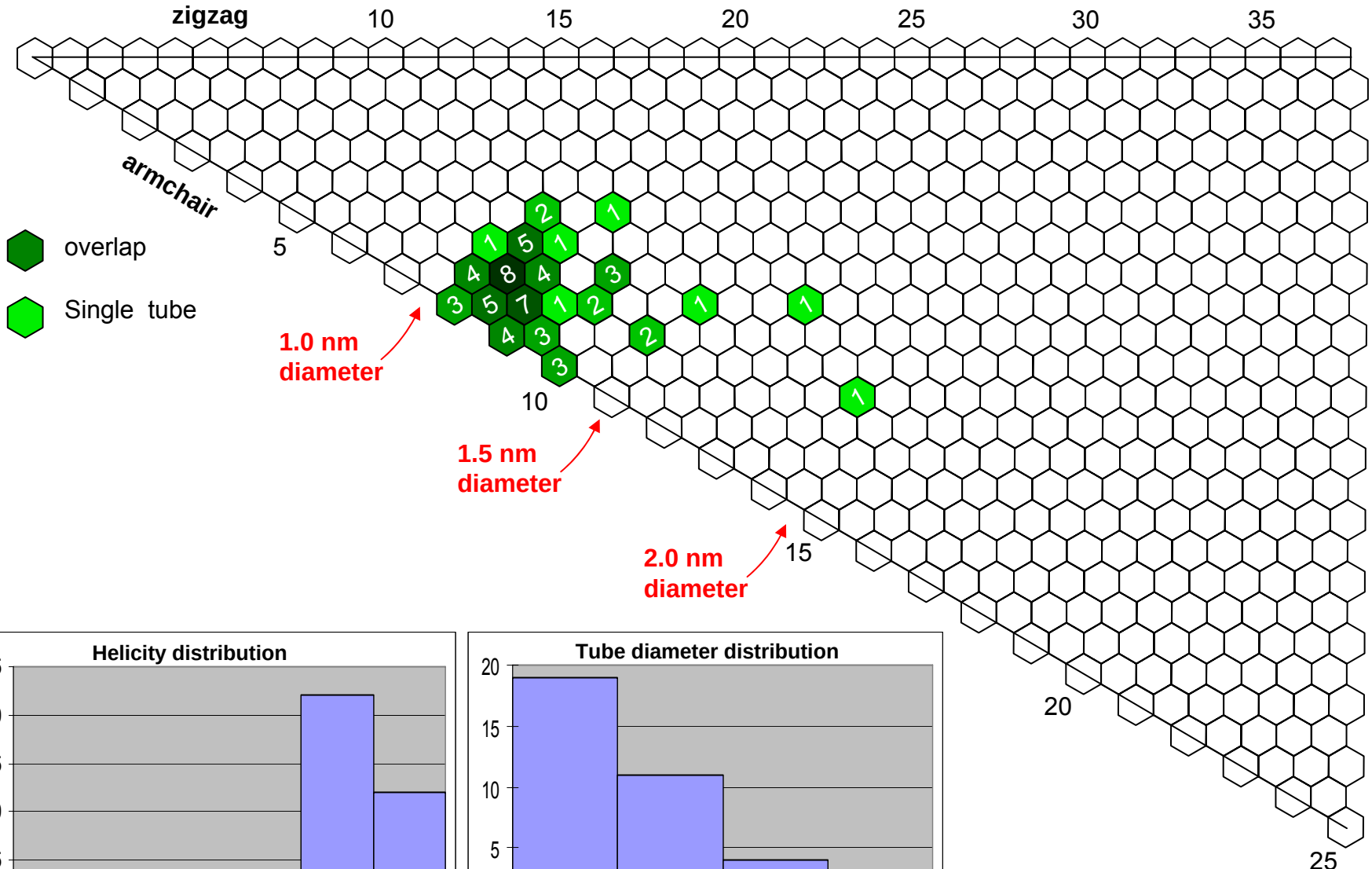


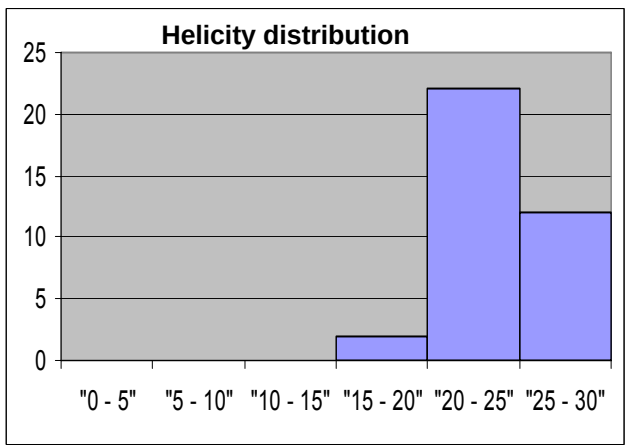
What's more? *--- computer-aid EDP analyzer*

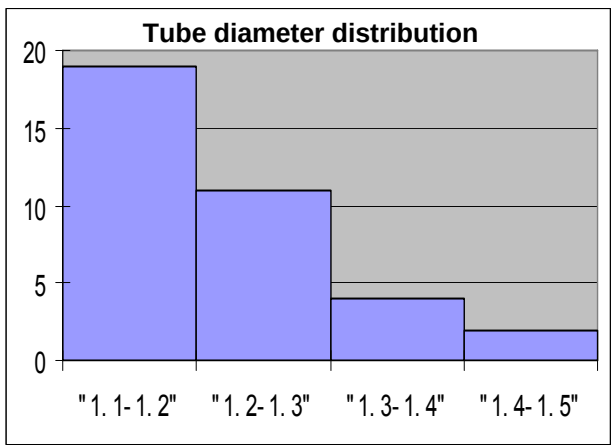
A Visual demonstration of the Program "*EDP Analyzer*"


D:\Jiang Hua\Otto\EdpAnalyzer
File Edit View Favorites Tools Help
CNT EDP Analyzer - k1 vgd EDP.txt
Image
Controls
Information
Open file...
Normalize
Calculate
Results
Delta: 4.584
Layer line distances:
d2: 37.500
d3: 48.500
d6: 83.500
Intrinsic layer line distances
xi2: 8.181
xi3: 10.580
xi6: 18.216
Apparent n,m
(23.543, 10.486)
(21.565, 11.475)
(24.532, 8.507)
Averages (23.213, 10.156)
Results:
(n,m) = (23,10)
(alpha,D) = (17.187, 0.000m)
Tube tilt angle: 10.400
Calibration: d3 = 4559211921.471m
EdpAnalyzer - startup
EdpAnalyzer 1.0
© Otto Vehviläinen 2007
ovehvila@cc.hut.fi
Helsinki University of Technology
Laboratory of Physics
Nanomaterials Group
http://www.fyslab.hut.fi/nanomat/
All rights reserved. See
README.txt for copyright and
licencing information.
HUT
N
G
M
NanoMaterials Group
Intrinsic layer line mode
Bessel function mode
Number of periods: 2
Manual delta value:
Exit
Intensity at 108.62005877983715: 100.0
Type: MS-DOS Batch File Date Modified: 6/19/2007 2:30 PM Size: 61 bytes
61 bytes
My Computer

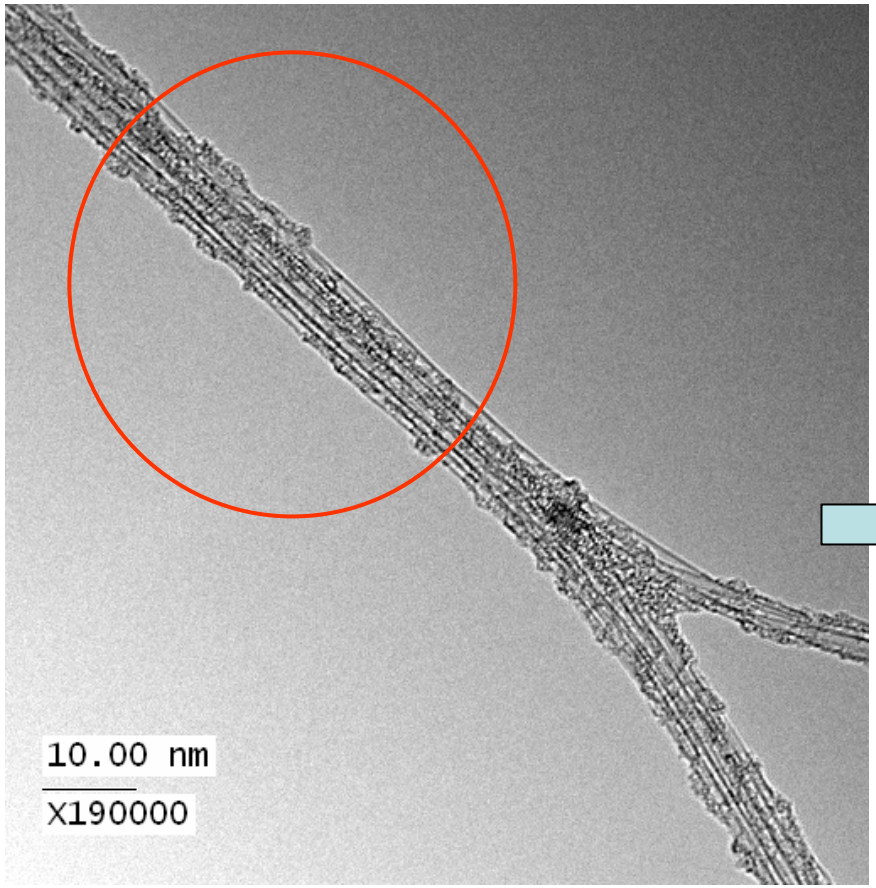
(n, m) map of TKK SWCNTs from CO with Fe cluster floating catalyst

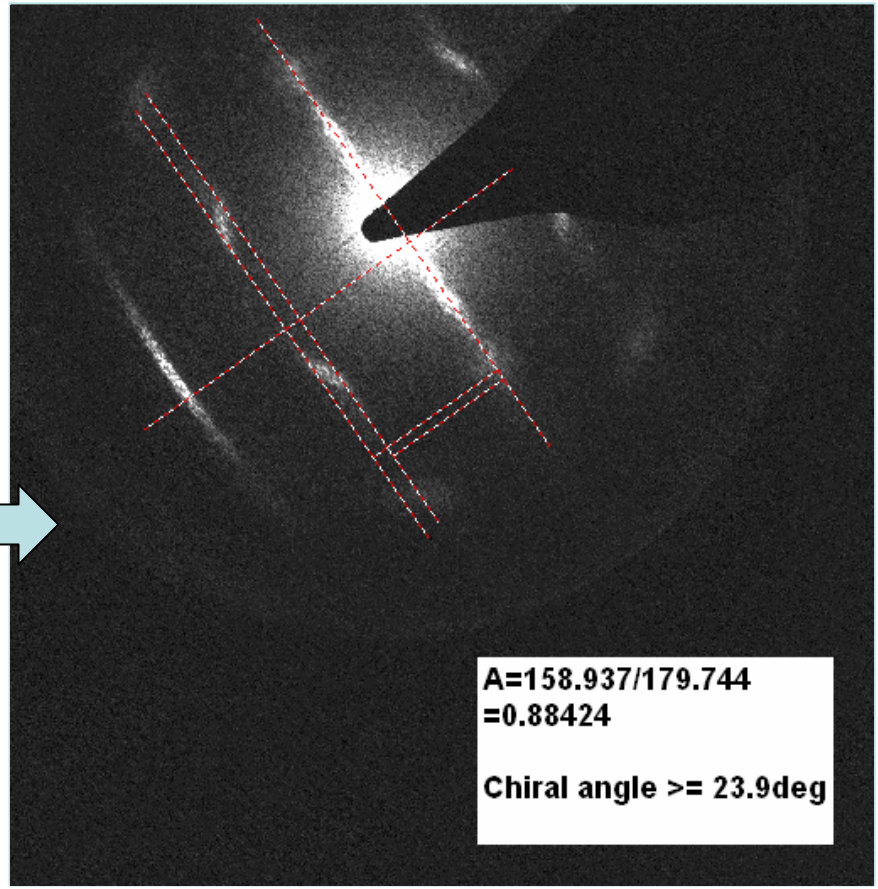






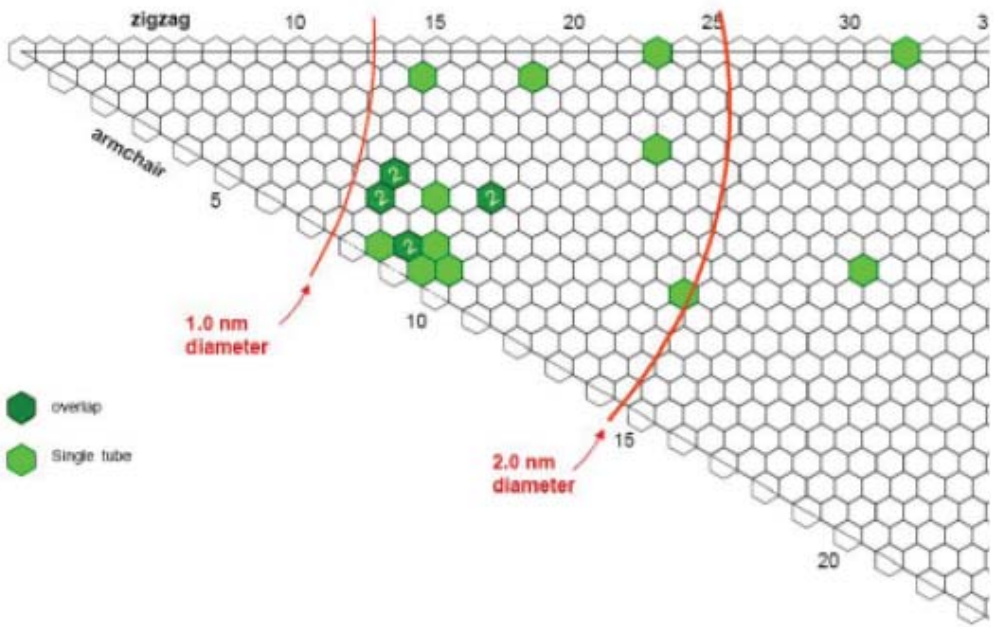
Electron diffraction from a bundle of TKK SWCNTs
CO + Fe cluster floating catalyst

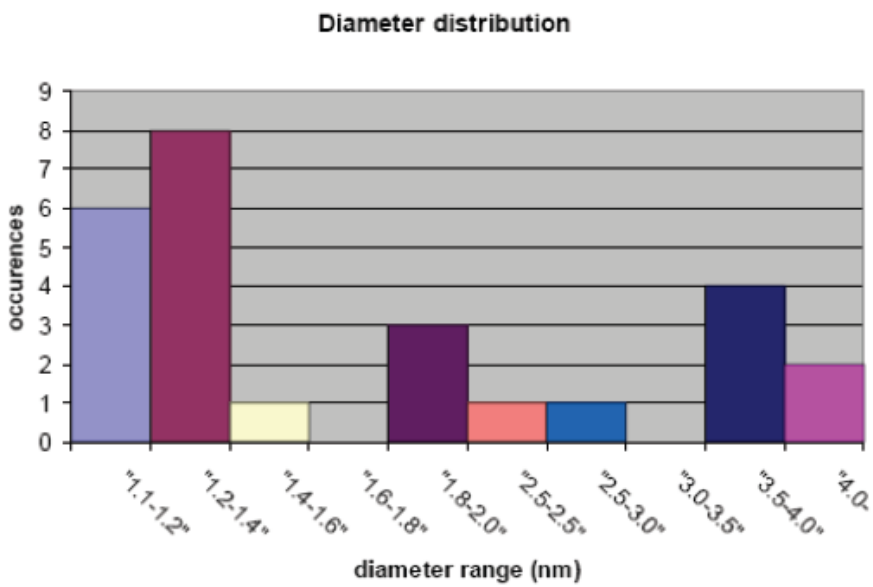




The chiralities of CNTs in the bundle have a narrow range of chiral angles which is determined from its electron diffraction pattern to be from 23.9 to 30 degrees, toward the near-armchair end.

(n, m) Map of Cambridge SiO_2 supported CVD SWCNT sample





Sample coursty: Dr. Simon Pisana and Dr. Stephan Hofmann
From Cambridge University

Carbon nanotubes are grown by chemical vapor deposition (CVD) on highly doped Si substrates with a 200 nm oxide layer. Different CVD growth conditions were used, as described in Refs. [42–44]. A grid structure is prepared on top of the nanotubes by electron beam lithography, thermal evaporation of 3nm Cr and 110nm Au, and a lift-off process. The sample is cleaved so that the structure is on the cleaved edge of the substrate (Fig. 1a). There are two possible etching processes to obtain the free-standing structure (Fig. 1b)

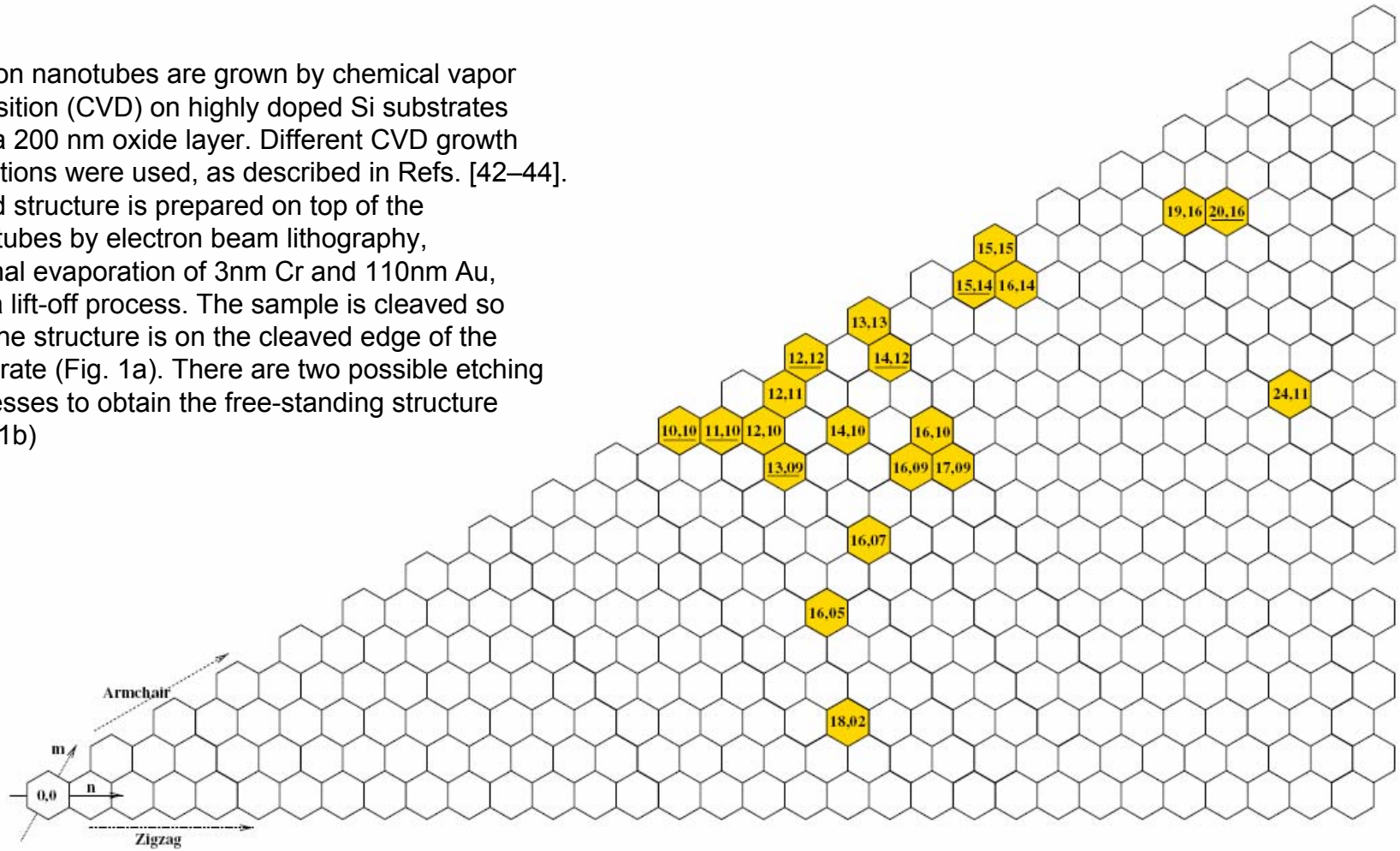
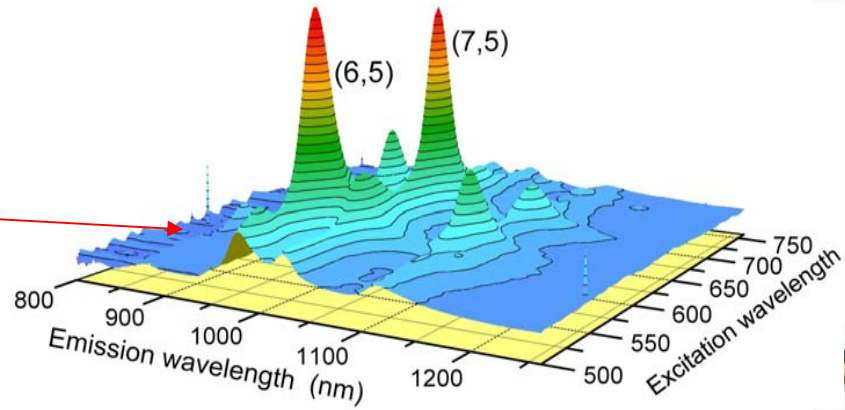
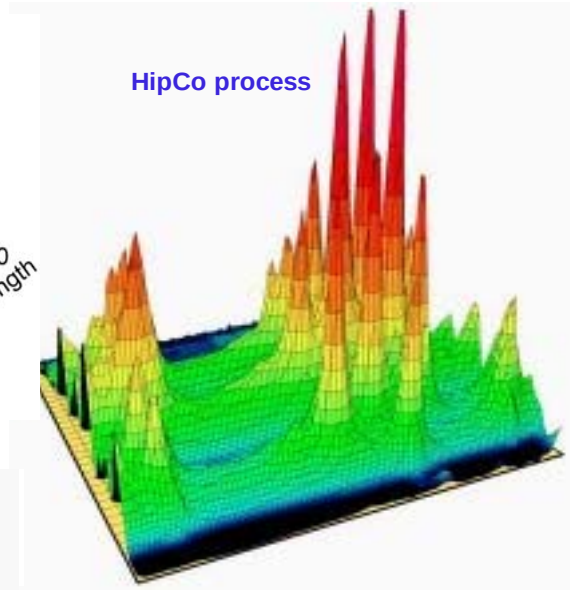
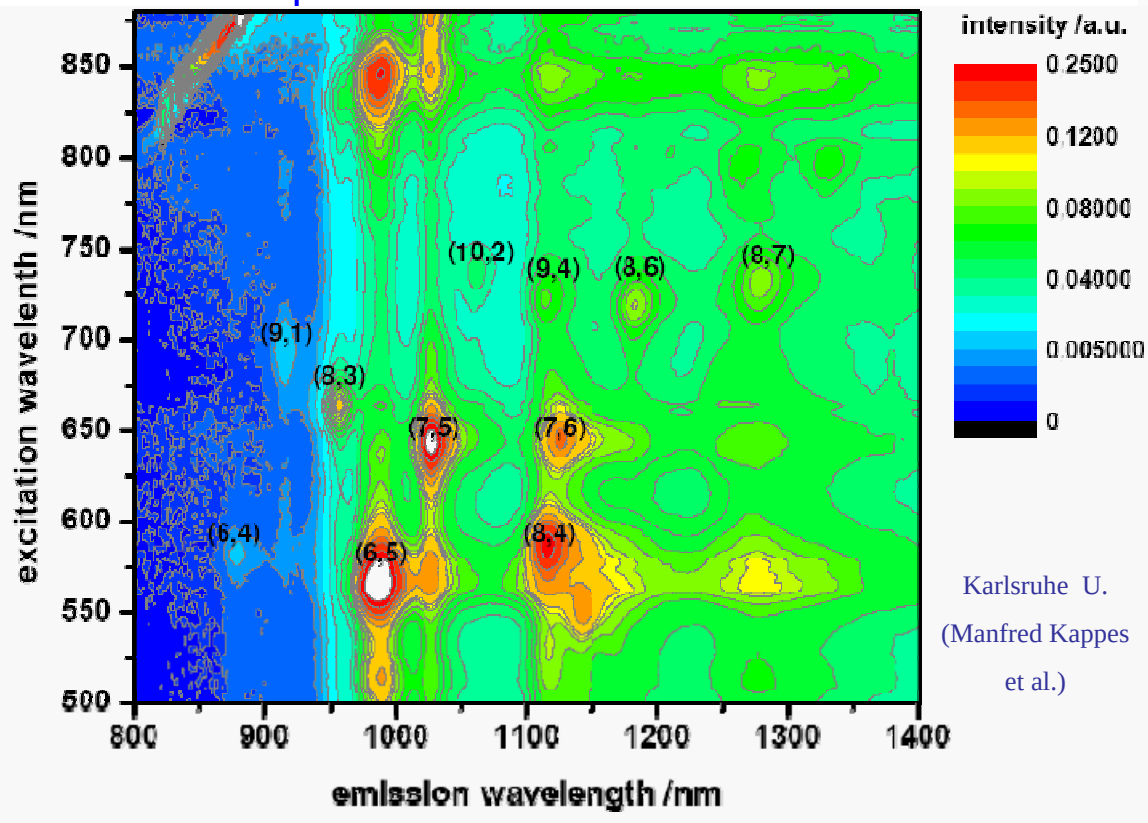


Fig. 9. Nanotube indices of 28 tubes grown in the same CVD process. The underlined indices were encountered twice. The rolling angle is not randomly distributed, but is close to the armchair direction (30°) in the majority of the nanotubes in this material.

CoMoCat







Karlsruhe U.
(Manfred Kappes et al.)

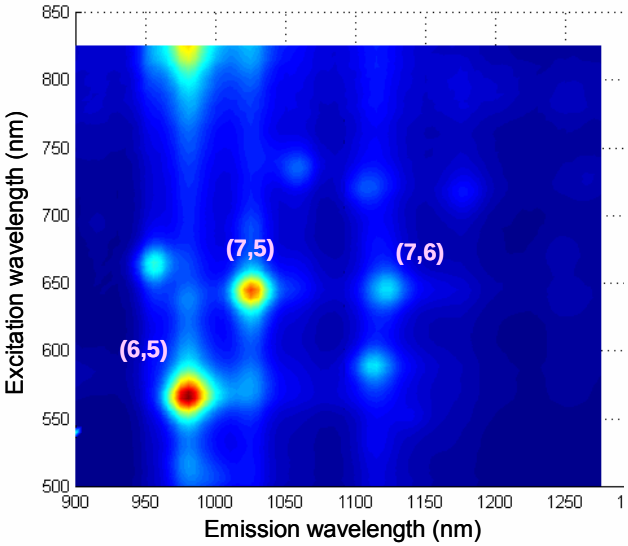
Comparison of (n,m) Distribution of CoMoCAT Vs. HIPCO PL - Photo-luminescence
SEMICONDUCTING TYBES ONLY

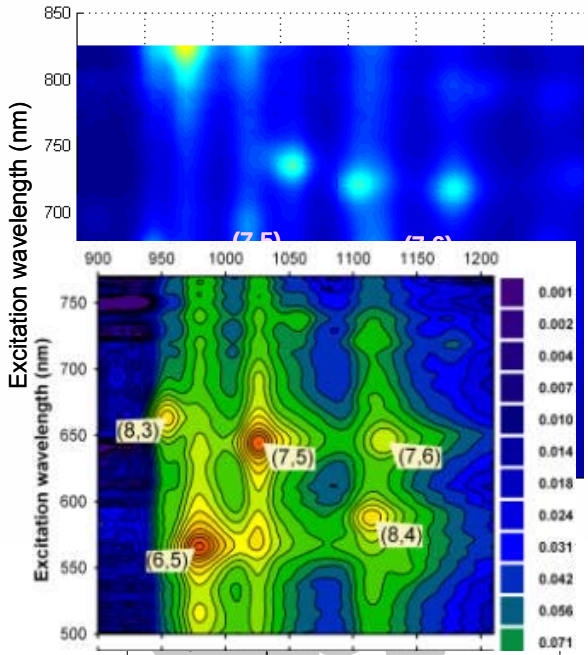
Courtesy –Prof. D. Resasco

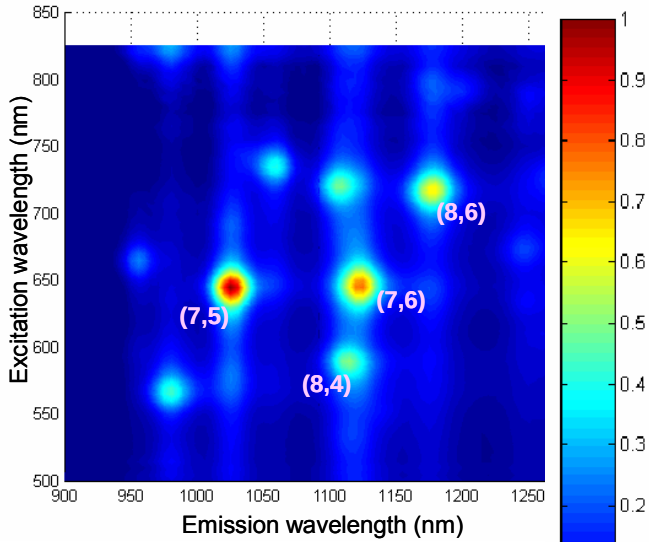
ACCVD Chirality – PL -Semiconducting

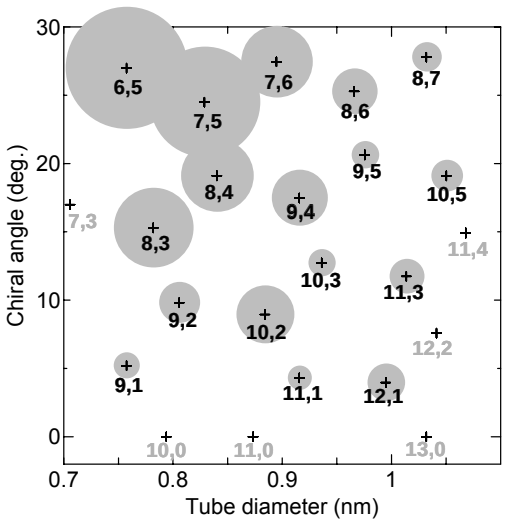
Carbon source : Ethanol, CVD time : 10min

S. Maruyama et al.

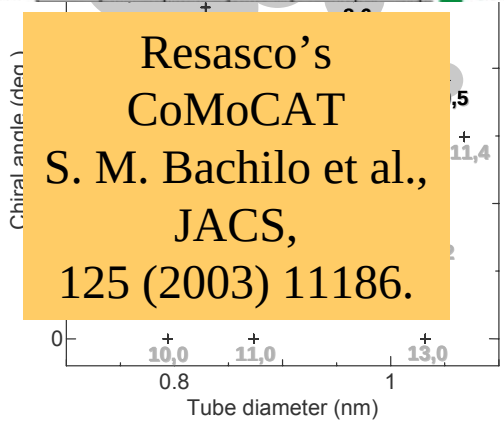






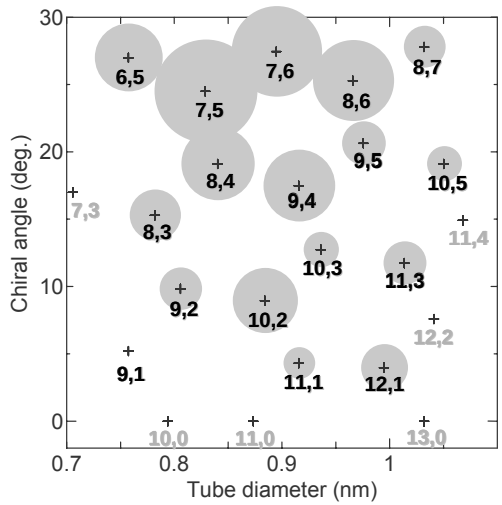


650℃



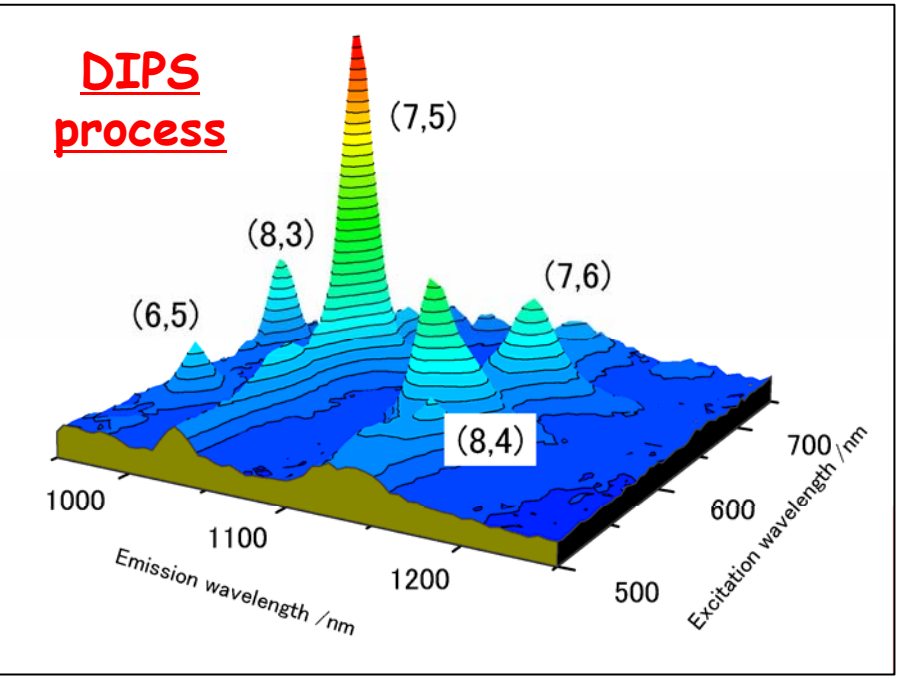
Resasco's CoMoCAT
S. M. Bachilo et al., JACS, 125 (2003) 11186.

750℃



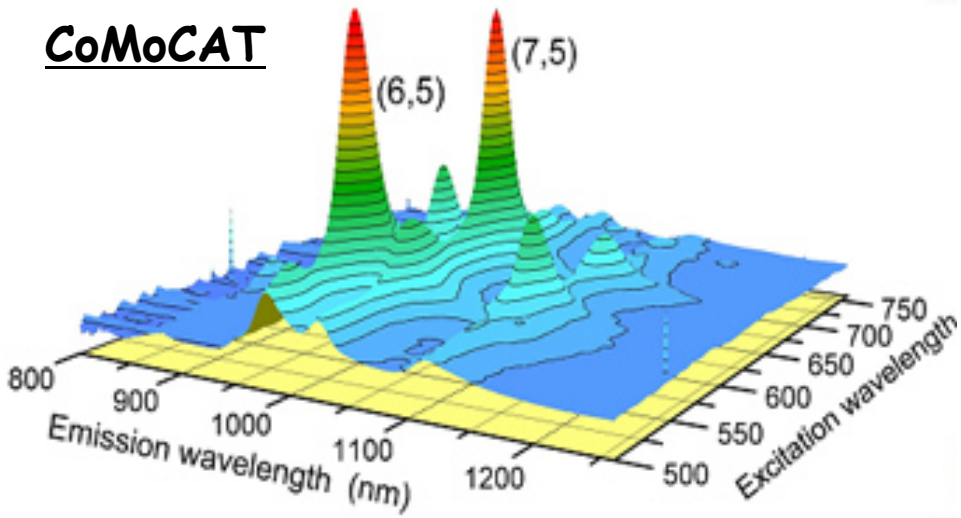
850℃

Comparison of DIPS and CoMoCat PL - Semiconducting fraction



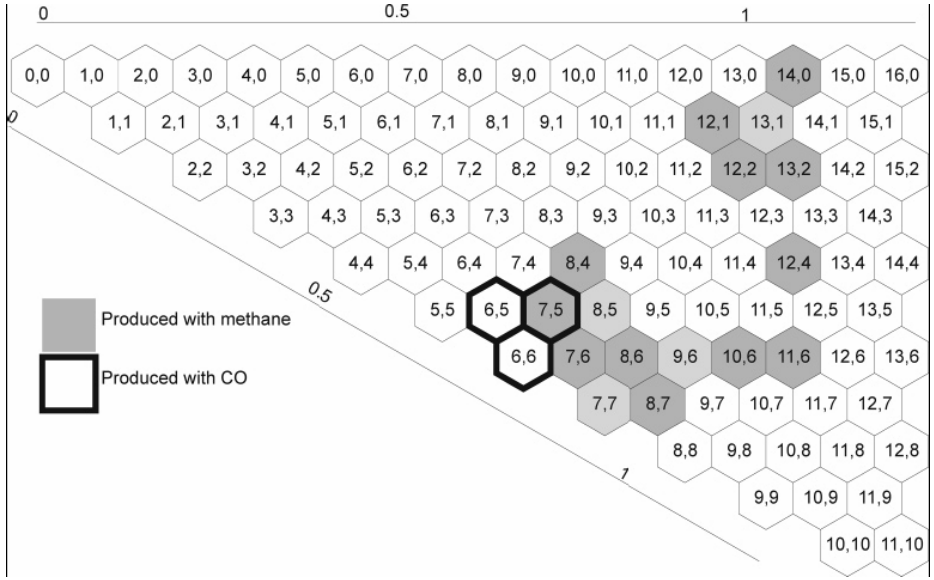
DIPS – bimetallic (Fe-Mo) catalyst

T. Saito, S. Iijima et al.

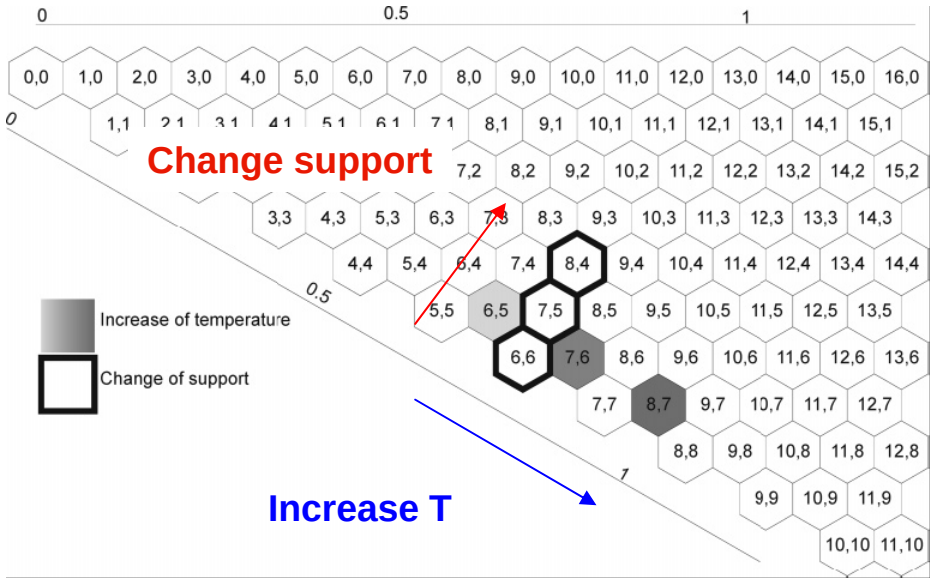


Spectrofluorimetric analysis (courtesy Prof. Weisman) of SWeNT™ (Left) and HiPCO™ (Right) samples. The comparison reflects the much narrower distribution of diameter and chirality

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

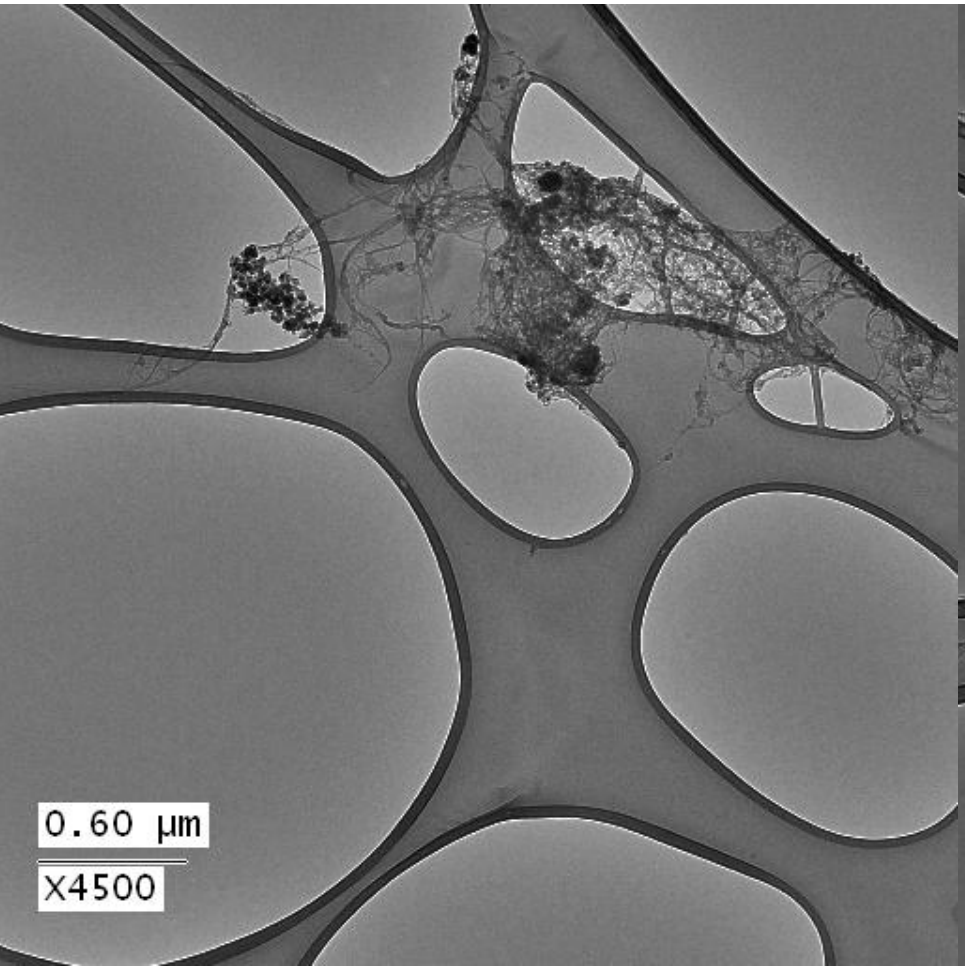


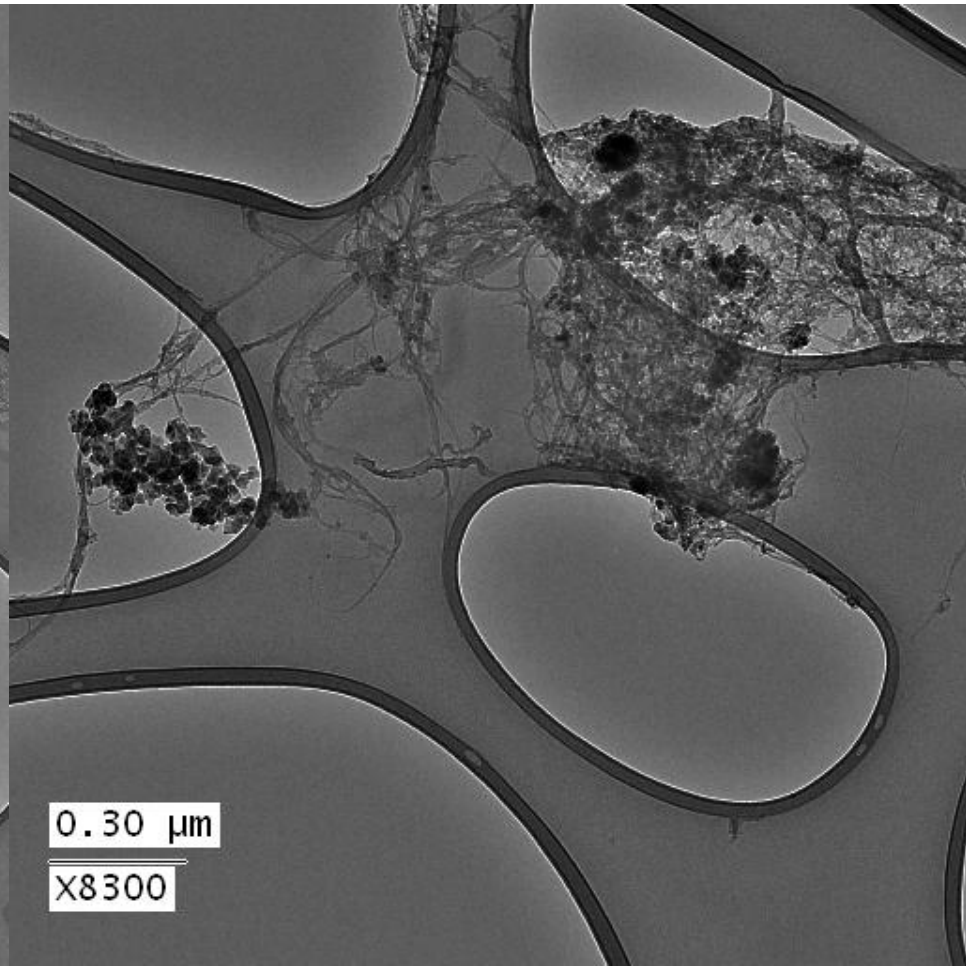
(*n*,*m*) map, effect of temperature and support morphology on the produced SWN



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

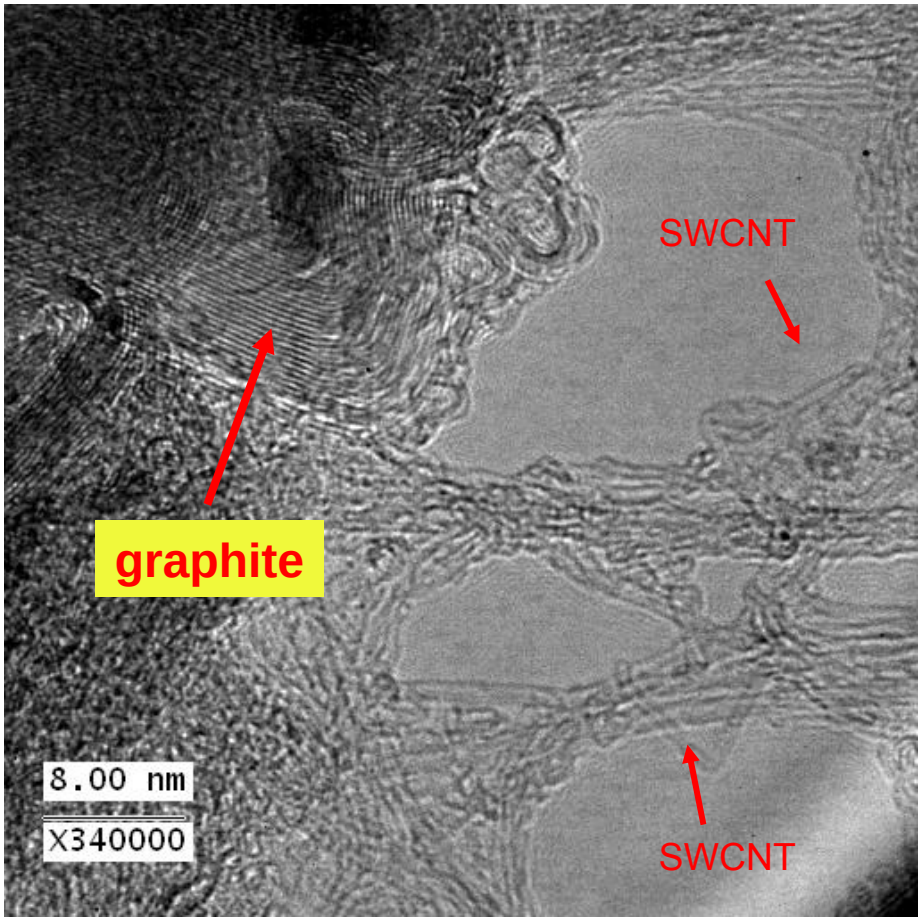
Purified CoMoCat SWCNTs (from CO) as dispersed in ethanol & drop to TEM grid

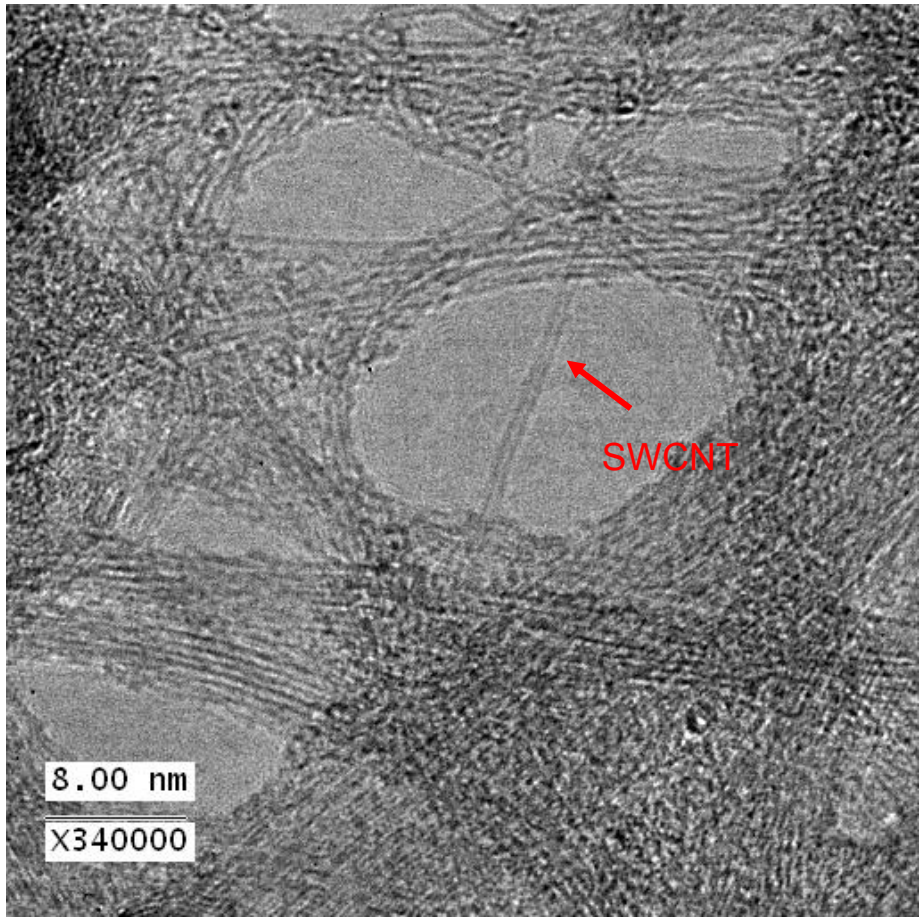




Overview images

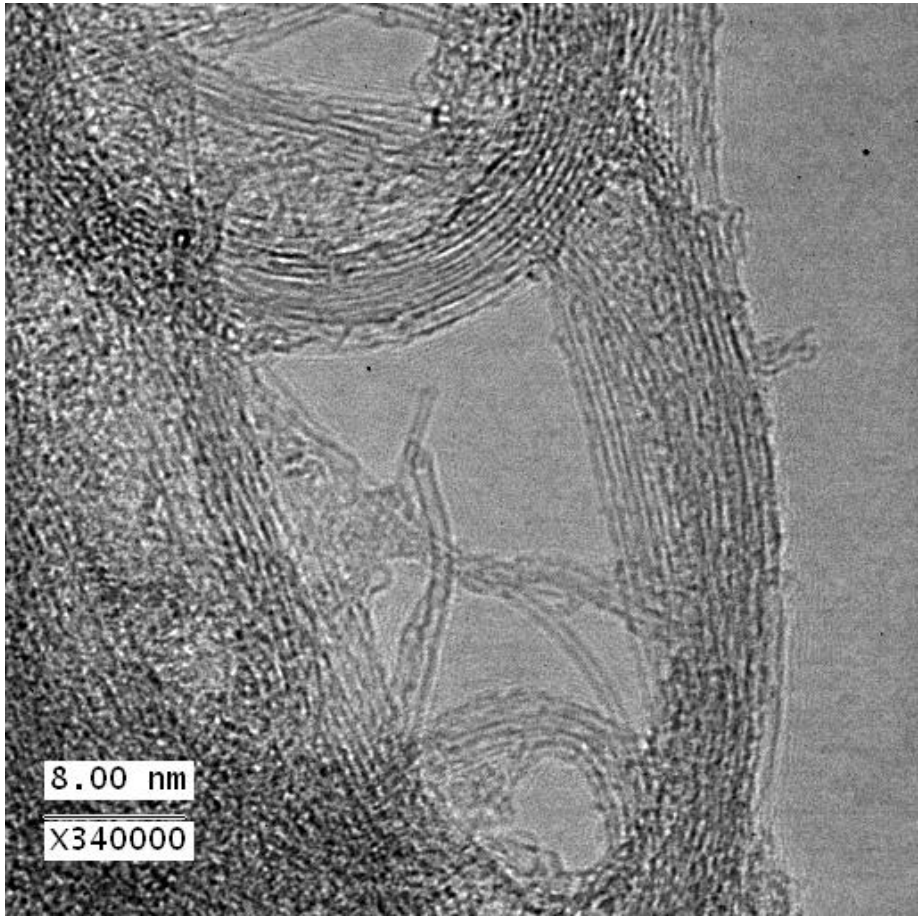
Purified CoMoCat as dispersed in ethanol & drop to TEM grid

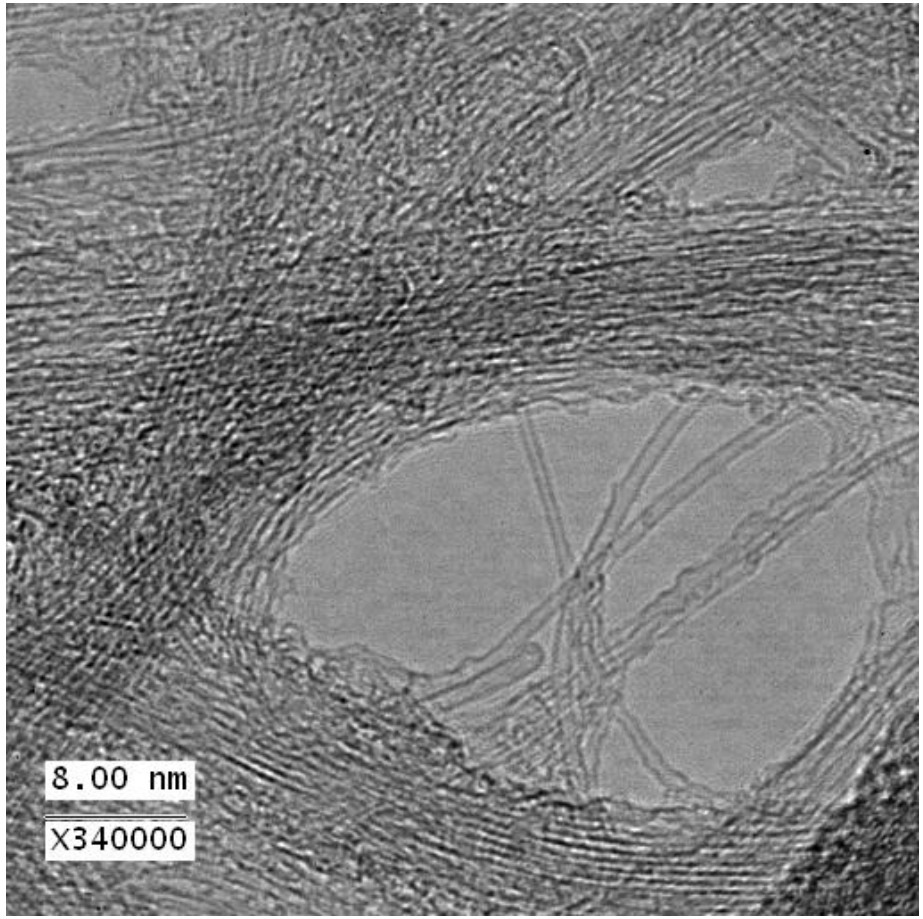




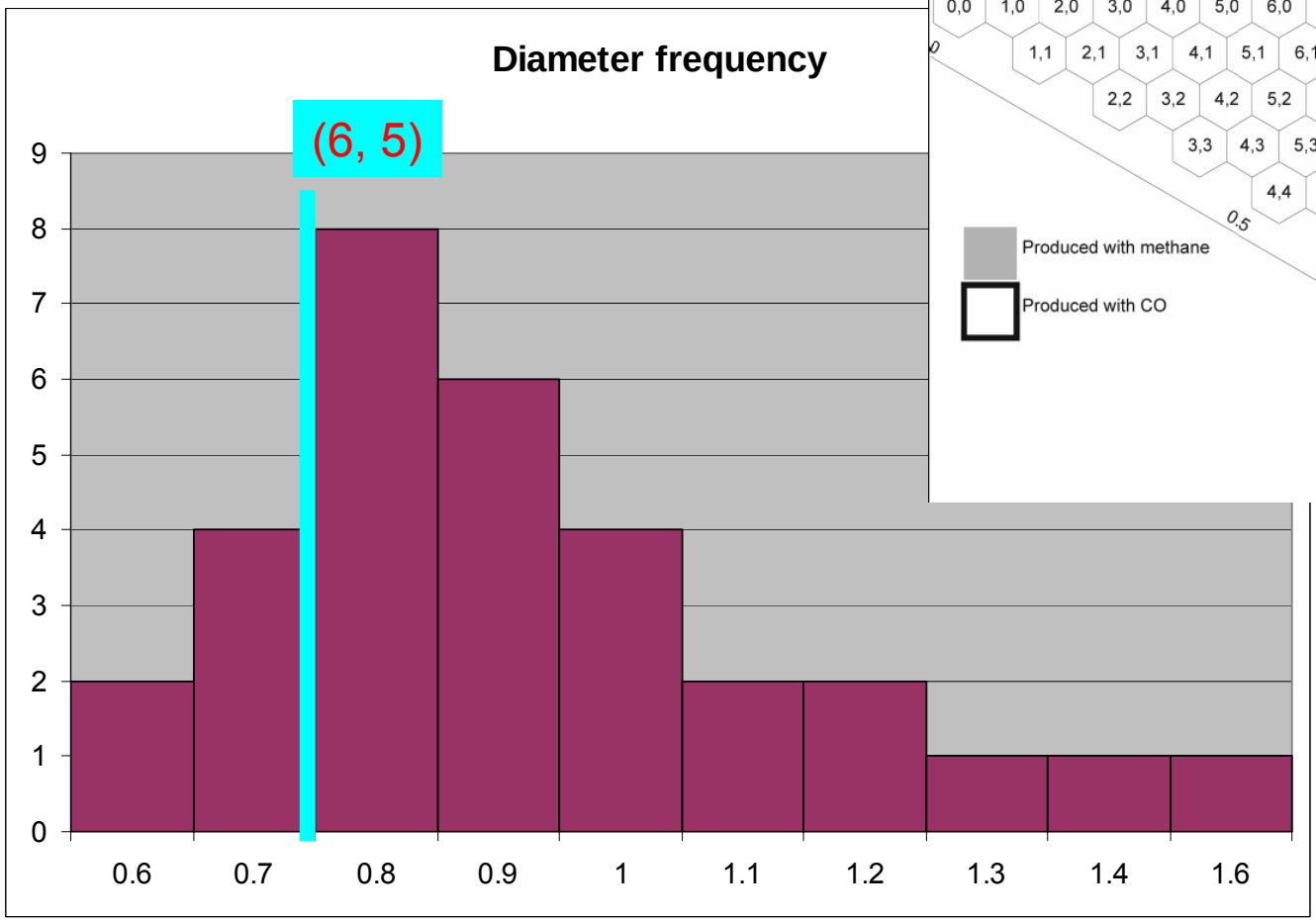
The magnification of the images are calibrated by using the graphite layer spacing of 0.345nm, as indicated in the image on the left.

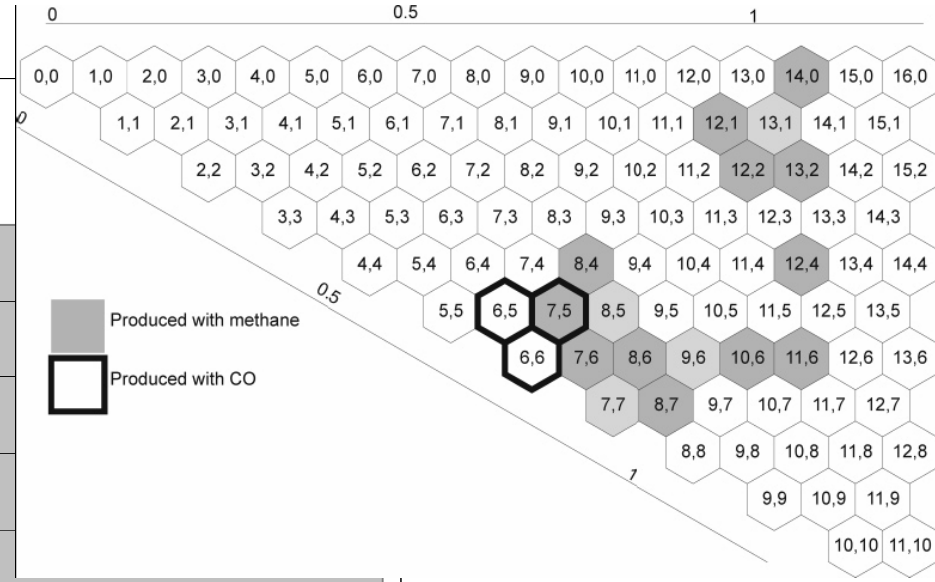
From the images, one can see SWCNTs with different diameters.





COMoCat - Distribution of tube diameters





In summary

- A *Simple idea* *of "intrinsic" layer-line distance"* brings us an *Easy solution* to *chirality (n, m) of carbon nanotubes*.
- A computer-aid EDP analyzer of SWCNTs being developed for the routine chirality analysis from EDPs.
- This new method makes it possible for fast and reliable mapping of chirality distribution in CNT sample by electron diffraction.
- The method can be extended to structural analysis of other nanotubes having structures similar to carbon nanotubes, such as boron nitride nanotubes
- *Sample preparation to deposit individual tubes very important*
- *Detailed comparison of optical, TEM/ED and STS needed*

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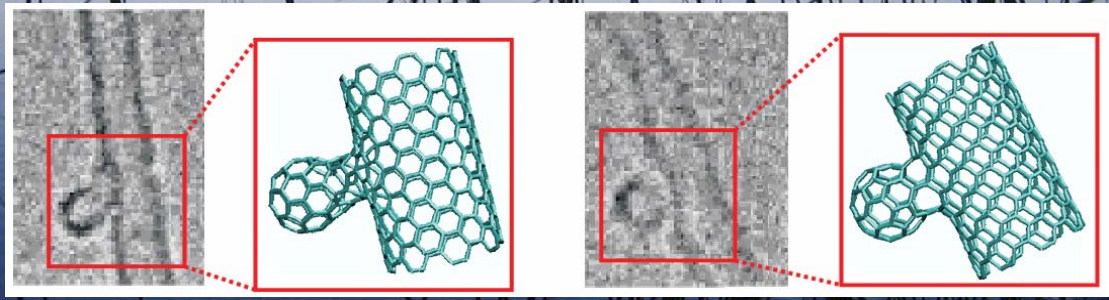
THANKS TO YOU FOR YOUR ATTENTION !