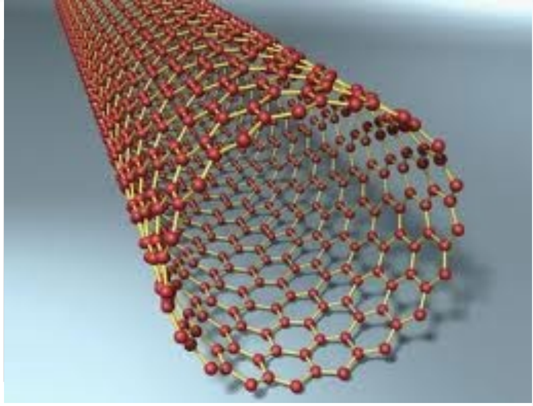
Aalto University

IRENA
Indium Replacement by Single-Walled Carbon Nanotube Thin Films



FLOATING CATALYST CVD SYNTHESIS OF SWNTs – LENSSONS EARNED AND FUTURE DIRECTIONS

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Content

- Status SWNT thin film transparent conductors (TCFs) and Thin Film Field Effect Transistors (TFT-FETs) via Direct Dry Deposition from FC-CVD reactor
- TEM of active catalyst particles – correlation of particle and tube diameters ?
- Comparison of (n,m) Distributions of SWNTs from Arc Discharge, Laser Vaporization and both Supported and Floating catalyst CVD & steps forward

Aalto University Novel dry, direct CNT film deposition method: *DPP – Direct Dry Printing*

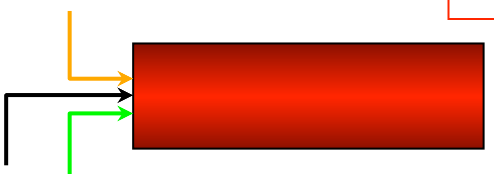
Industrial manufacturing – Canatu Oy

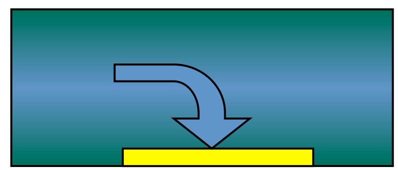
Synthesis

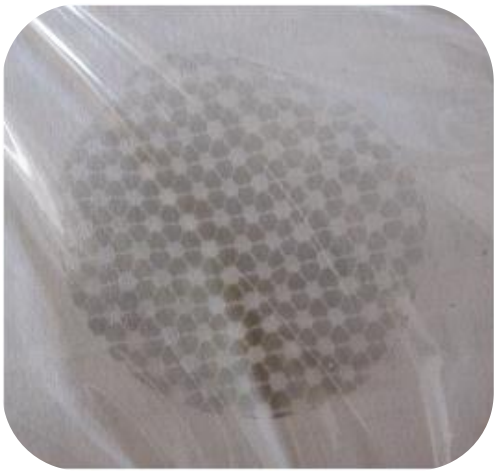
Deposition

Thin Films

SWCNTs in the reactor gas

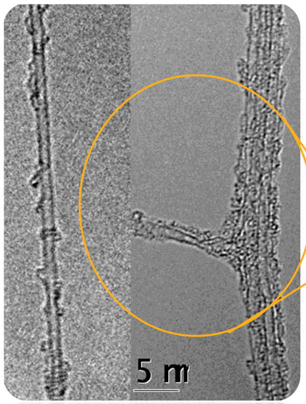


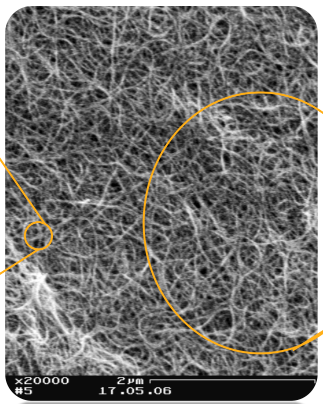


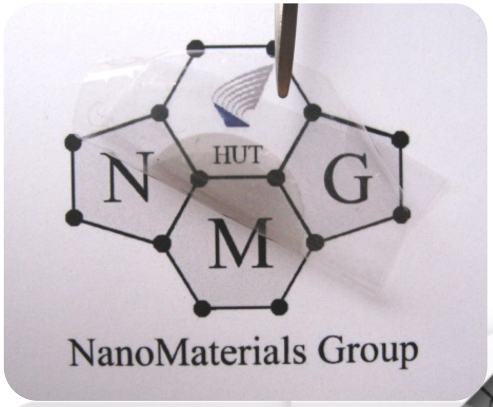


Control of SWCNT properties

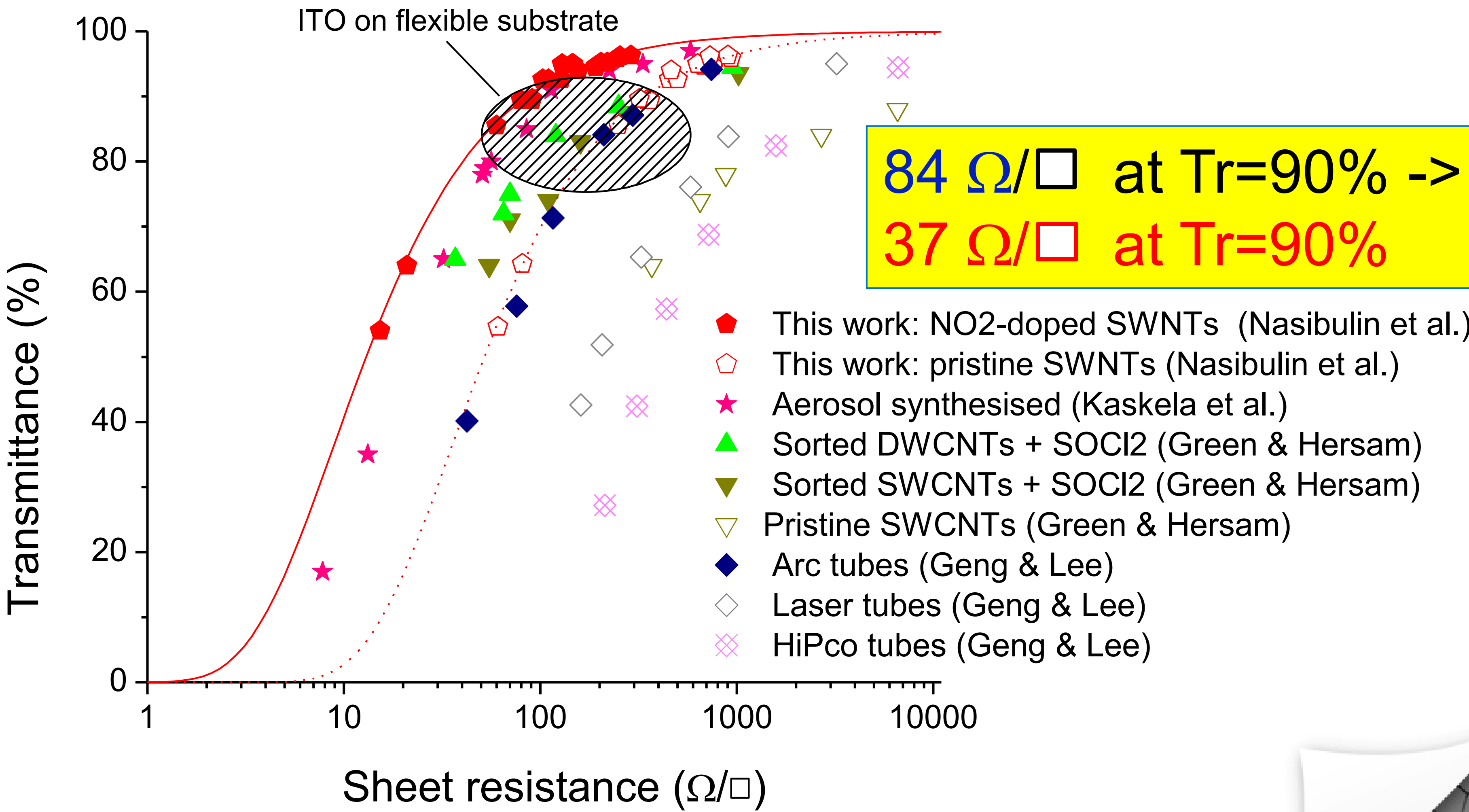
Patterned/non-patterned







Record performance level of SWCNT-based transparent electrodes (1.7 nm tubes)

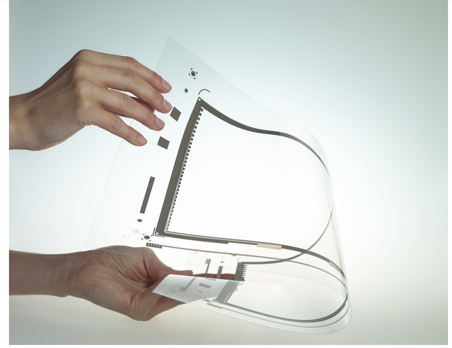


84 Ω/□ at Tr=90% ->
37 Ω/□ at Tr=90%

Nasibulin, Kaskela, Mustonen, Anisimov, Kauppinen, *et al.* (2011)
ACS Nano, 5(4), p.3214

CANATU

Touch the Future



Transparent conductive films for flat, flexible or formable touch devices

CNB™ sheet resistivity	CNB™ transmission	CNB™ reflectivity	CNB™ haze
100 Ω/□	94%	0,20%	0,15%
150 Ω/□	96%	0,20%	0,15%
300 Ω/□	98%	0,20%	0,15%

Carbon Nanobuds® increase display contrast

Canatu is a leading manufacturer of transparent conductive films for an entirely new class of touch applications. Canatu's **CNB**™ films are based on a new type of carbon nanomaterial (**Carbon NanoBud®**), and a new Roll-to-Roll manufacturing process (**Direct Dry Printing®**), which combines the synthesis of the Carbon NanoBuds directly from carbon gases and direct deposition to the substrate in one single process. Canatu offers its customers in consumer electronics and automotive industry next level of design freedom with its innovative technologies.

Canatu to talk at High Value Manufacturing Graphene Conference 2013

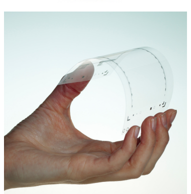
Canatu releases new transparent conductive films with ultra-low reflections and record flexibility

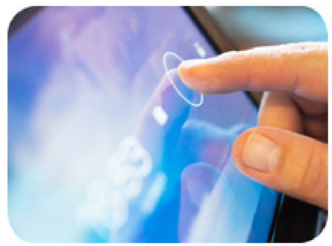
Canatu has been invited to talk about flexible touch sensors in the upcoming global trade events

Canatu to showcase and launch Generation 5 Carbon NanoBud® films in FPD International 2013

Canatu will give a talk on advanced printed touch sensors at the ICFPE conference in Korea

Meet Canatu at FPD International 2013





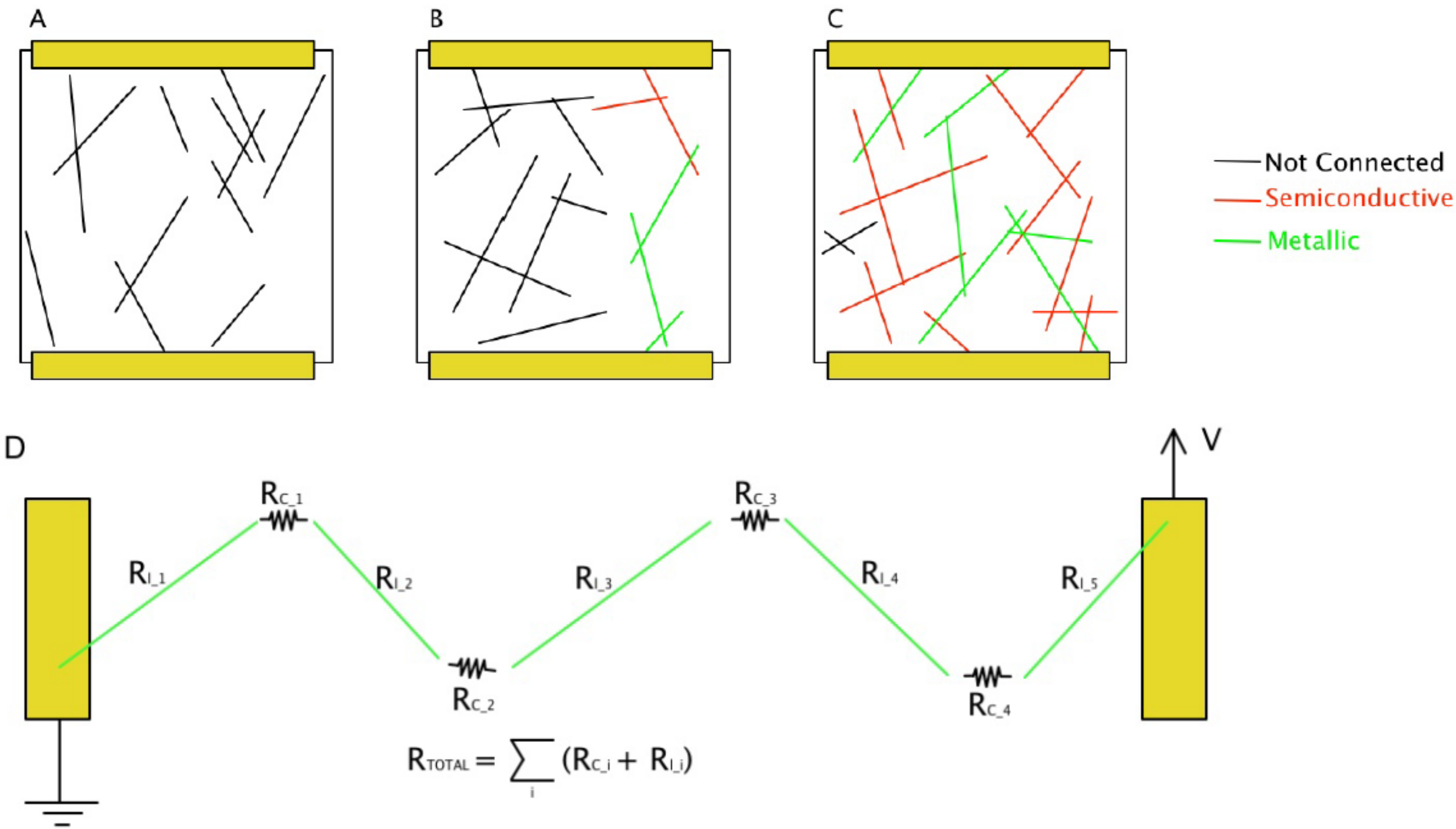
Canatu's CNB™ transparent conductive films are designed for demanding touch sensors, paving the way for high-contrast touch displays also in flexible, foldable and 3D format.

Canatu's high-quality CNB™ films serve touch module and display companies in the rapidly-expanding markets of mobile phones, tablets, cameras, wearable consumer devices, white goods, home appliances and automotive. Canatu also supplies CNB™ touch sensors for touch module prototyping and small to medium volume production.

Canatu can help electronics hardware companies and brand names who are seeking ways to differentiate products, reduce production costs and increase product performance. Existing materials such as silicon, metals and metal oxides are expensive, not flexible, stretchable or transparent, and require complex and bulky support structures. Moreover, these traditional technologies are reaching their performance limits. With Canatu's CNB™ films it is possible to replace Indium Tin Oxide (ITO) in capacitive touch sensors using existing driving electronics.

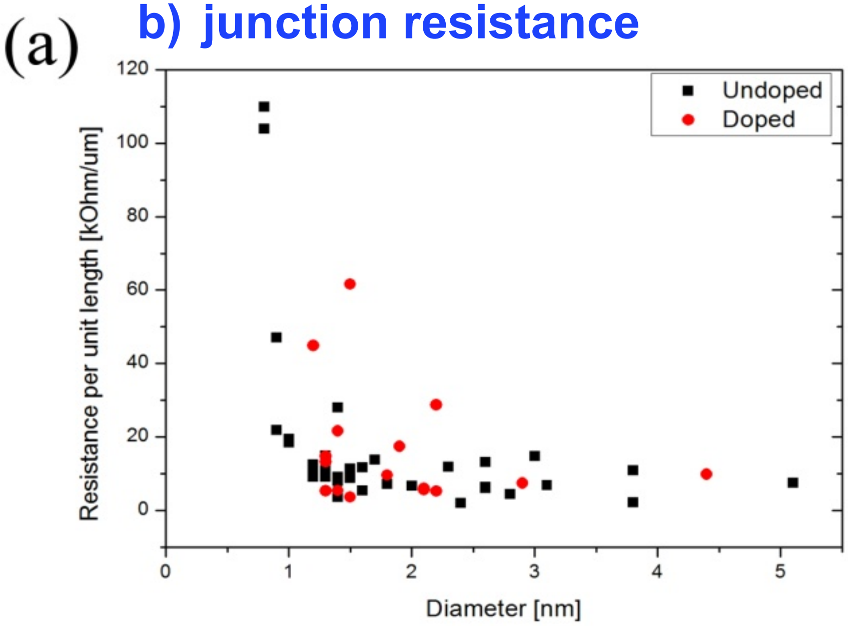
Canatu Ltd: 96% T @ 150 Ohm/□ for PET+CNT film => 97% T @ 150 Ohm/□ for SWNT film only. Stability: T240 h @ 60˚C/ 90%RH with < 20% variation of sheet resistance

Simplified resistance model for SWNT network

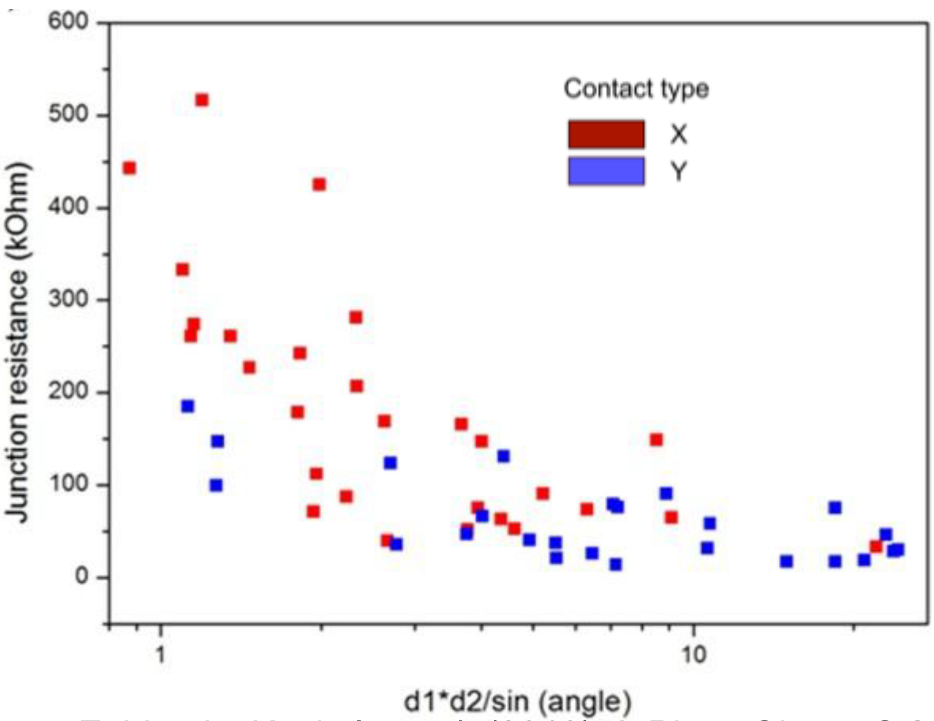


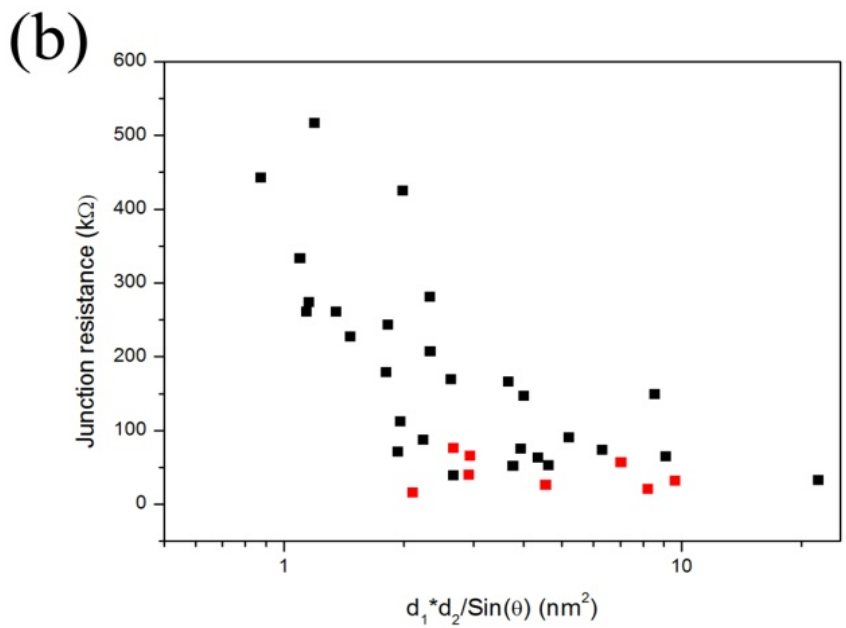
Tube-to-tube contact resistance as well along tube resistance measurement of pristine SWNTs with conductive atomic force microscope (C-AFM)

The effect of acid doping on
a) resistance per unit lenght and
b) junction resistance



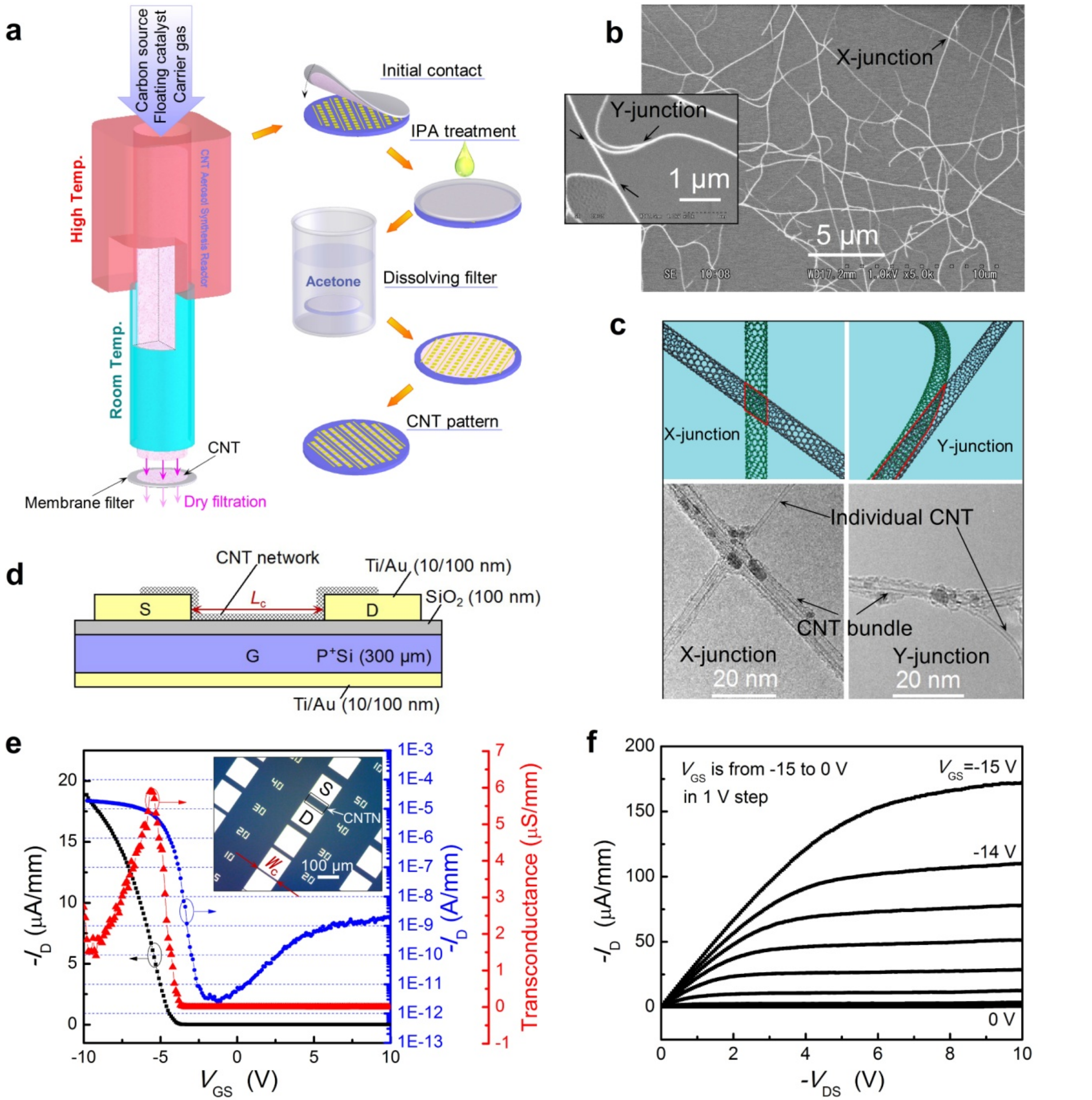
The junction resistance versus interfacial area. d1 = tube 1 diameter D2= tube 2 diameter.





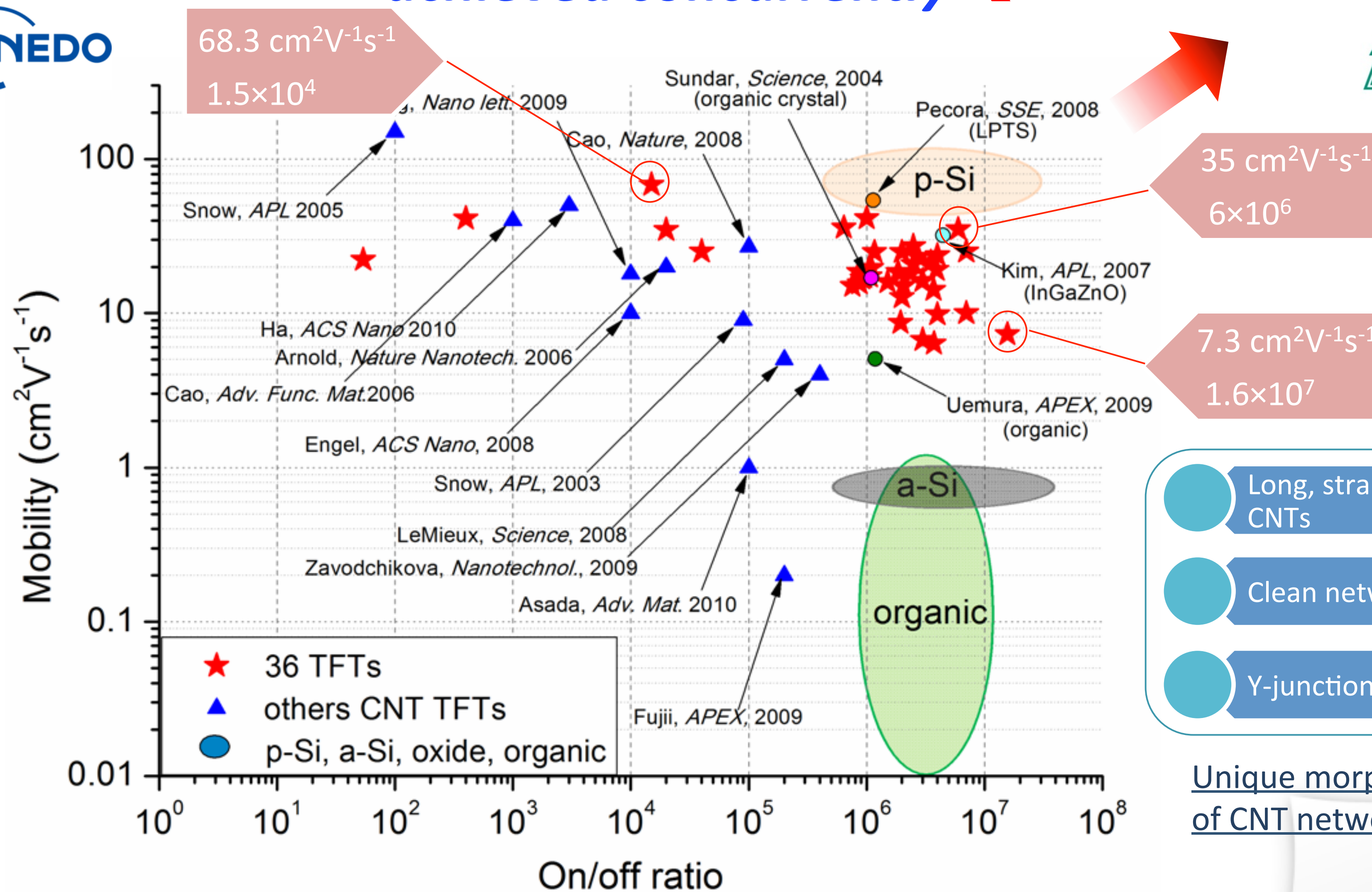
Znidarsic, Kaskela et al. (2013) *J. Phys. Chem. C* **117**, 13324-13330.

Dissolve Filter (DF): High mobility & large on/off ratio CNTN-FETs by better controlling SWCNT bundle length, orientation and SWCNT chiral distribution (Sun, Zavodchikova, Tian, Nasibulin, Kauppinen, Kishimoto, Mitzutani & Ohno (2011), Nature Nanotechnology)



High performance carbon nanotube TFTs

- High mobility (thin film capacitance model) and high on/off achieved concurrently ←



- Long, straight CNTs
- Clean network
- Y-junction

Unique morphology of CNT network

Sun, Timmermans, Tian, Nasibulin, Kauppinen, Kishimoto, Mizutani and Ohno, *Nature Nanotechnology* (2011) **6**, 156–161.

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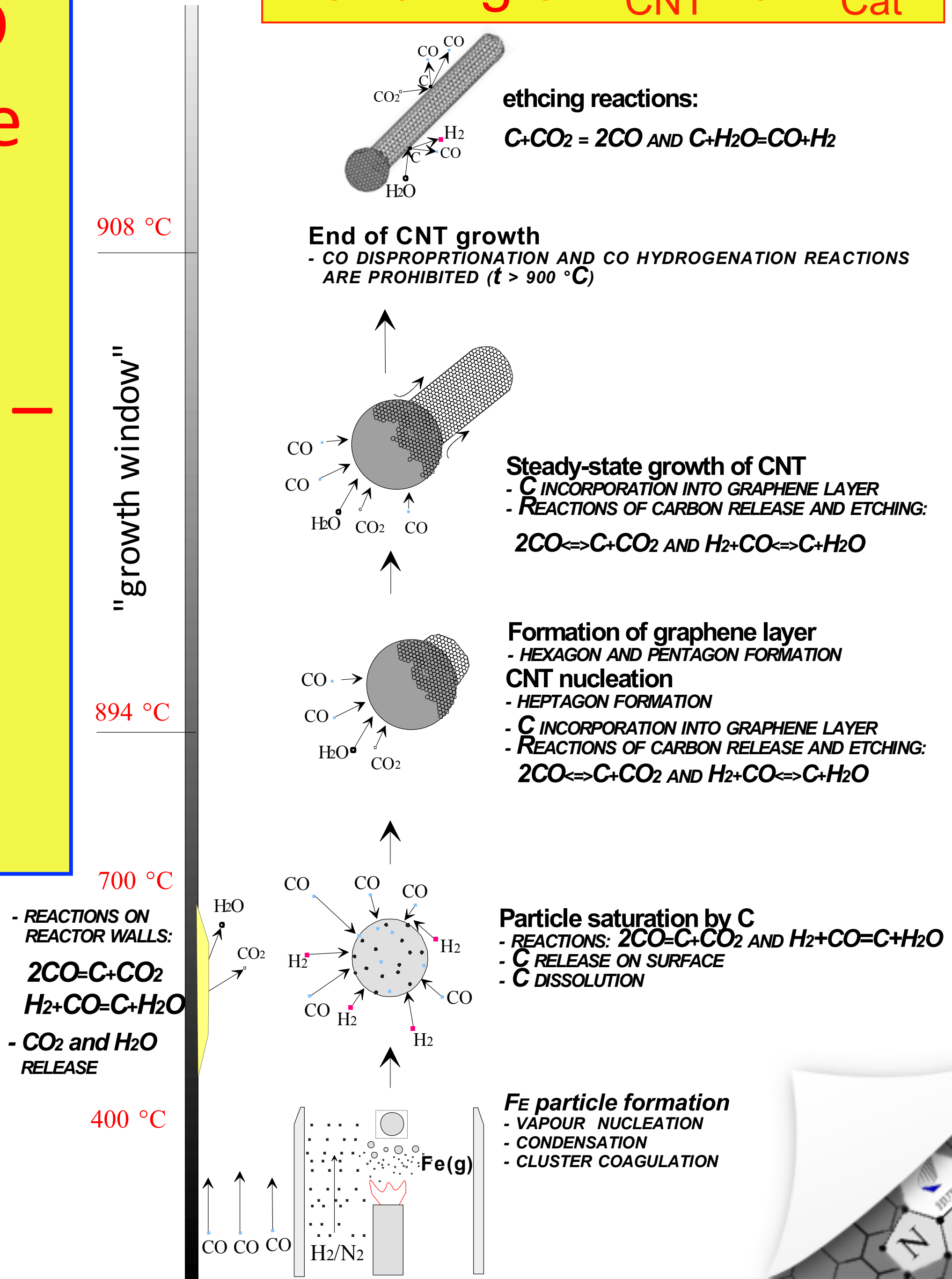
Schematics of FC-CVD reactor with pre-made Fe catalyst clusters formed inside the SWNT reactor via PVD – catalyst growth and SWNT nucleation coupled (Nasibulin et al., 2005)

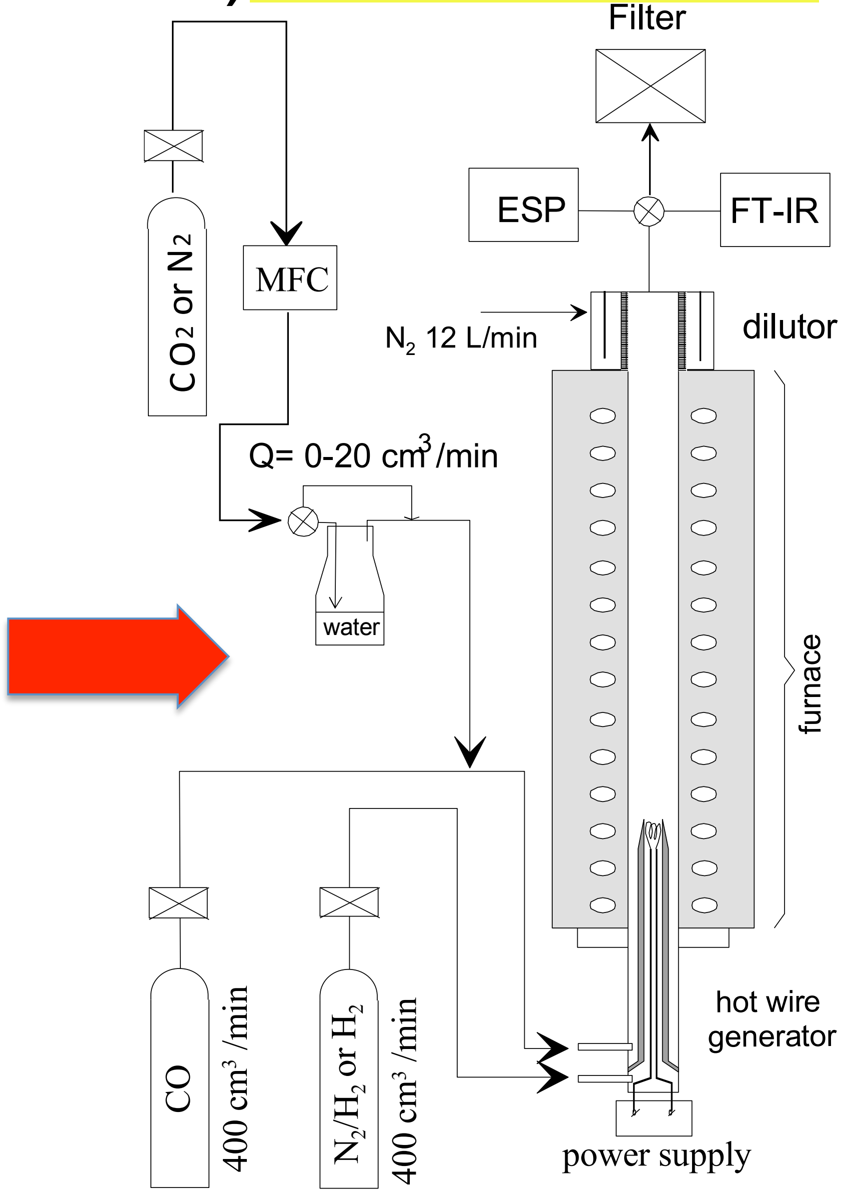
Bundling α N_{CNT}^2 α N_{Cat}^2



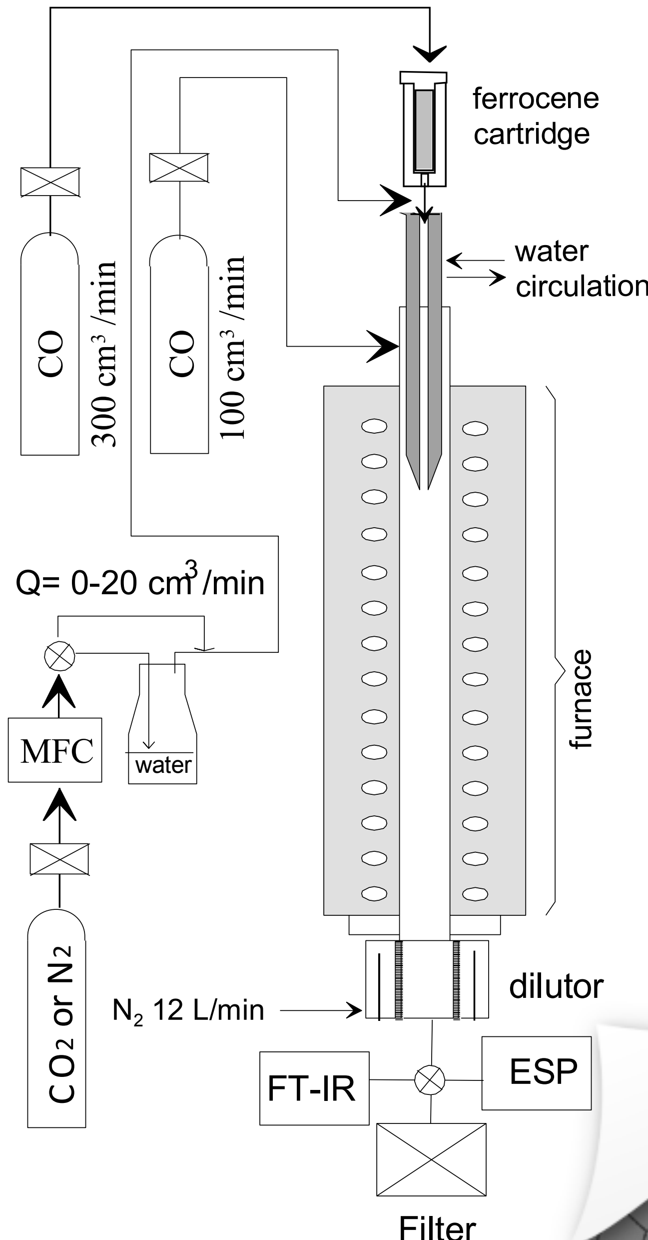
Controll :
- Diameter and length via temperature and oxidant (e.g. CO_2, NH_3, H_2O) concentration
- Bundling via catalyst concentration

Floating Catalyst Methods for CNT Synthesis

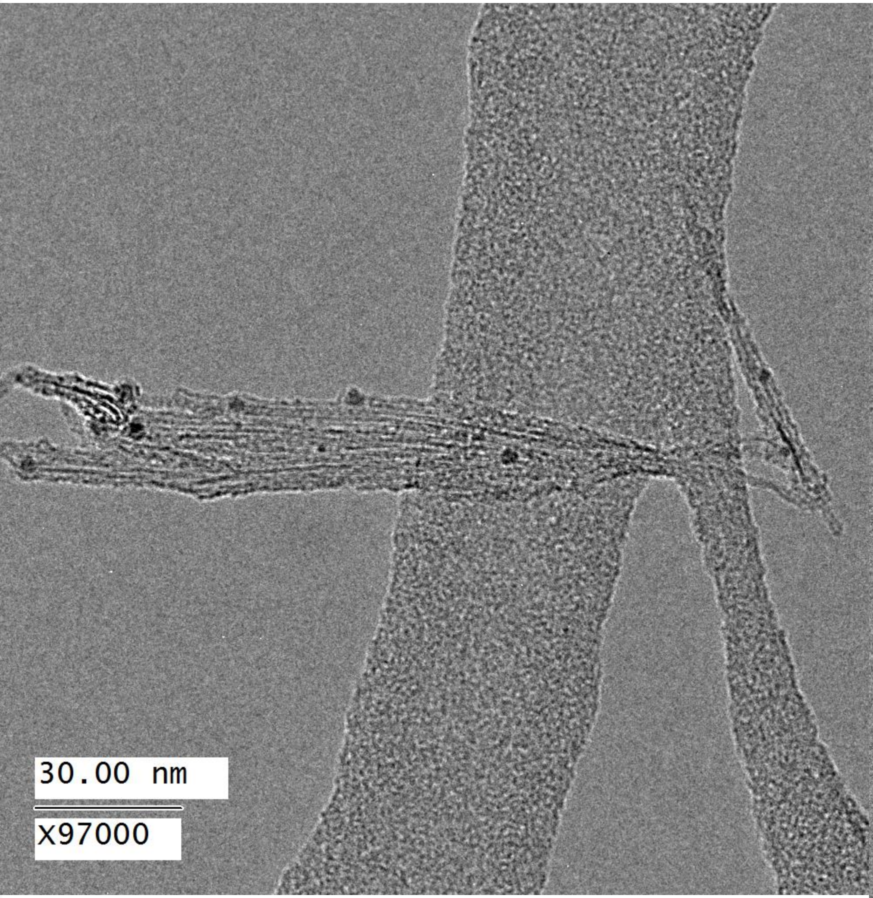
a) **HWG-based CVD of CO**

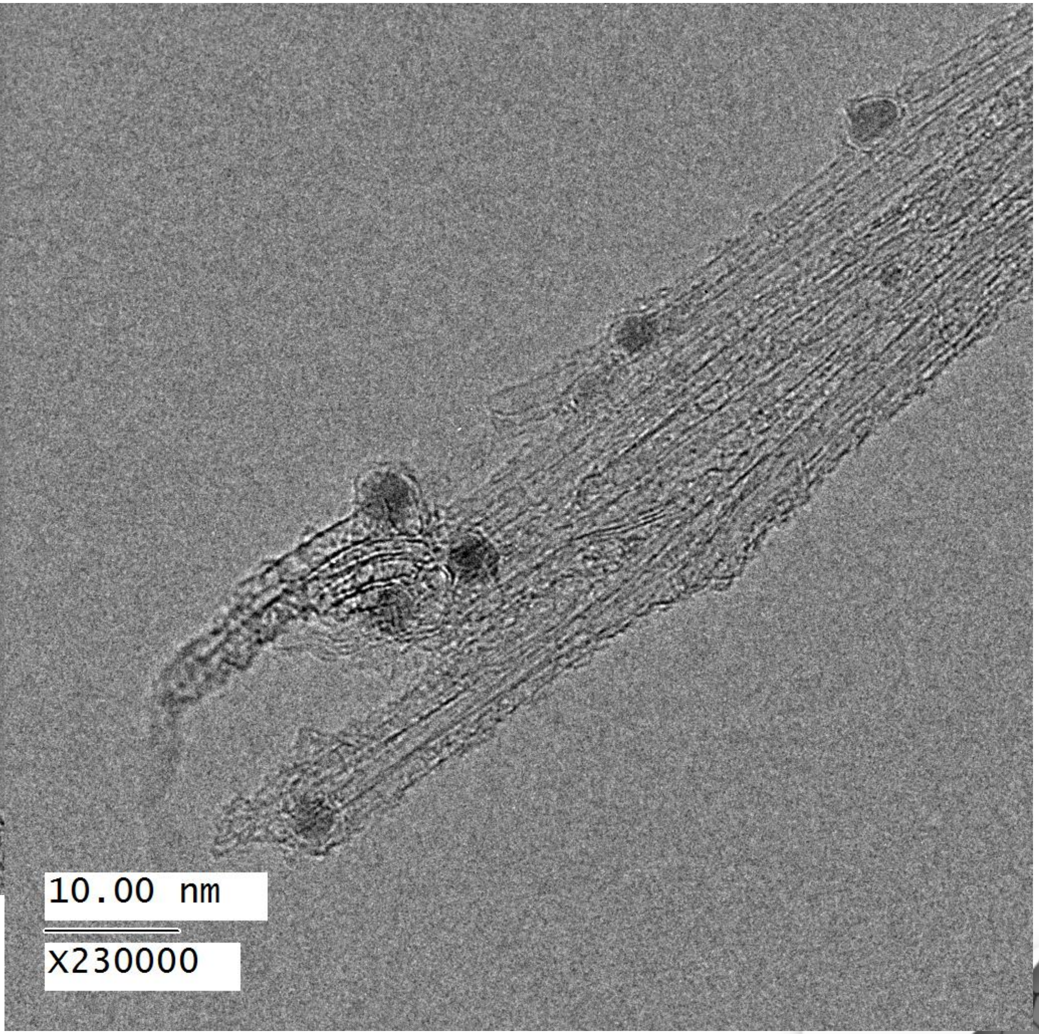


b) **Ferrozene-based CVD of CO**

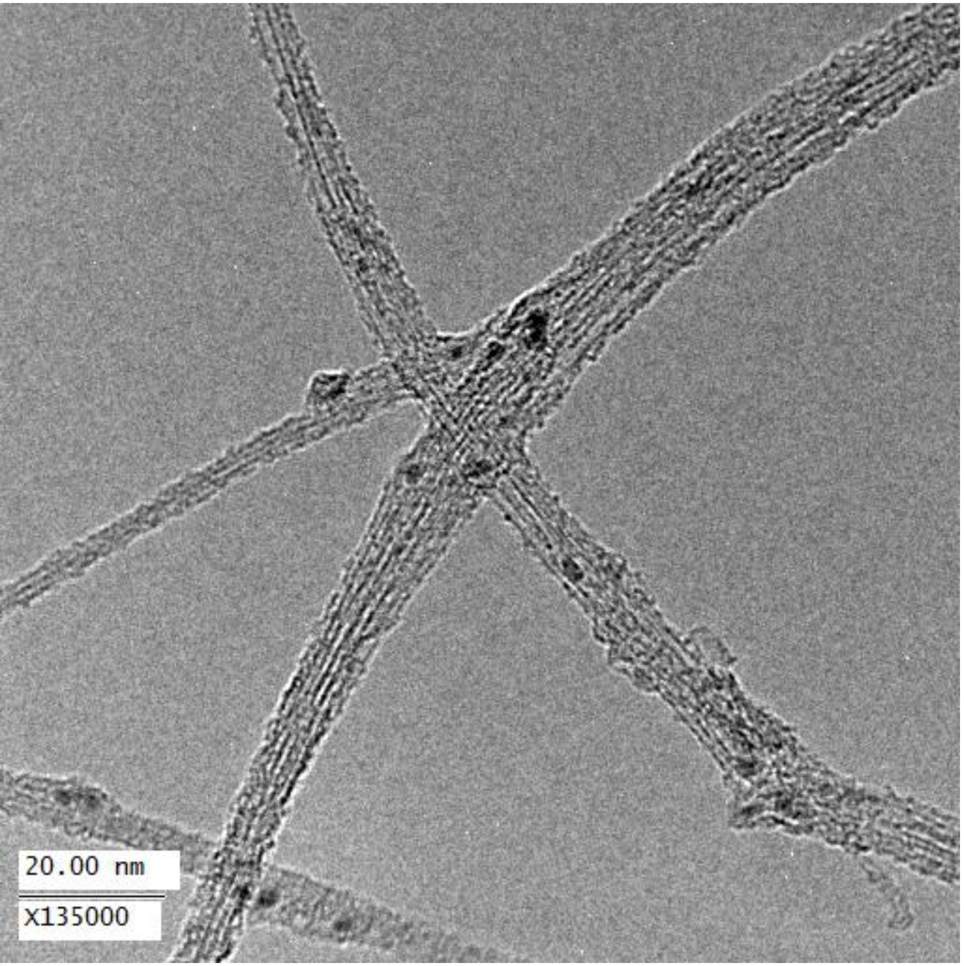


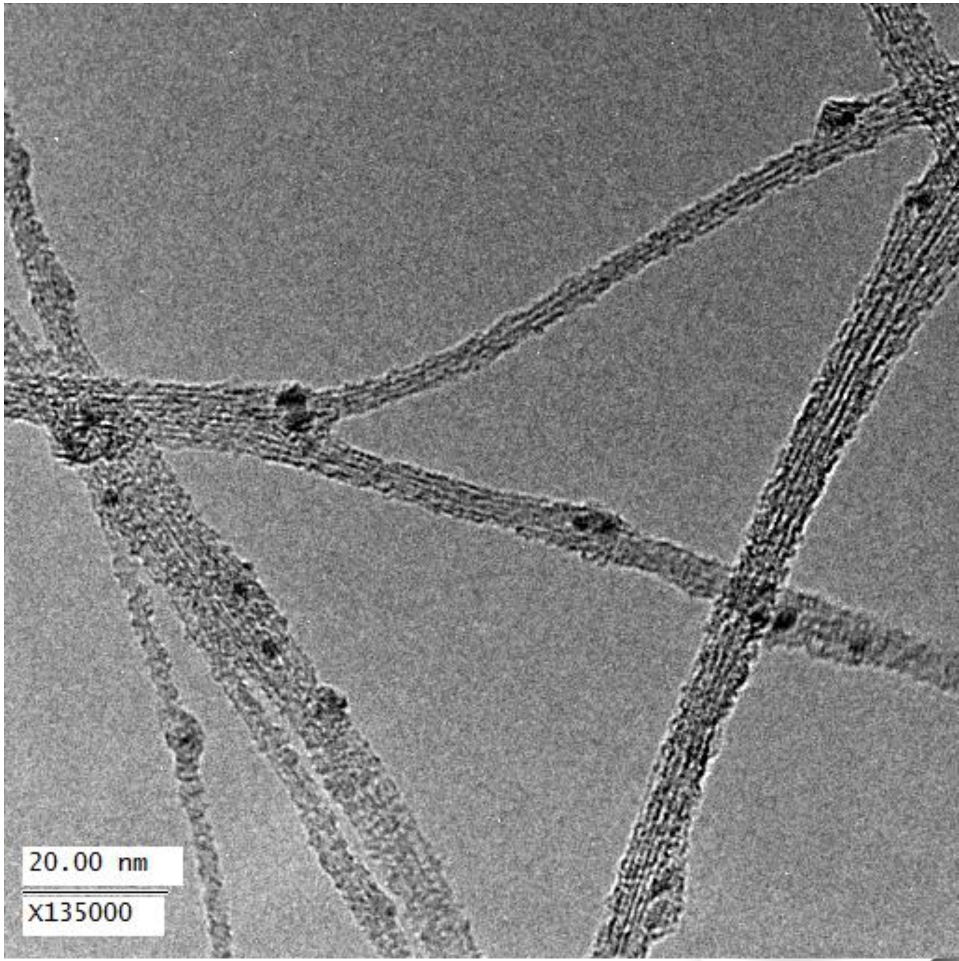
TEM of short SWNTs with Fe catalyst particles made from CO with HWG FC-CVD reactor 2002 200 kV, no heating prior imaging



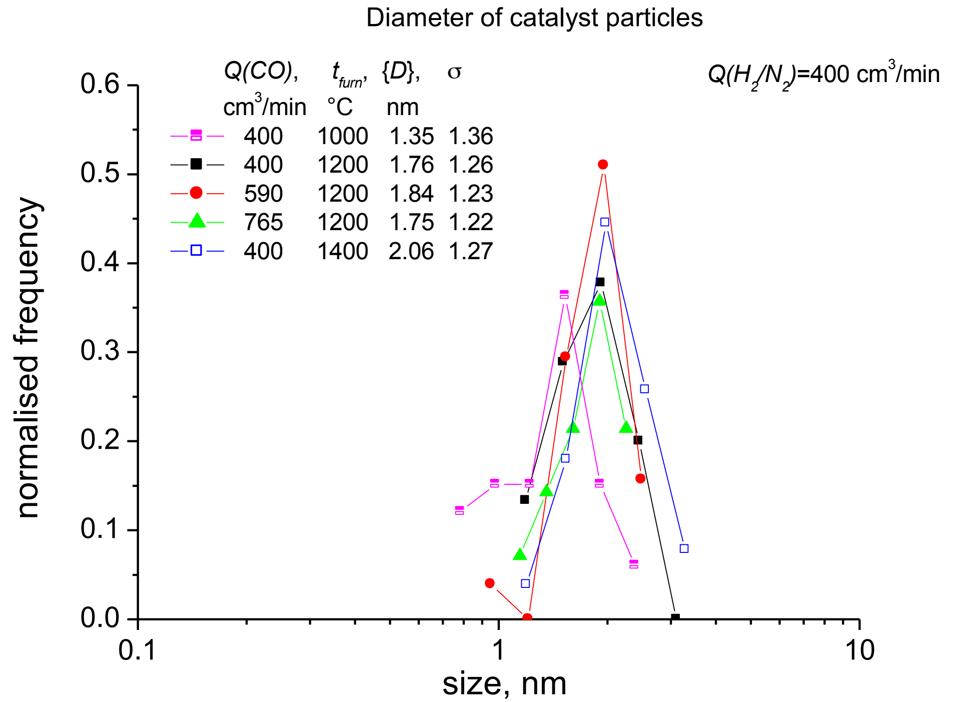


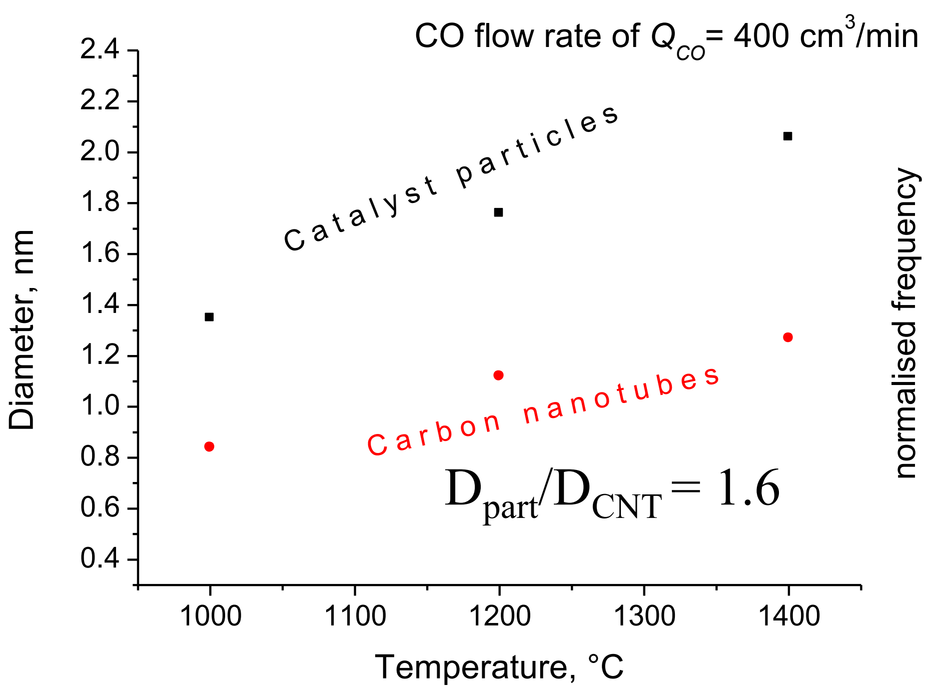
TEM of SWNTs with Fe catalyst particles made from CO with HWG FC-CVD reactor 2003 200 kV, no heating prior imaging

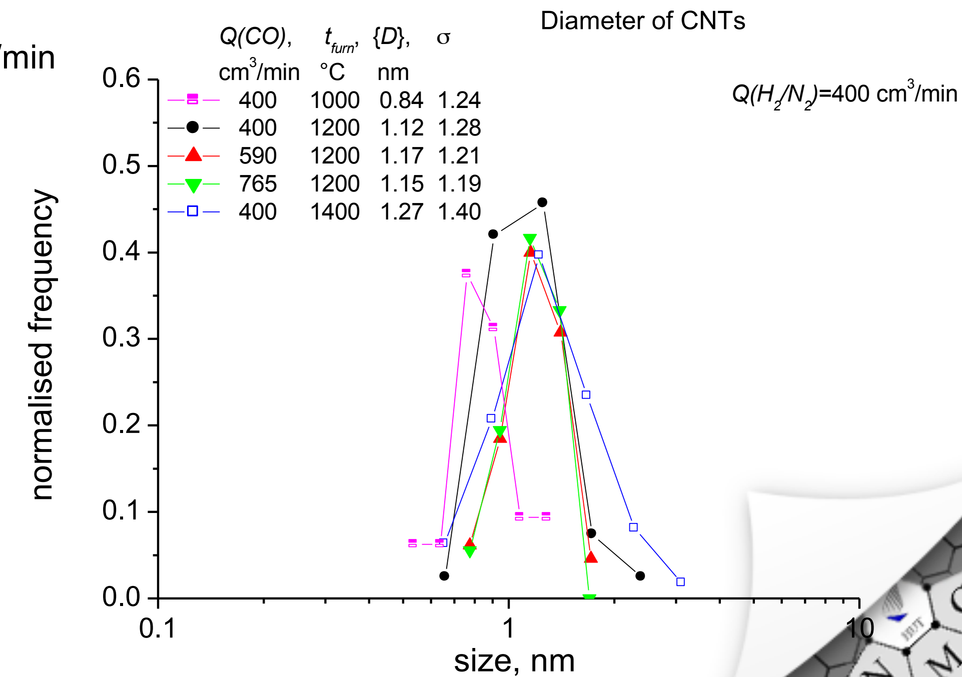




Correlation between diameter of Fe particles and SWCNTs – control of catalyst size







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}, cm^3/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 :

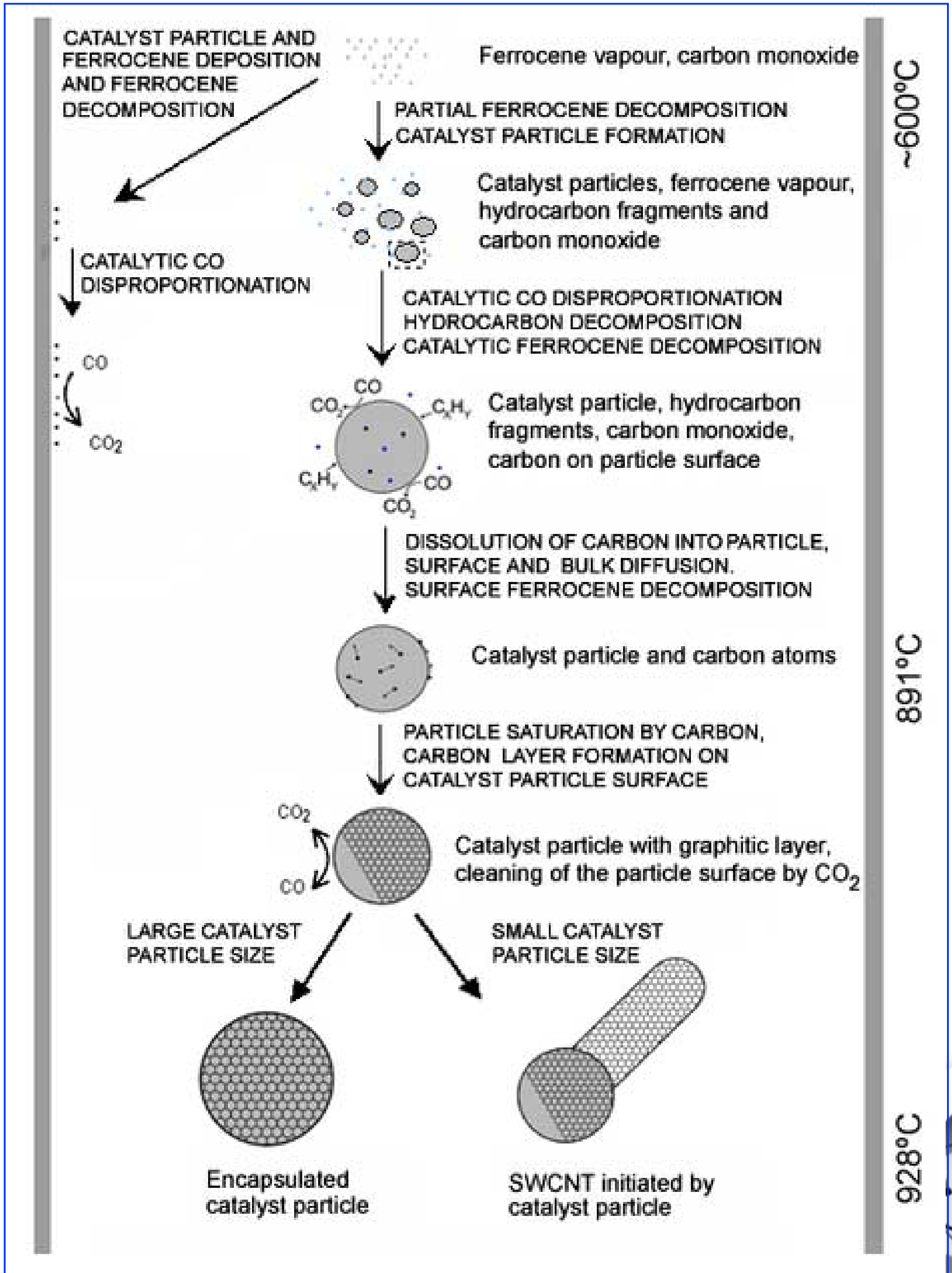
Ferrocene vapor decomposition in CO at 1150 °C
D_{CNT} = 1.3 nm, D_{part} = 3.1 nm
D_{part}/D_{CNT} = **2.4**
MORE DETAILS LATER

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

Catalyst formed in-situ during ***ferrocene*** decomposition in ***CO/CO₂*** – catalyst nucleation & growth and SWNT nucleation coupled.

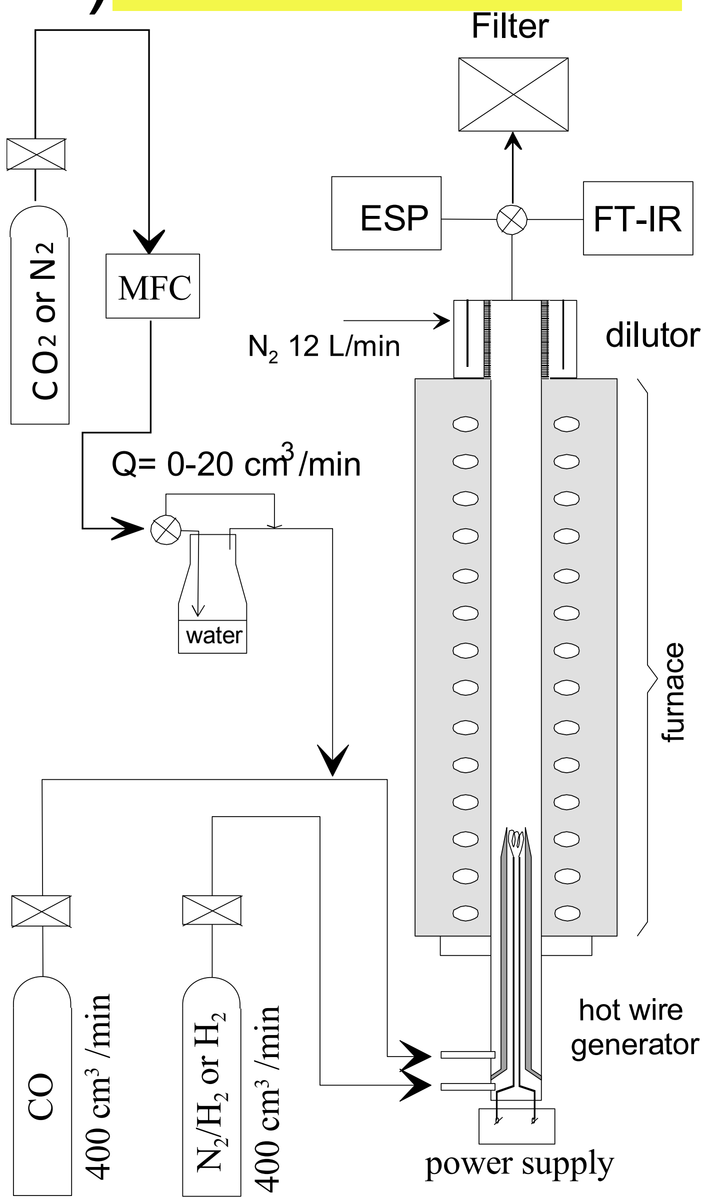
Moisala et al., CES 2006

Ferrocene decomposition slow – overlapp between CNT nucleation & growth and cerrocene decomposition – CVD growth of Fe clusters

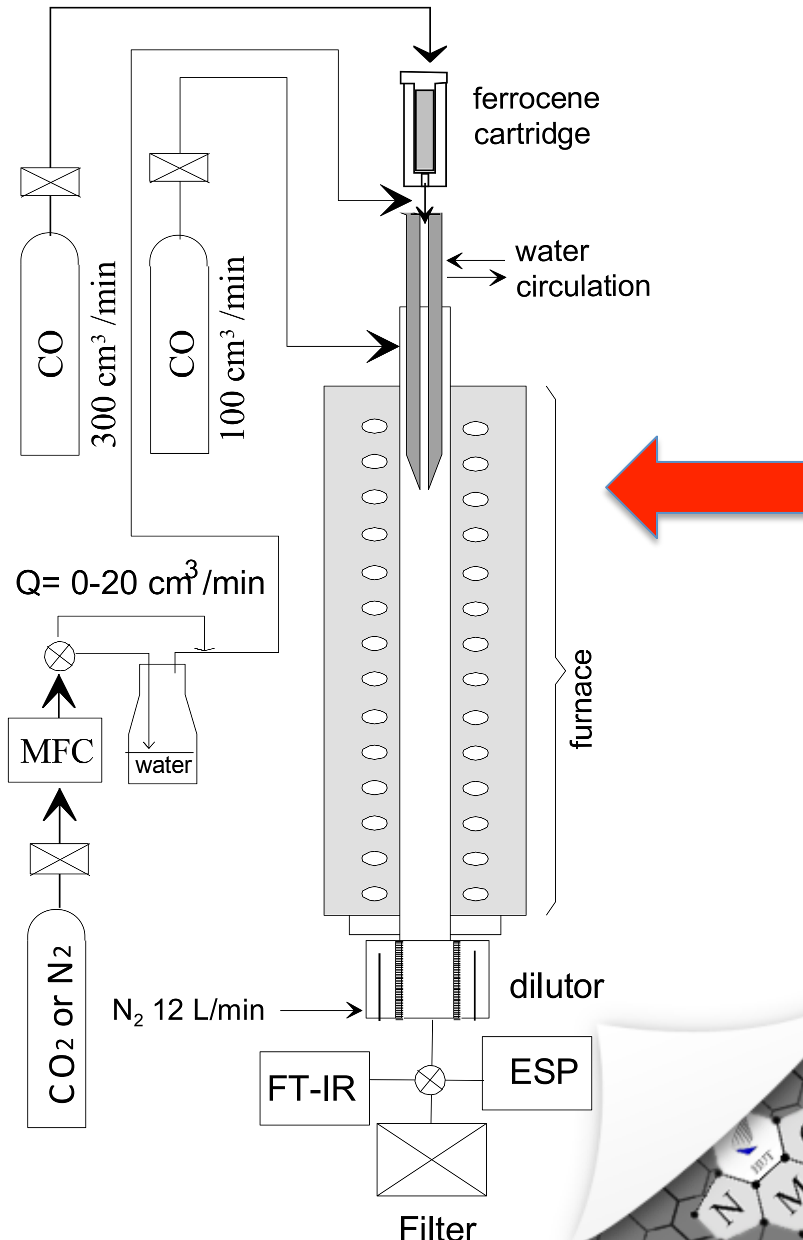


Floating Catalyst Methods for CNT Synthesis

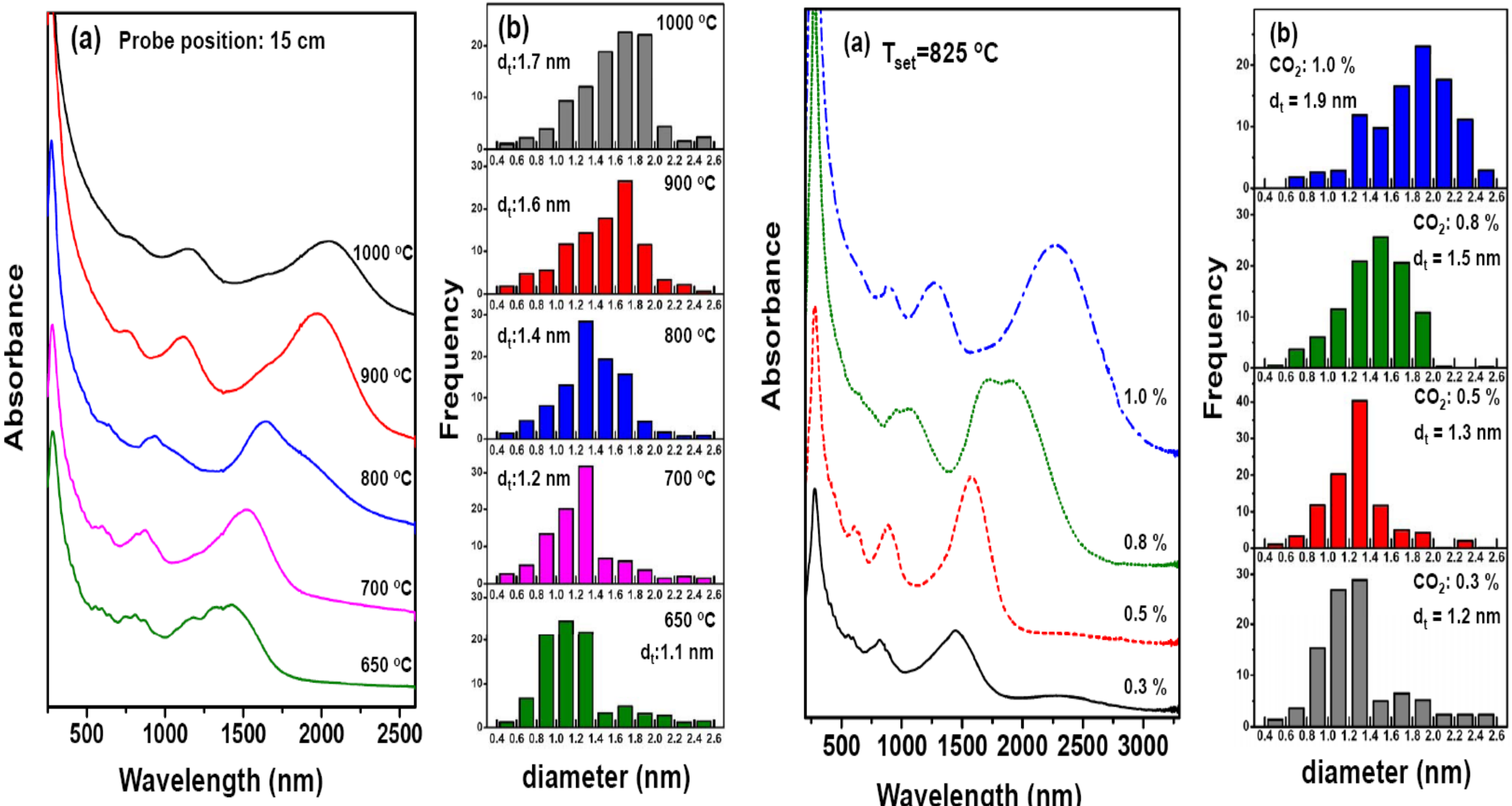
a) **HWG-based CVD of CO**



b) **Ferrozene-based CVD of CO**

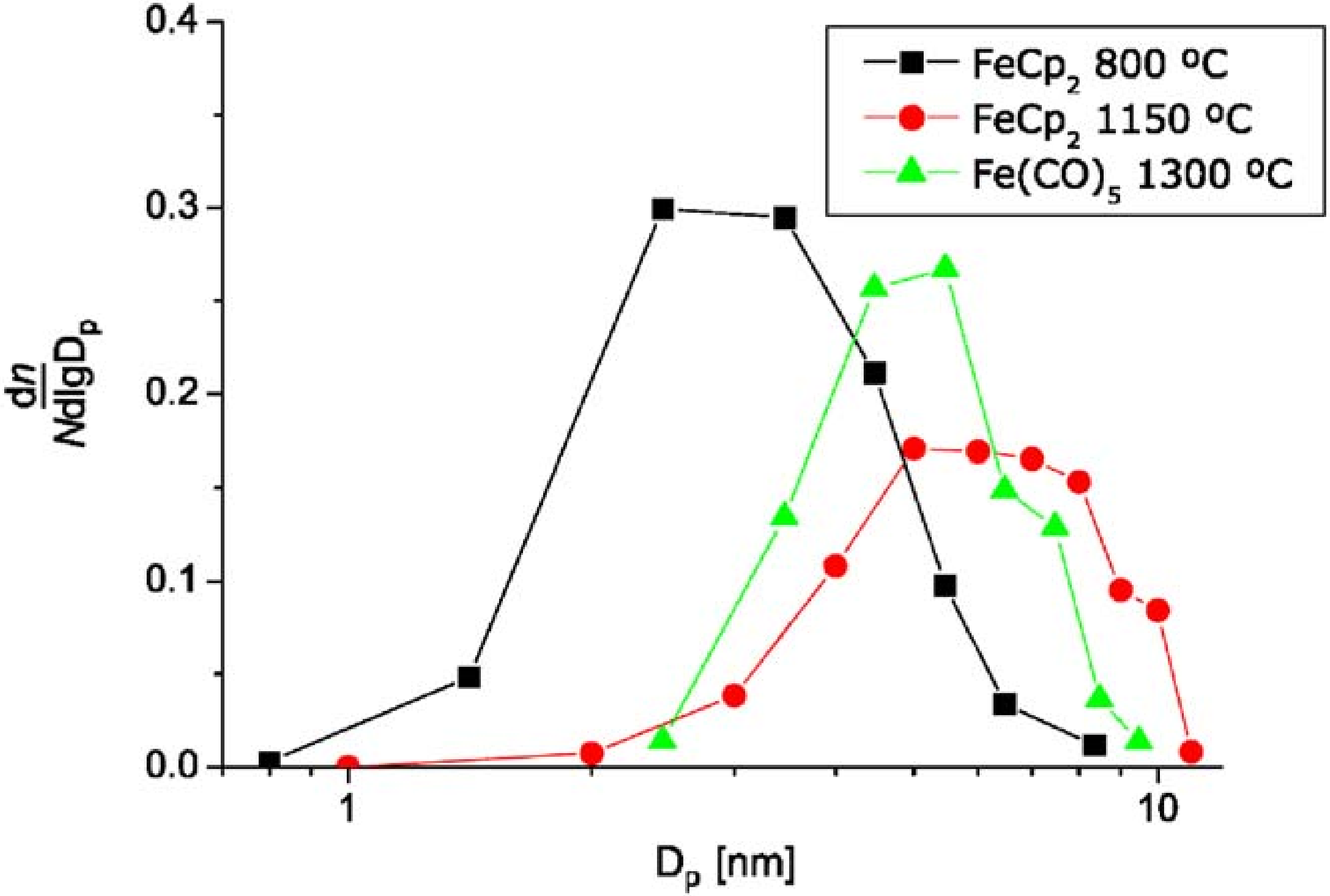


Optical absorption derived SWCNT diameter distributions vs. wall temperature and vs. CO_2 concentration



Ying et al. (2011) Carbon

Catalyst particle size distribution in SWNTs produced with ferrocene reactor. SWNT mean diameter about 1.3 nm.

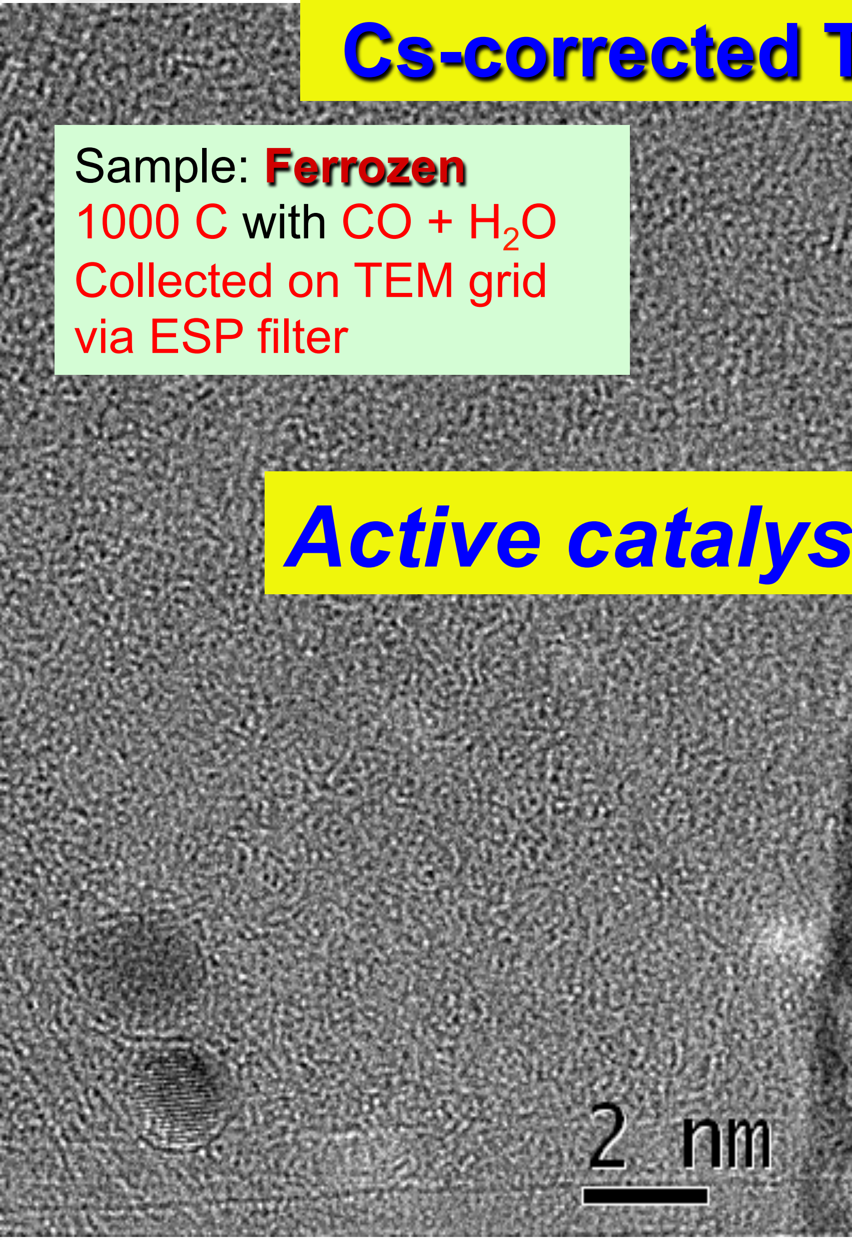


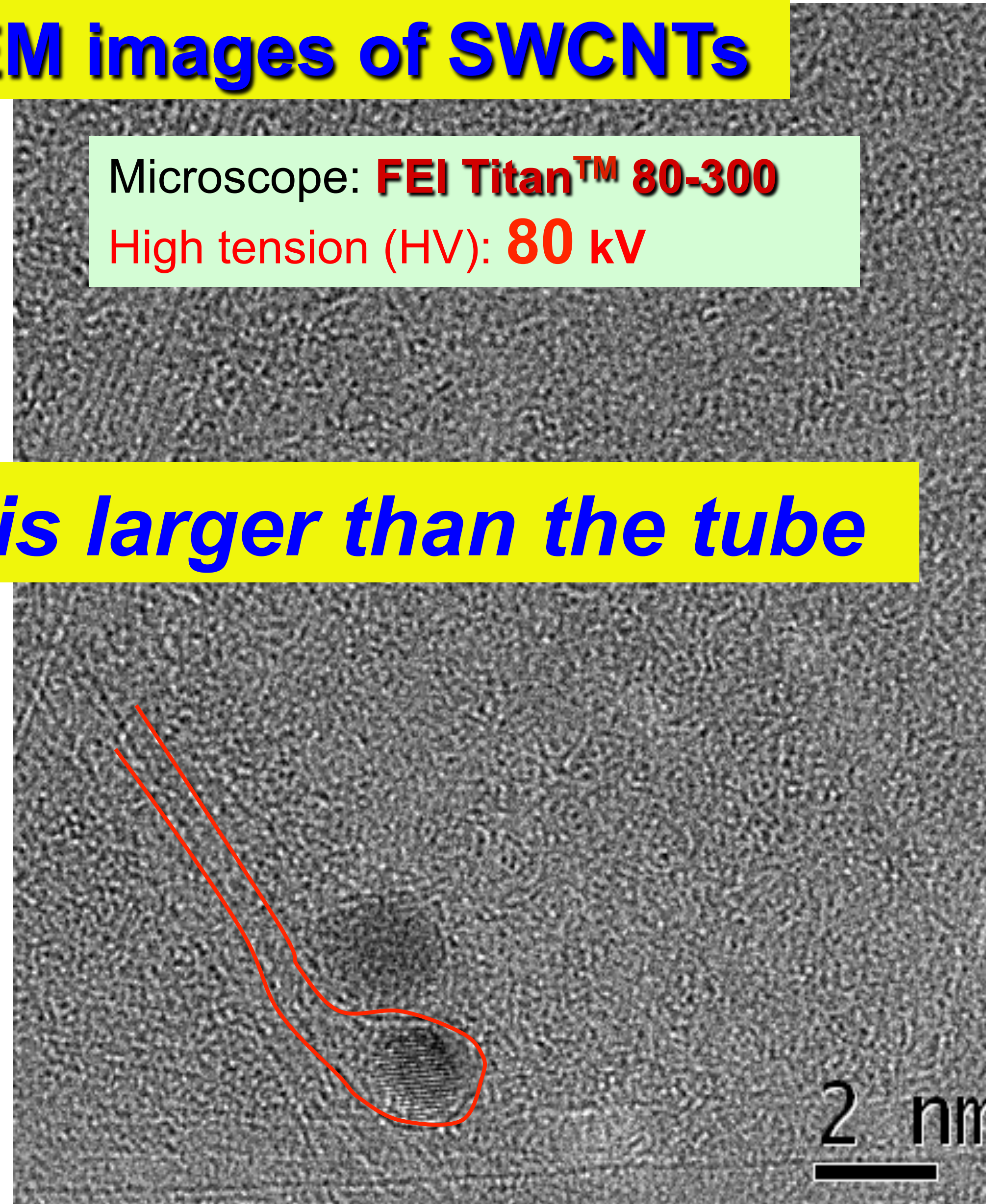
Cs-corrected TEM images of SWCNTs

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

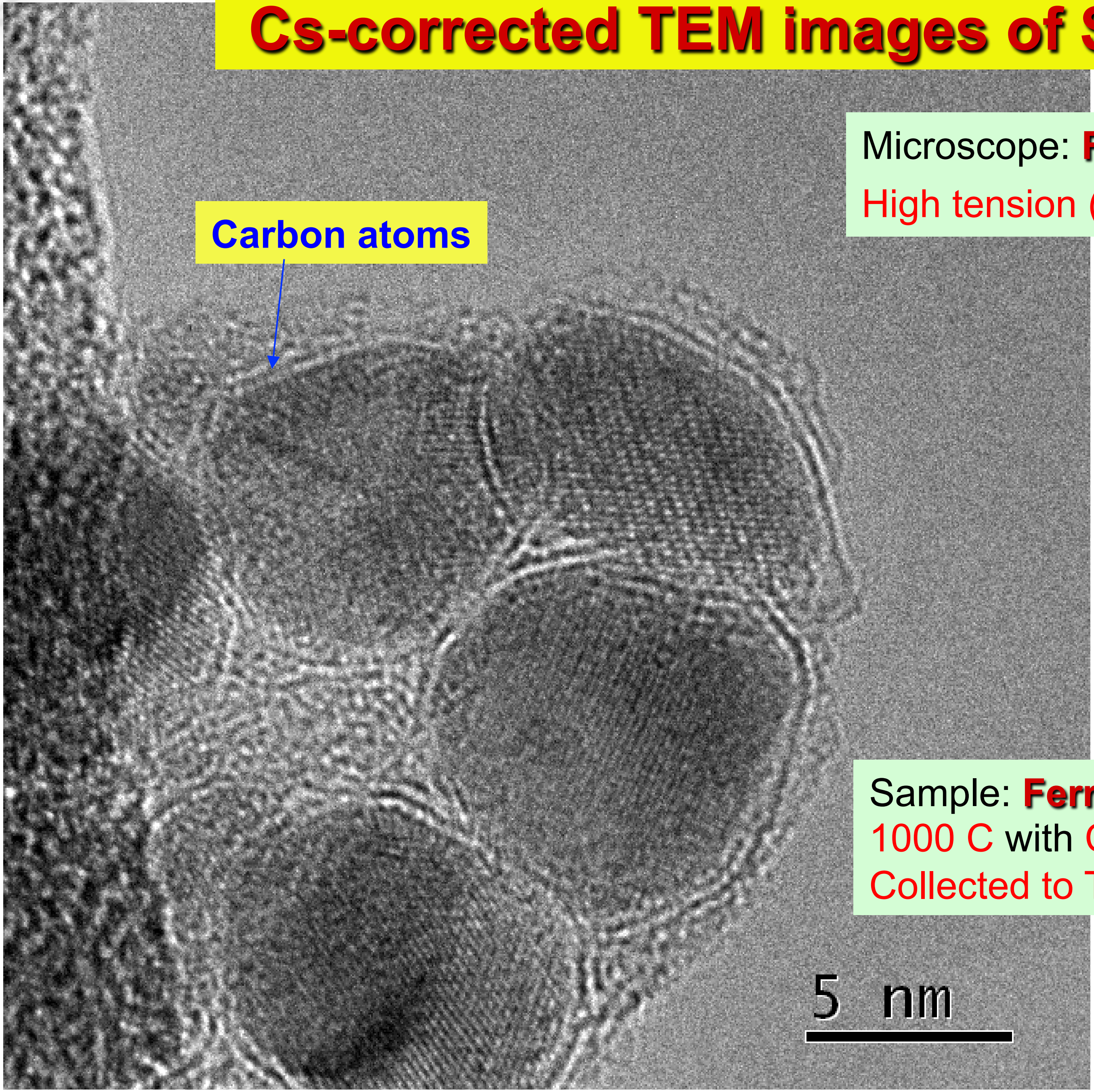
Microscope: **FEI Titan™ 80-300**
High tension (HV): **80 kV**

Active catalyst is larger than the tube





Cs-corrected TEM images of SWCNTs



Microscope: **FEI Titan^{TM} 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

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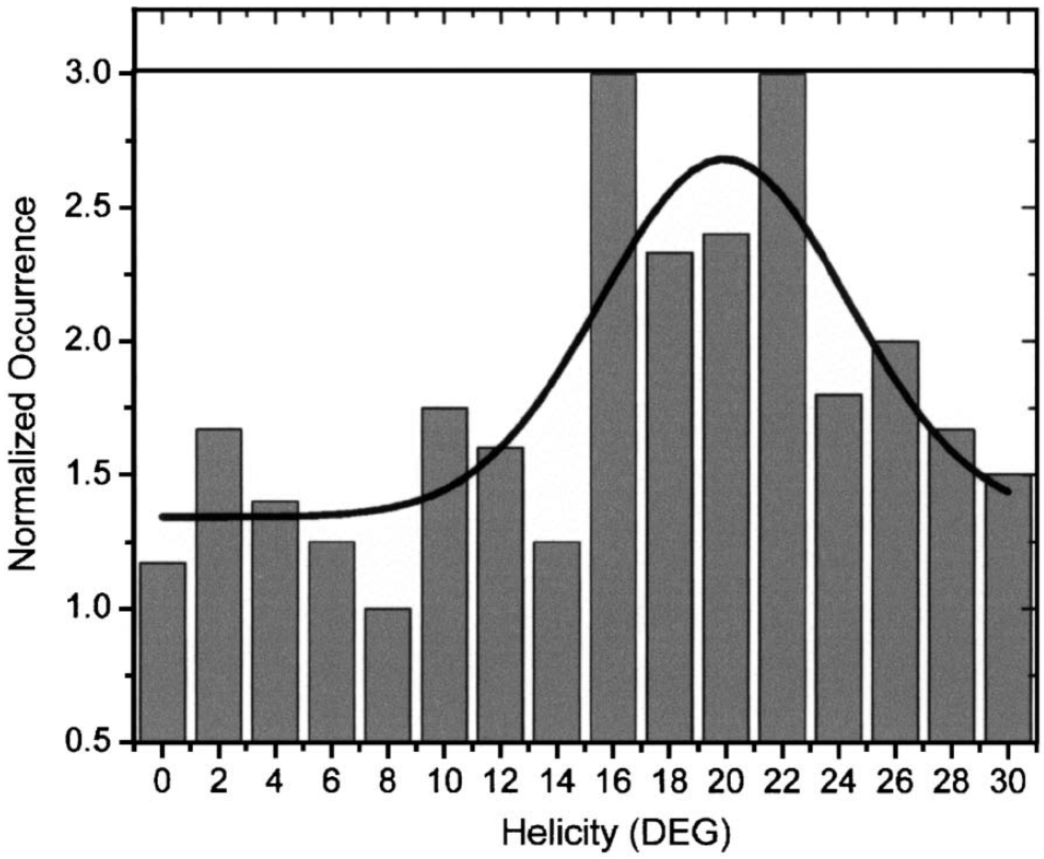
Chiral angle distributions for a SWCNT sample produced by arc discharge[1]



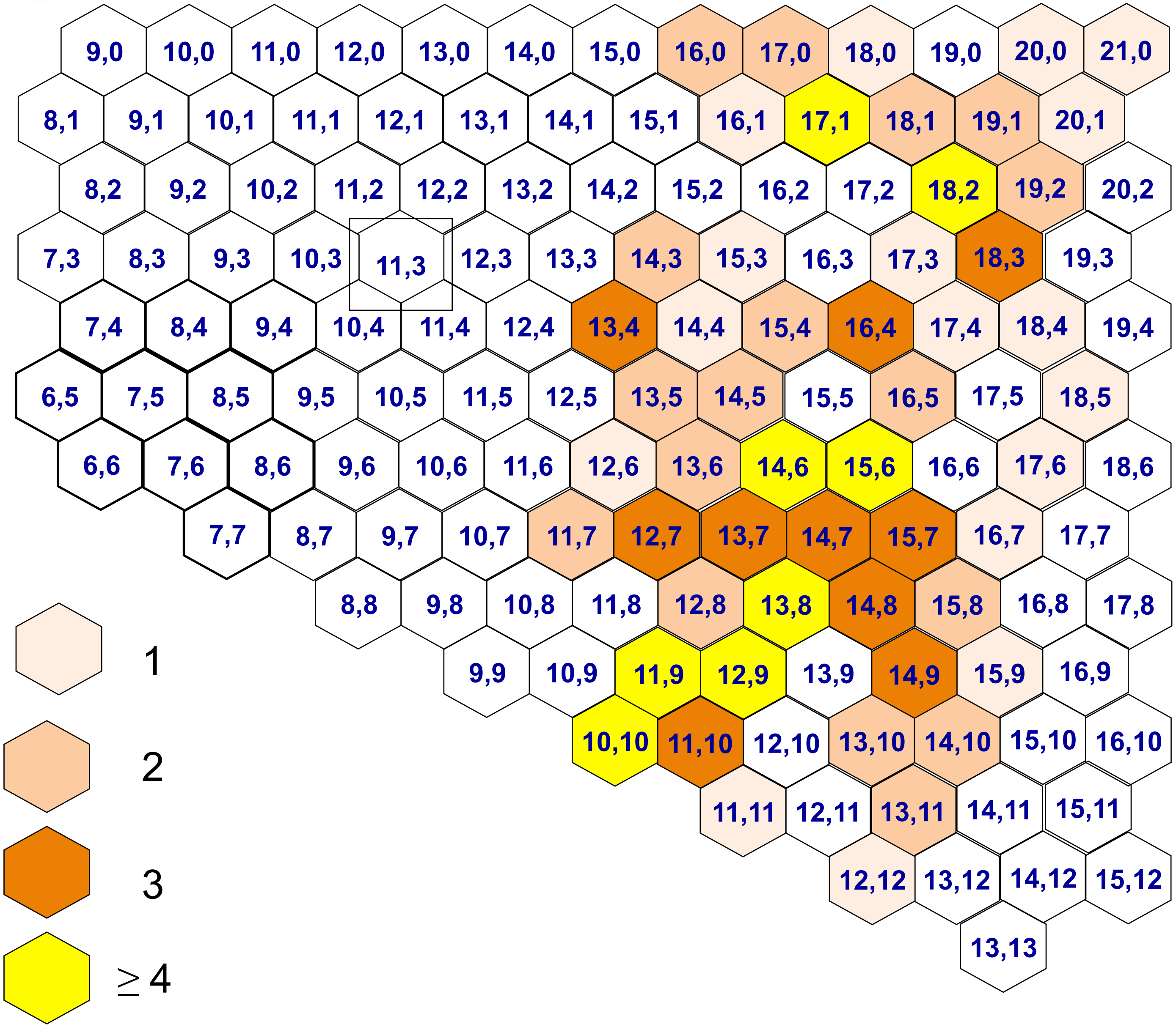
Chiral angle distribution of 124 individual SWNTs characterized experimentally by nano-beam **electron diffraction** analysis.

The histogram shows normalized number (normalized by dividing the observed number of nanotubes by the number of nanotube species at each helicity) of characterized individual nanotubes with different helicities.

-- Qin et al., *Phys. Rev*. **B 71,** 245413 (2005)

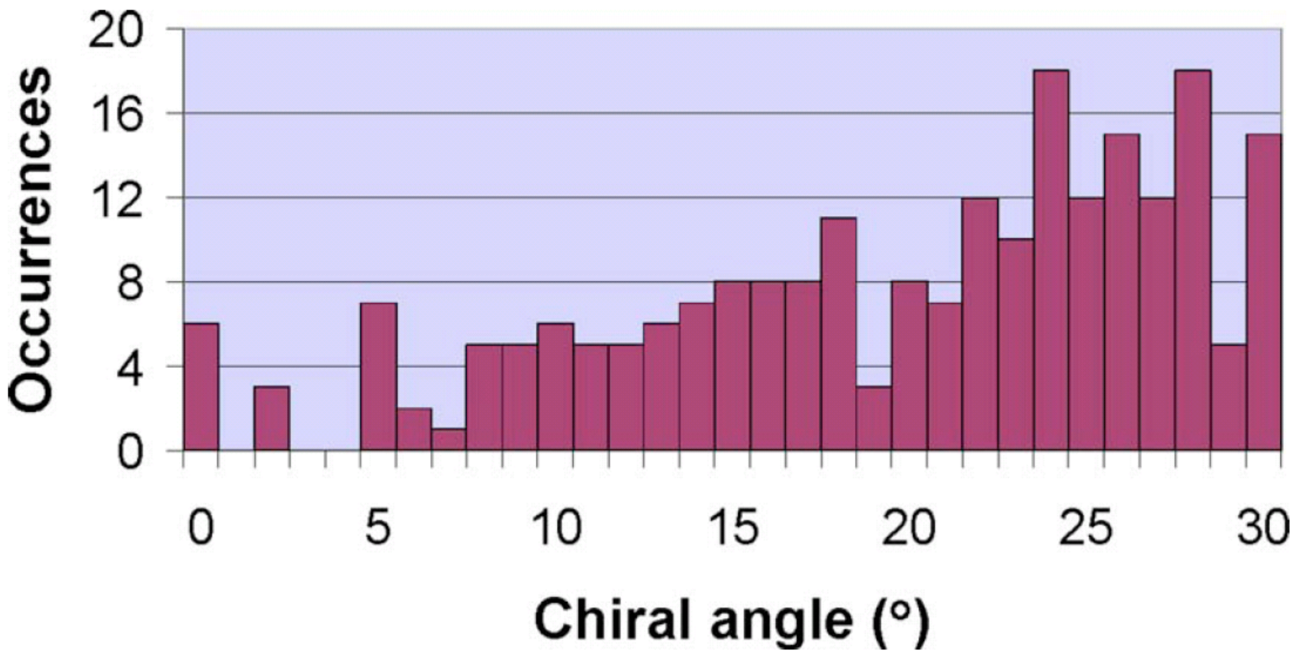
1. C. Journet, W. K. Maser, P. Bernier, A. Loiseau, M. Lamy de la Chappelle, S. Lefrant, P. Deniard, R. Lee, and J. E. Fischer, Nature (London) **388**, 756 (1997).

Arc SWNTs



PHYSICAL REVIEW B **71**, 245413 (2005)

Chiral angle distributions for a SWCNT sample produced by laser ablation[2]

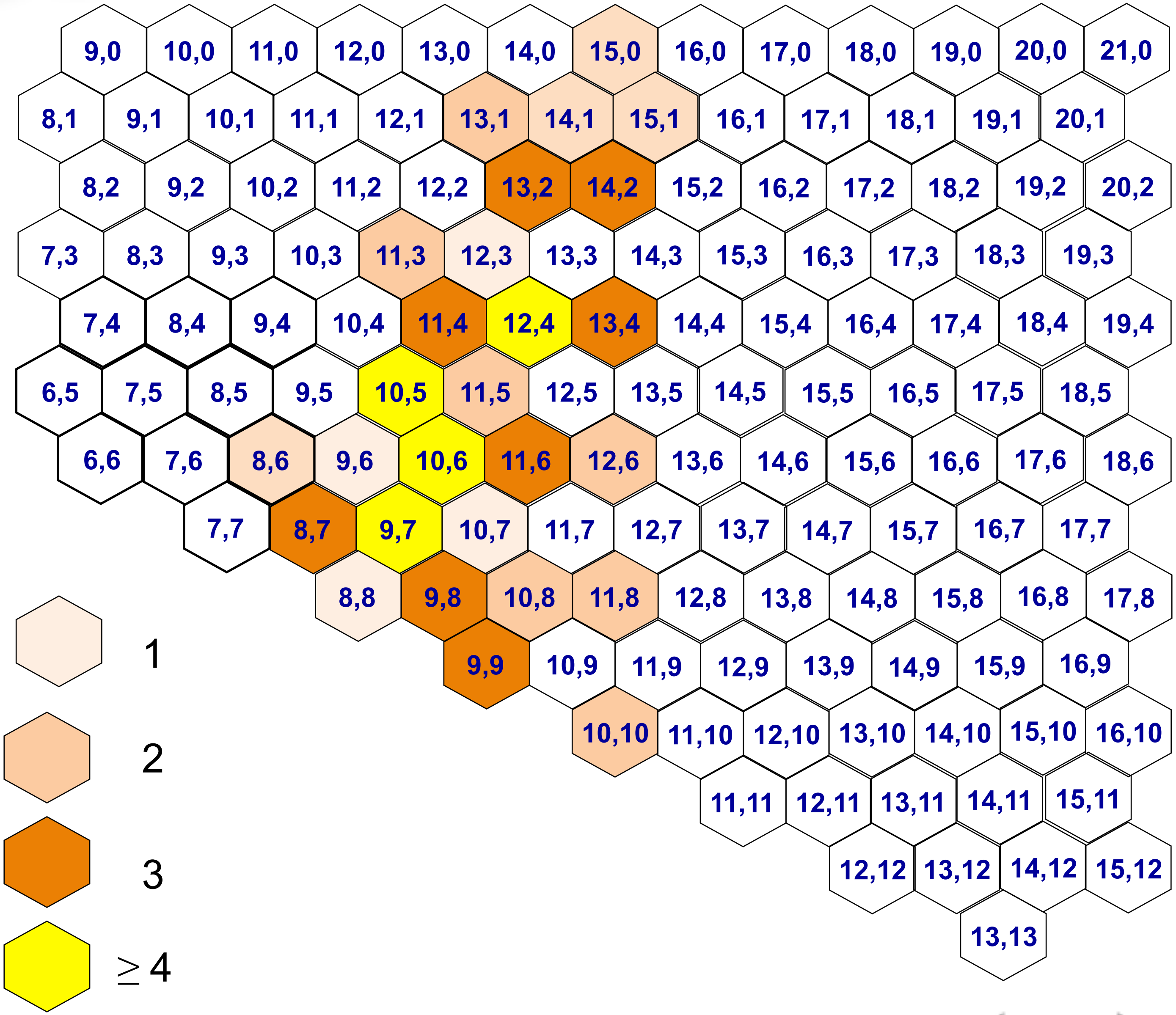


Chiral angle distribution for a laser-ablation SWCNT sample. The measurement was based on **electron diffraction analysis** of 48 SWCNT bundles and 10 individual SWCNTs which results in a total occurrence of 228 helicities for statistic.

-- Jiang et al., *Appl. Phys. Lett*. **93,** 141903 (2008)

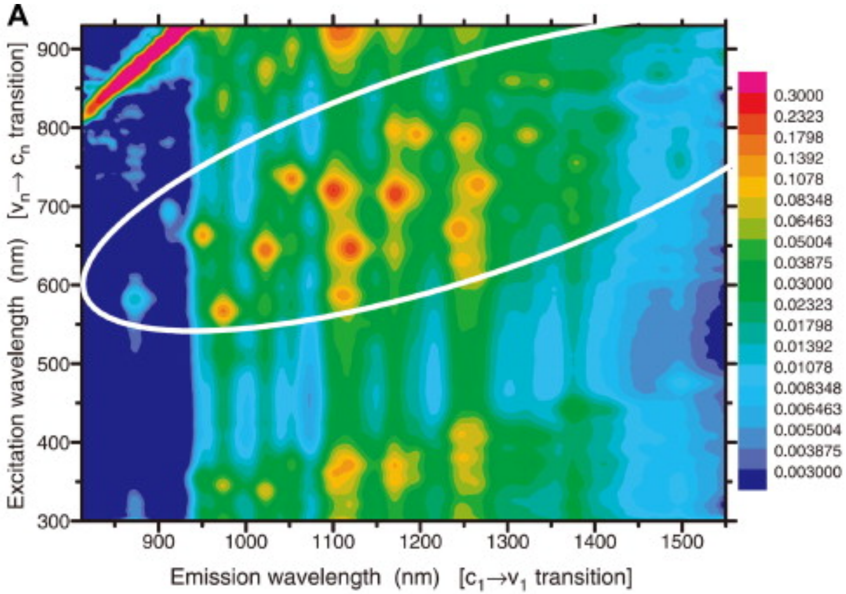
2. T. Guo, P. Nikolaev, A. Thess, D. T. Colbert, and R. E. Smalley, Chem. Phys. Lett. **243**, 49 (1995).

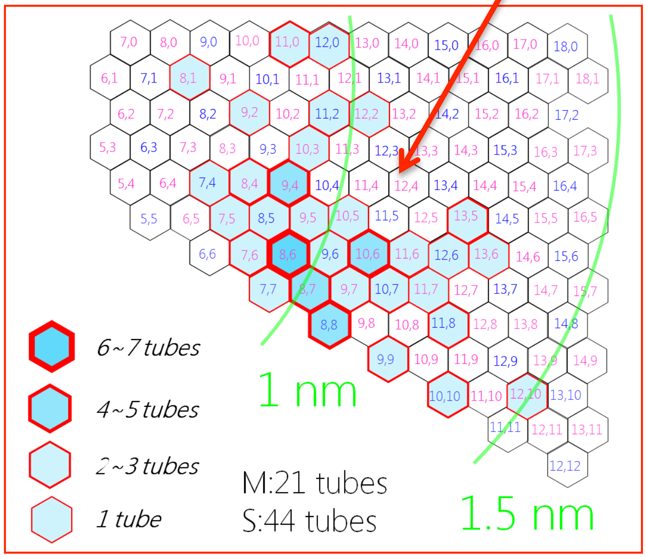
Laser SWNTs (optical)

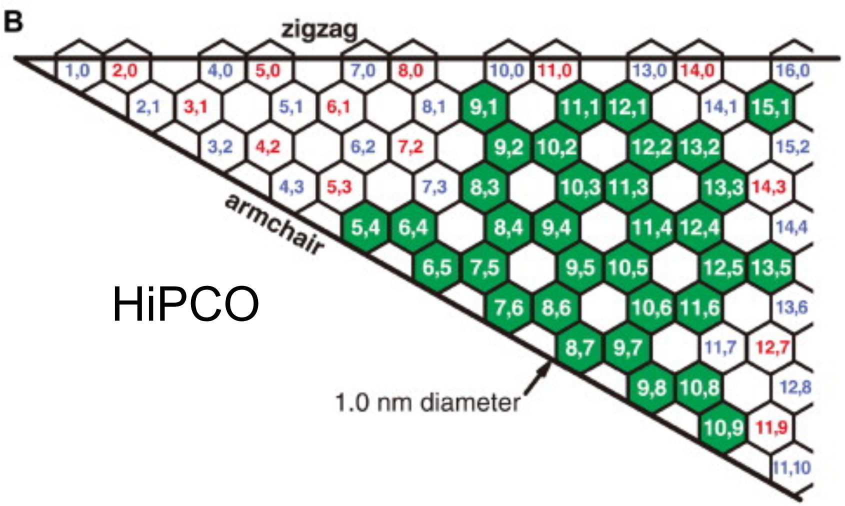


Nano Res (2009) 2: 818−827

High pressure CO FC-CVD SWNTs (HiPCO; optical data) – very broad vs. chiral angle when compared to ambient pressure FC-CVD

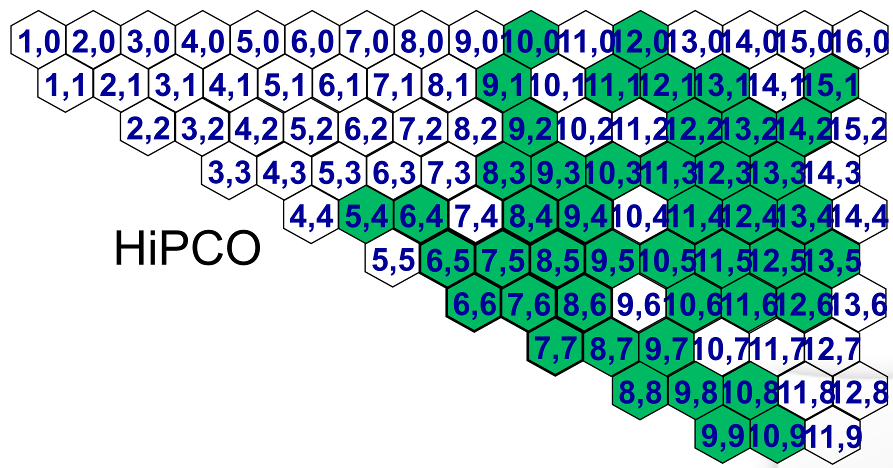






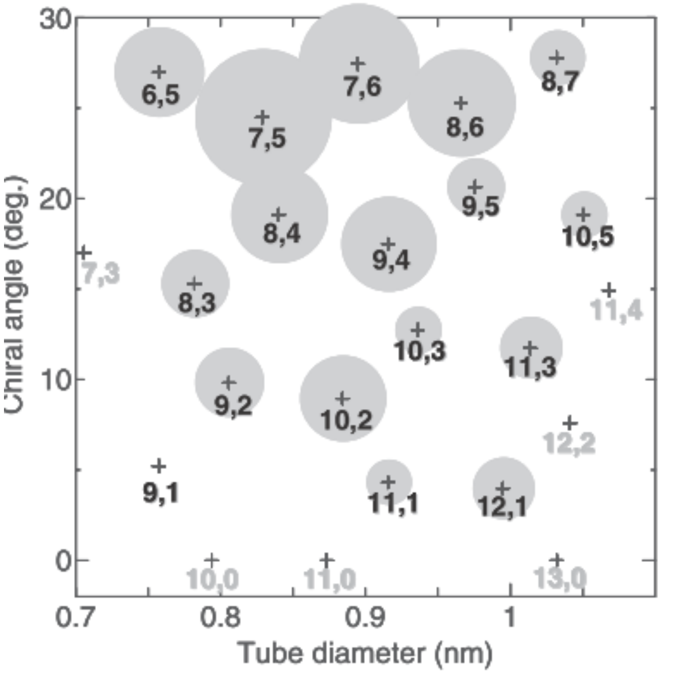
HiPCO

Include metallic tubes

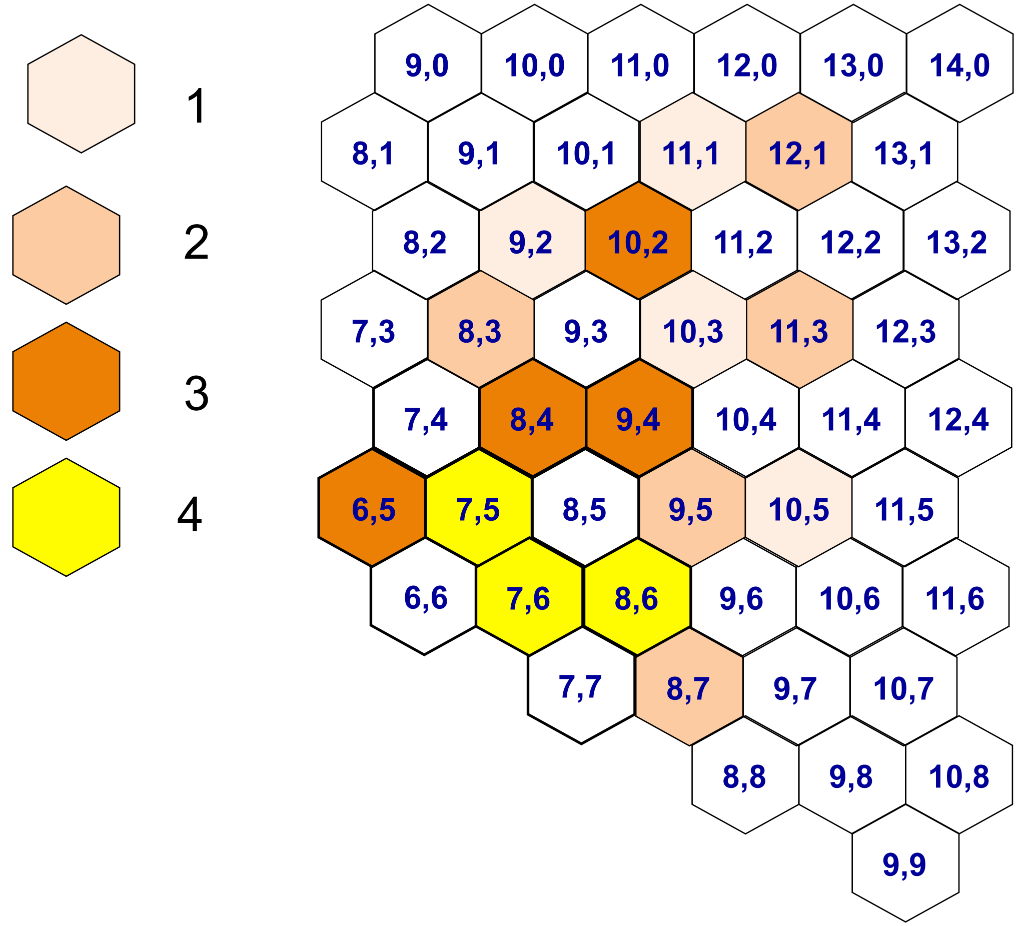


HiPCO

Alcohol SWNTs (PL – did not find ED)

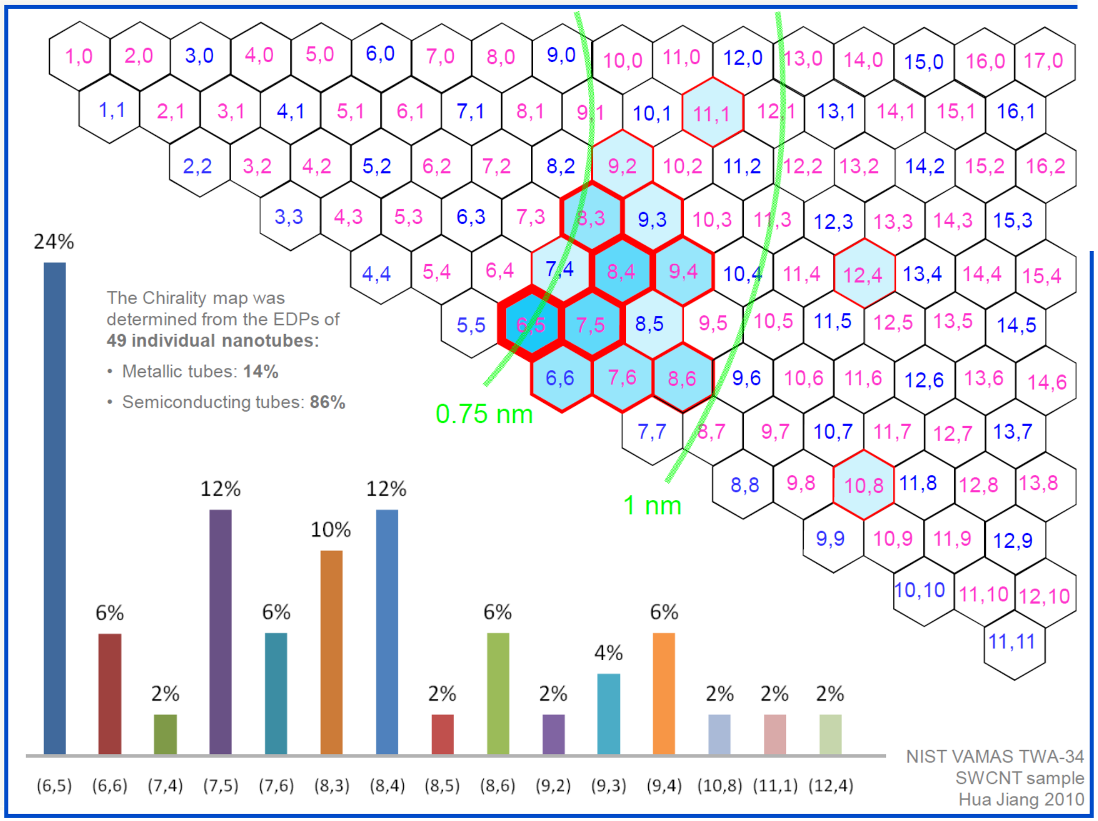


(a) ACCVD



New Journal of Physics **5** (2003) 149.1–149.12

CoMoCat – comparison of TEM/ED and PL



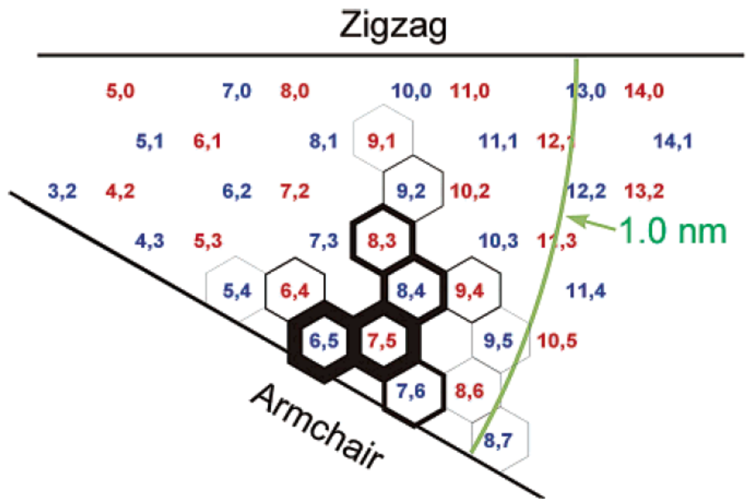


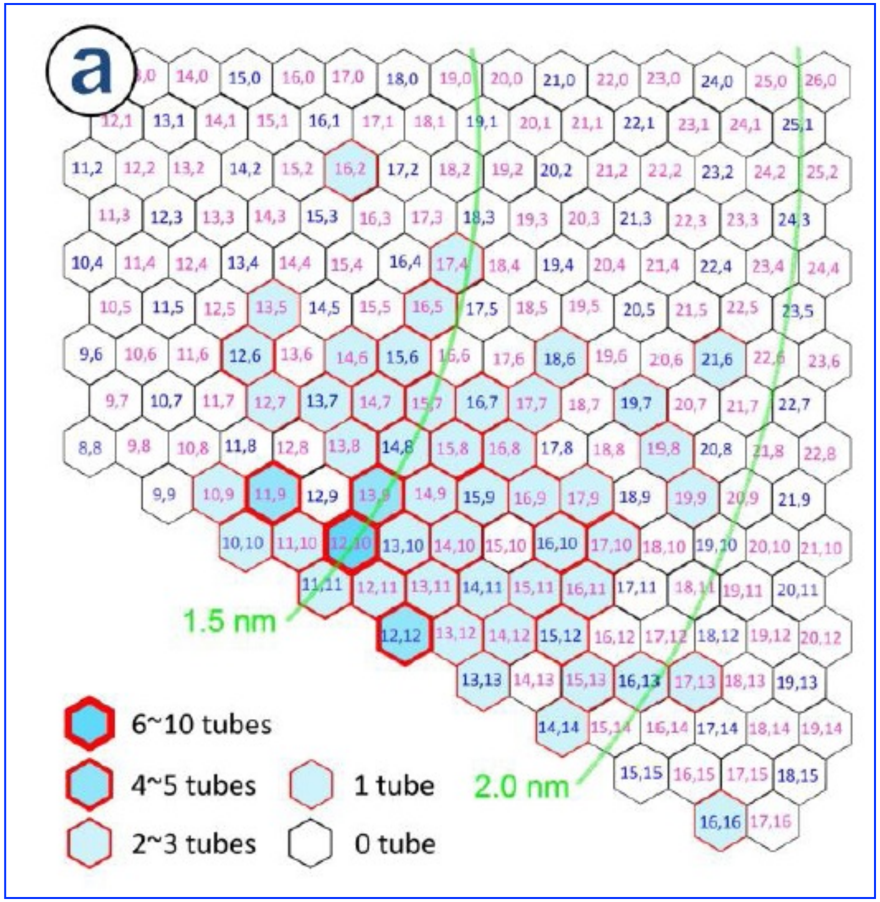
Table 1. (*n,m*)-Resolved Spectral Intensities from SWNT Samples

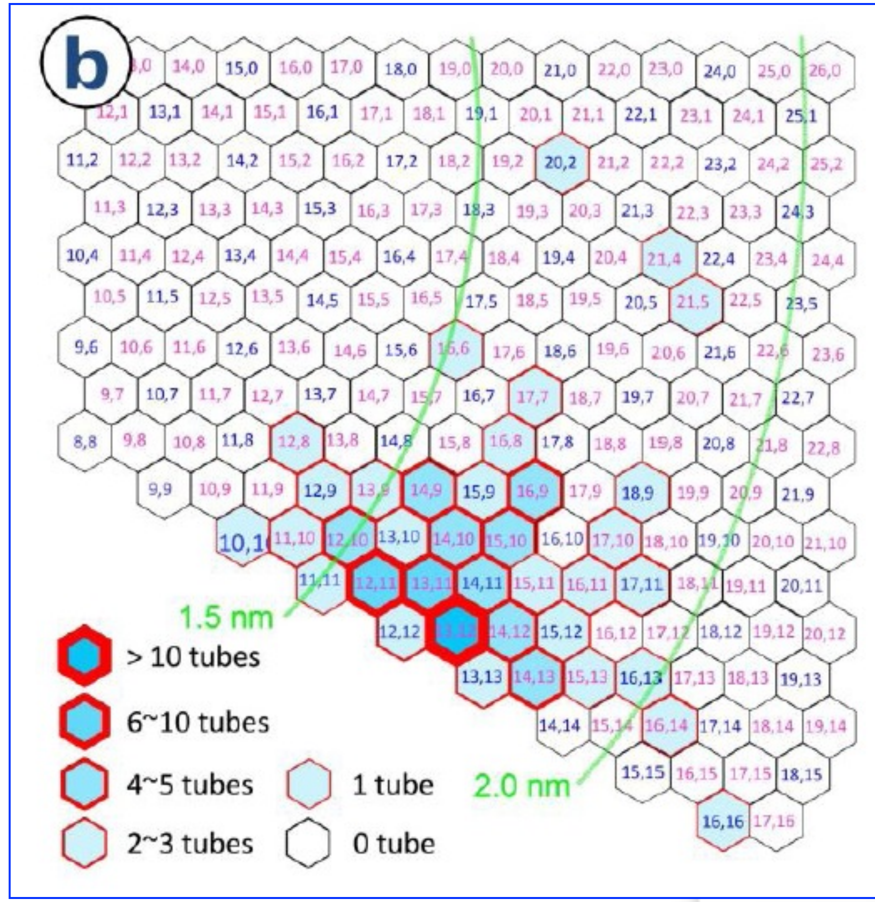
n,m	diameter (nm)	chiral angle (deg)	fractional intensity (%), CoMoCAT	fractional intensity (%), HiPco
5,4	0.620	26.3	0.3	0.0
6,4	0.692	23.4	2.8	0.3
9,1	0.757	5.2	0.8	0.2
6,5	0.757	27.0	28	3.7
8,3	0.782	15.3	11	2.9
9,2	0.806	9.8	1.7	0.4
7,5	0.829	24.5	28	4.9
8,4	0.840	19.1	14	4.2
10,2	0.884	9.0	0.0	4.5
7,6	0.895	27.5	8.5	7.1
9,4	0.916	17.5	2.3	7.6
10,3	0.936	12.7	0.0	4.3
8,6	0.966	25.3	0.8	8.3
9,5	0.976	20.6	0.3	5.7
9,5	0.976	20.6	0.0	5.7
12,1	0.995	4.0	0.0	3.8
11,3	1.014	11.7	0.0	4.6
8,7	1.032	27.8	0.3	5.6
10,5	1.050	19.1	0.0	4.6

TEM/ED individual tube data - Jiang et al. unpublished

Sergei M. Bachilo, Leandro Balzano, Jose E. Herrera, Francisco Pompeo, Daniel E. Resasco and R. Bruce Weisman
J. AM. CHEM. SOC. 2003, 125, 11186-11187.

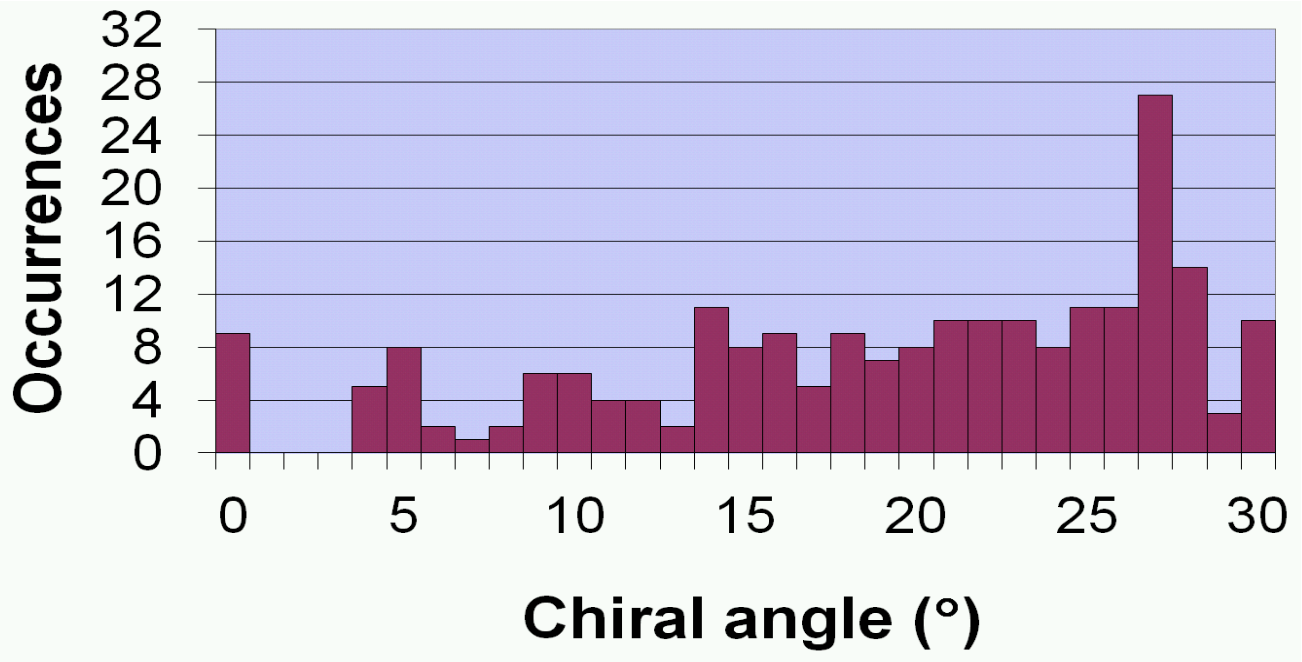
Chirality i.e. (*n,m*) maps for samples produced with (a) 0 ppm NH3, and (b) 500 ppm NH3 as determined with electron diffraction of individual SWCNTs – *large chiral angle due to enhanced etching of low chiral angle tubes*





Jiang et al., *JACS* **133,** 1224 (2010)

Chiral angle distributions for the NIST VAMAS TWA-34 SWCNT sample (CoMoCAT)[3]



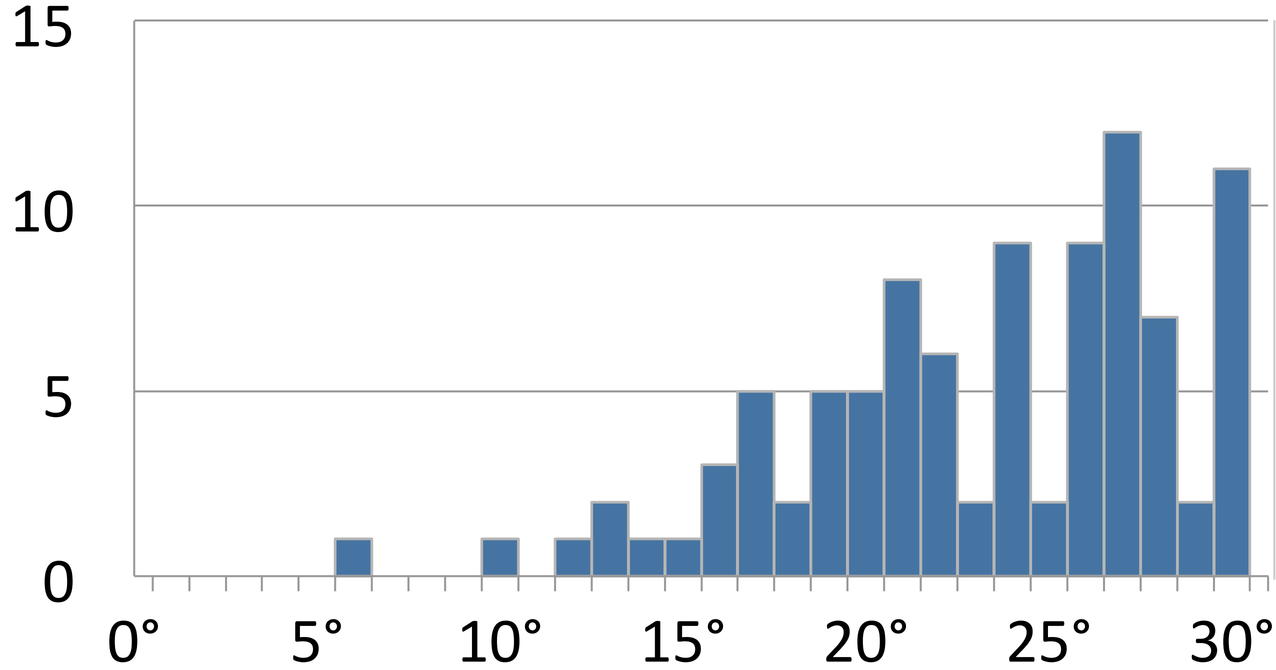
Chiral angle distribution for a CoMoCAT SWCNT sample. The measurement was based on **electron diffraction analysis** of 44 SWCNT bundles and 49 individual SWCNTs which results in a total occurrence of 269 helicities for statistic.

-- Jiang *et al.*, unpublished (2010)

3. Provided by NIST VAMAS TWA-34 project.

Chiral angle distributions for a SWCNT sample produced from CO by a floating catalyst (aerosol) CVD process

introduced with 0 ppm NH_3 (blue)



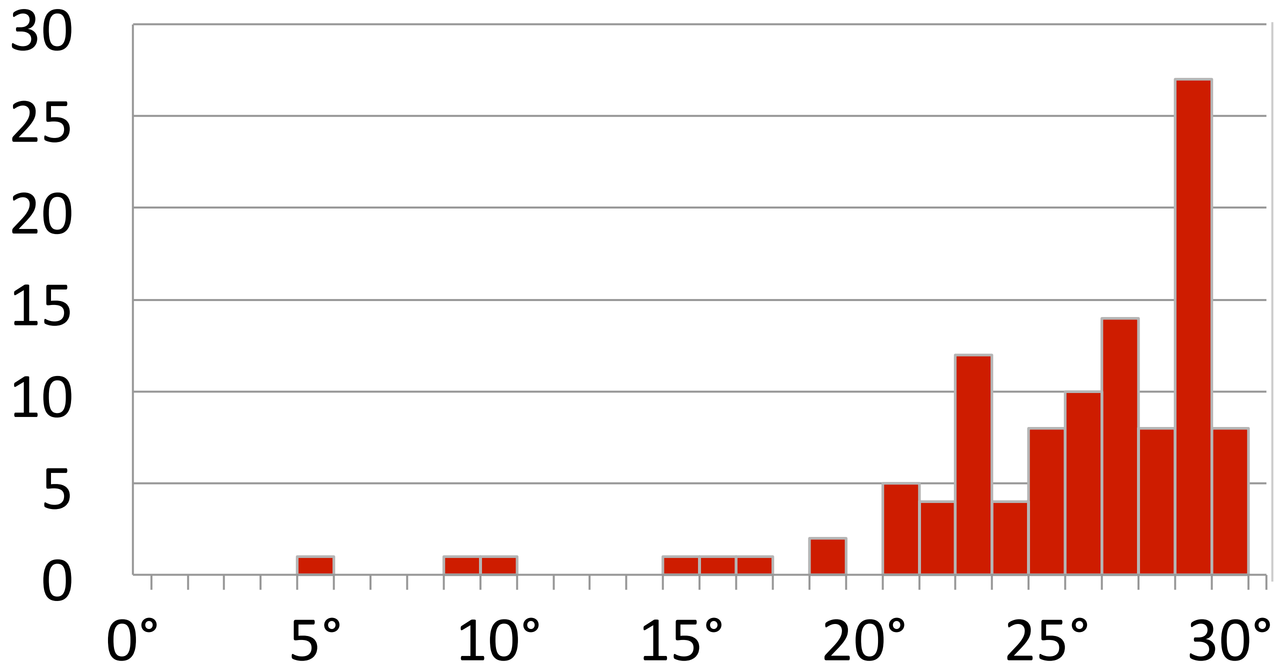
Chiral angle distribution for a SWCNT sample produced without NH_3 introduced. The measurement was based on electron diffraction analysis of totally **95** individual SWCNTs.

CO flow rate@400 cm³/min, CO2 flow rate@2 cm³/min, Temperature@ 880 °C

-- Jiang et al., *JACS* **133,** 1224 (2010)

Chiral angle distributions for a SWCNT sample produced from CO by a floating catalyst (aerosol) CVD process

introduced with 500 ppm NH_3 (Red)



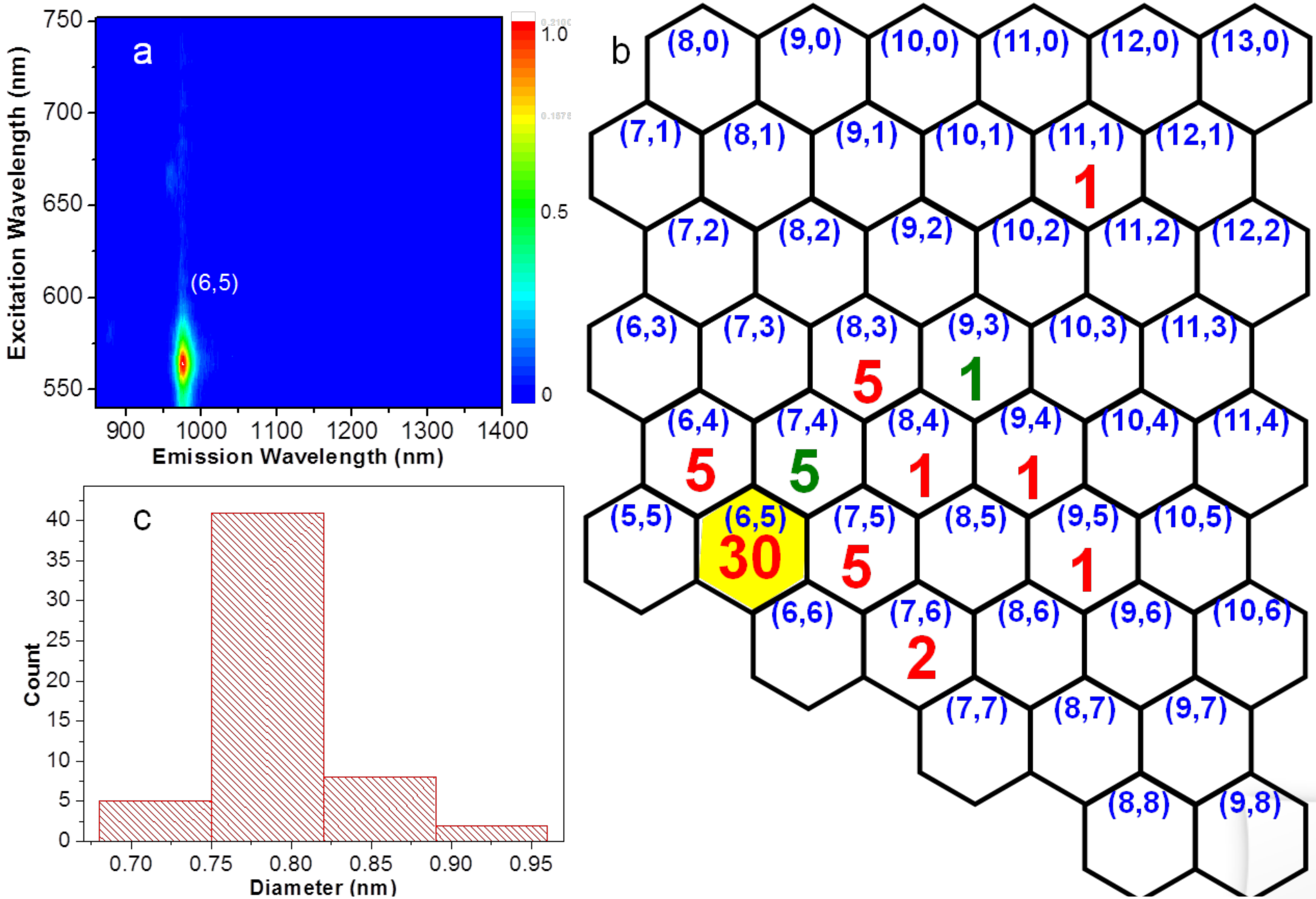
Chiral angle distribution for a SWCNT sample produced with 500 ppm NH_3 introduced. The measurement was based on electron diffraction analysis of totally **108** individual SWCNTs.

CO flow rate@400 cm³/min, CO2 flow rate@2 cm³/min, Temperature@ 880 °C

-- Jiang et al., *JACS* **133,** 1224 (2010)

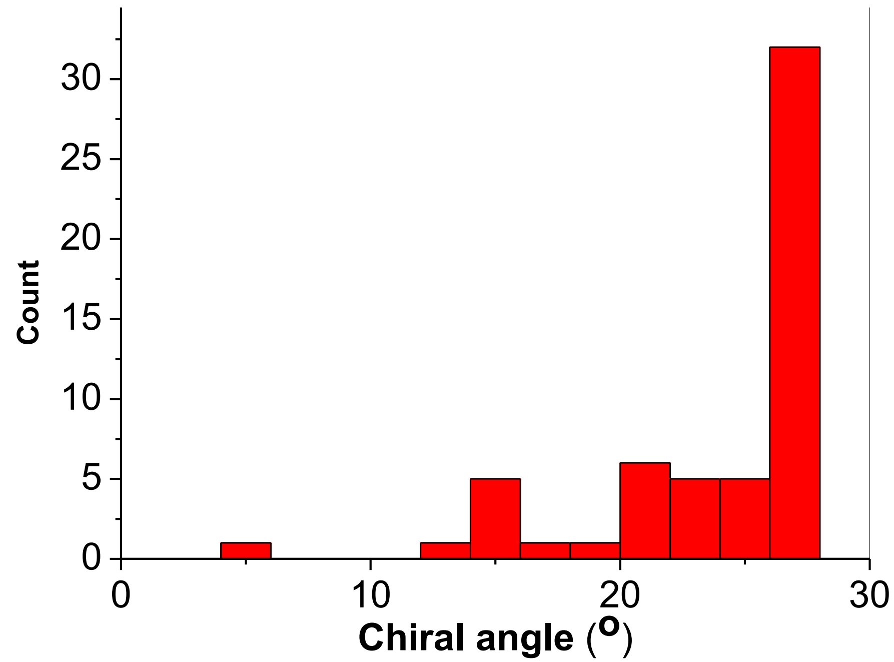
Characterization of SWNTs grown at 500 C, 1 atm

Co-MgO II by impregnation



Preferential growth of semiconducting SWNTs (～90%)

Chiral angle distributions for a SWCNT sample grown on lattice-mismatched epitaxial Co Nanoparticles



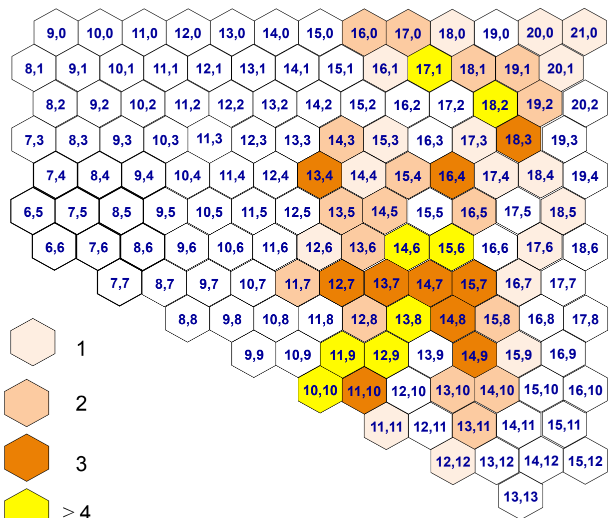
No armchair tubes !

Chiral angle distribution for a Co grown SWCNT sample (500 ^{o}C). The measurement was based on **electron diffraction analysis** of 57 individual SWCNTs.

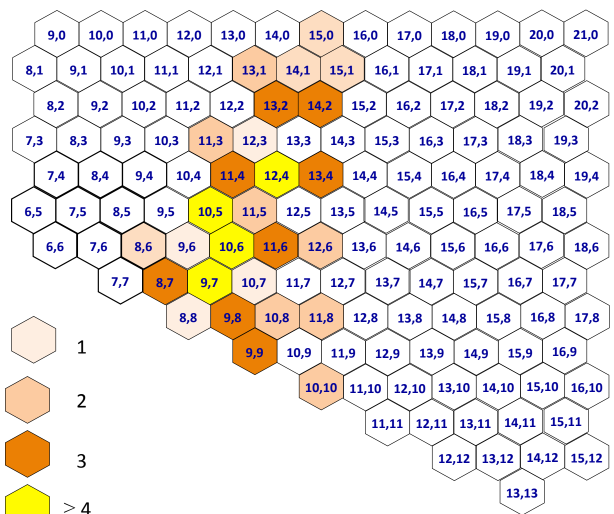
-- He et al., *Scientific Reports* **3,** 1460 (2013)

(n,m) maps of SWNTs via ED

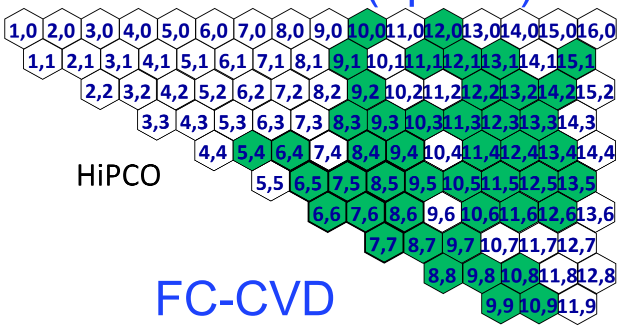
Arc SWNTs



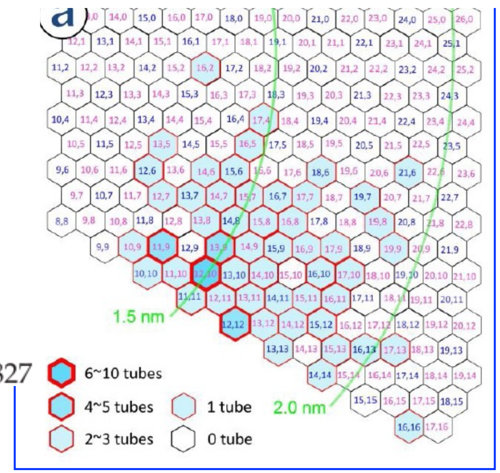
Laser SWNTs (optical)



HiPCO (optical)

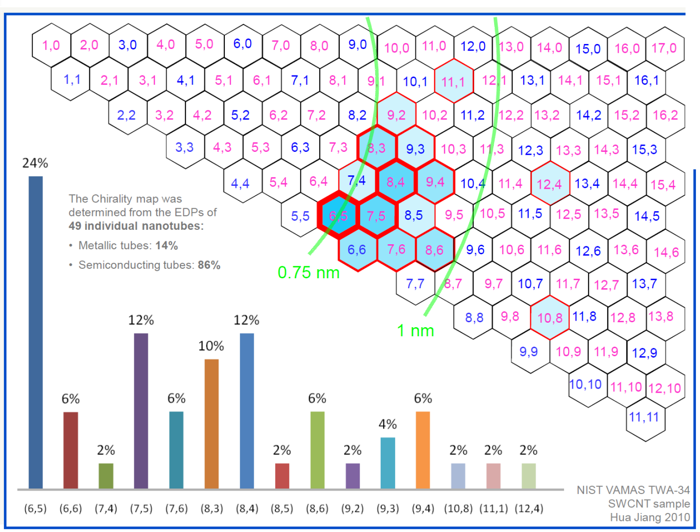


FC-CVD

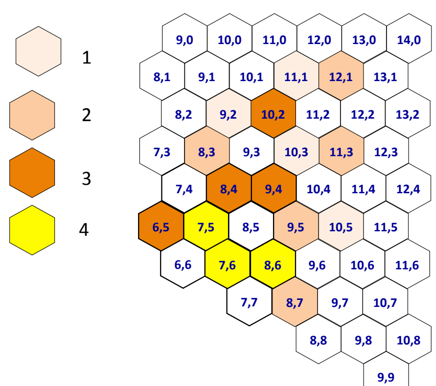


Nano Res (2009) 2: 818–827

CoMoCAT

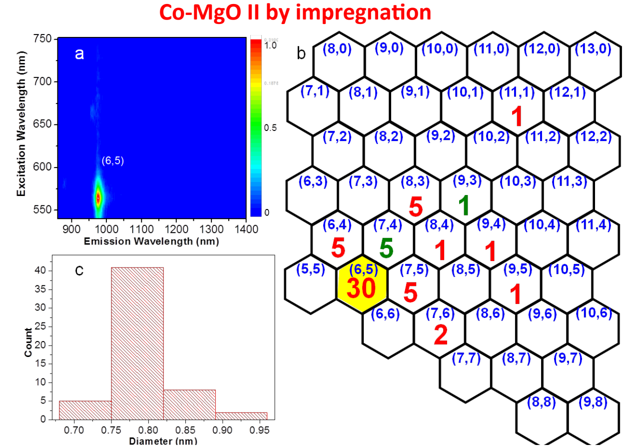


A-CVD (optical)



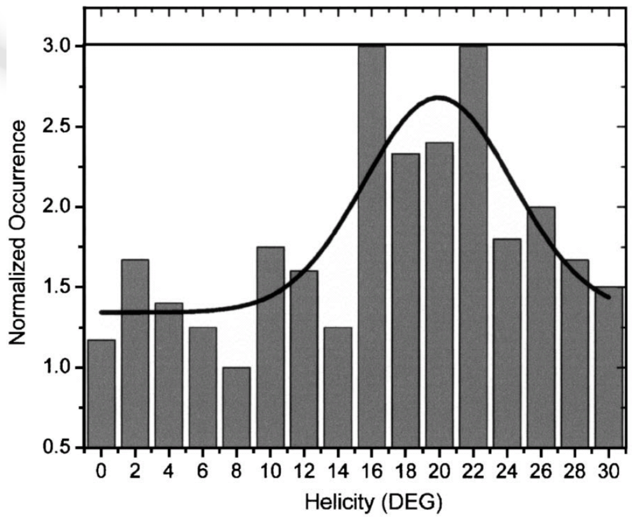
CVD –" locked" catalyst

Co-MgO II by impregnation

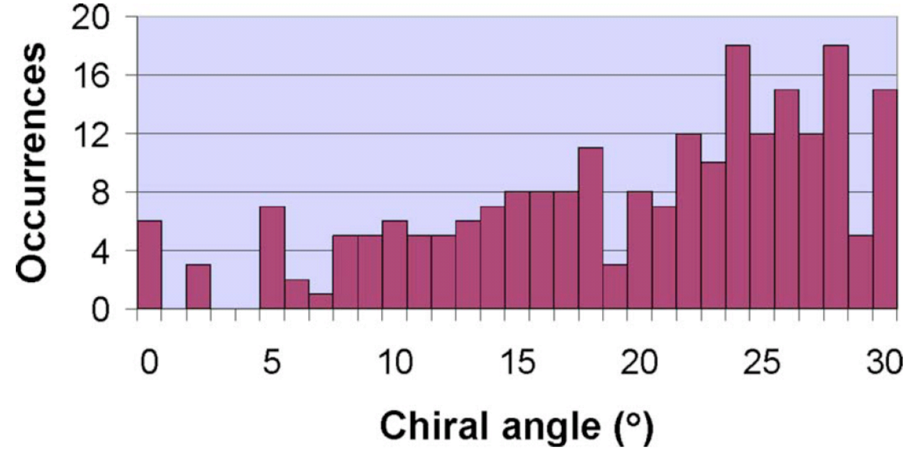


Preferential growth of semiconducting SWNTs (~90%)

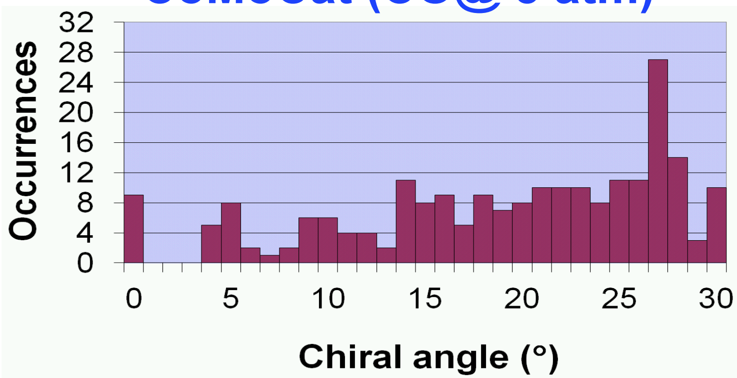
Arc



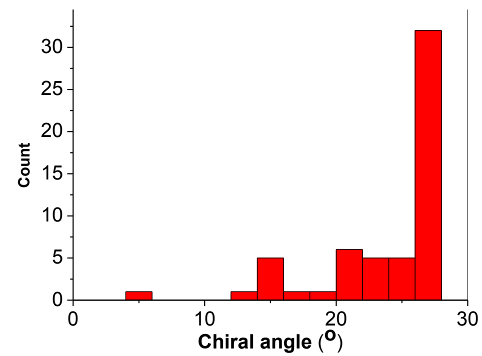
Laser



CoMoCat (CO@ 5 atm)

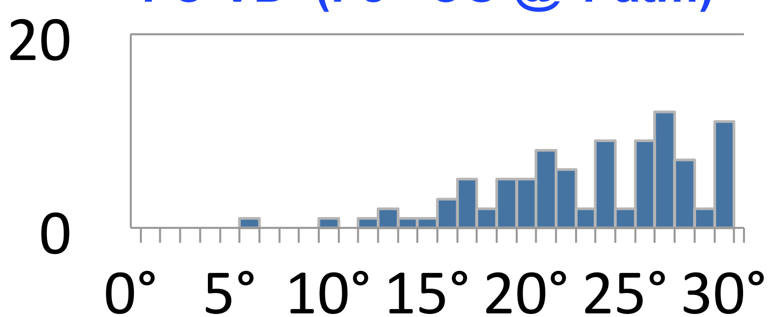


Lattice-mismatched epitaxial Co on MgO CO @ 1 atm, 500 oC

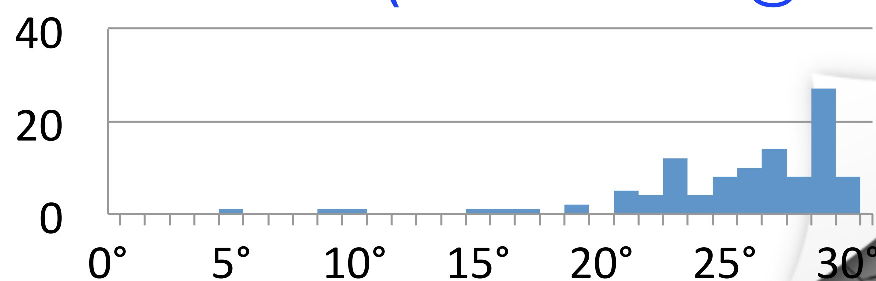


Peking U. Prof. Y. Li with faceted catalyst: close to just one (n,m) ?

FC-VD (Fe +CO @ 1 atm)



FC-CVD (Fe + CO + NH3 @ 1 atm)



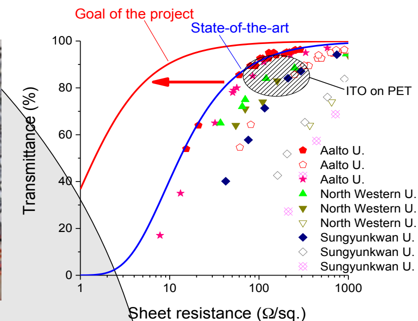
New Project

EU-Japan 2013-17

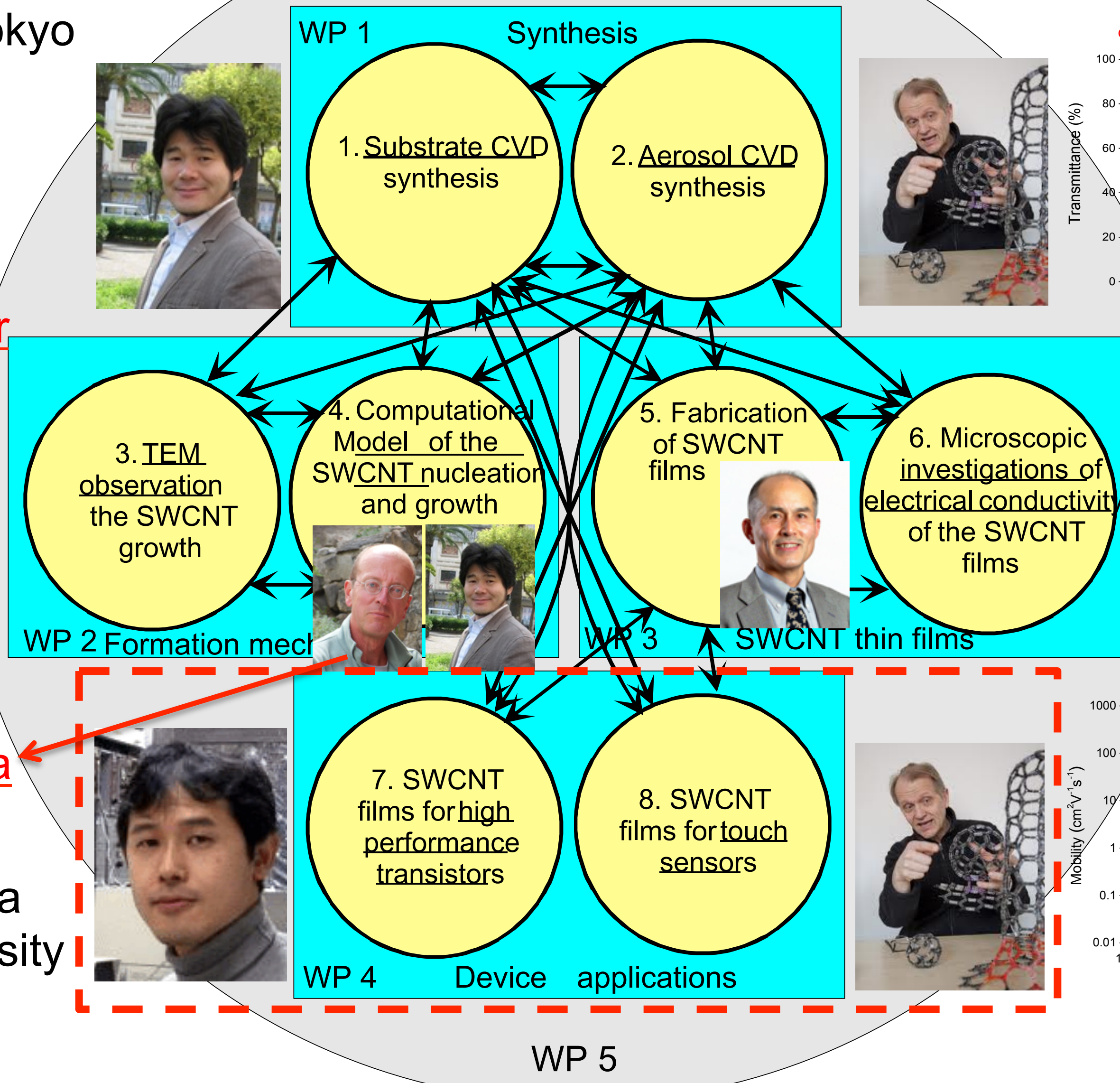
IRENA
Indium **Re**placement by Single-Walled Carbon **Na**notube Thin Films

The University of Tokyo

Aalto University

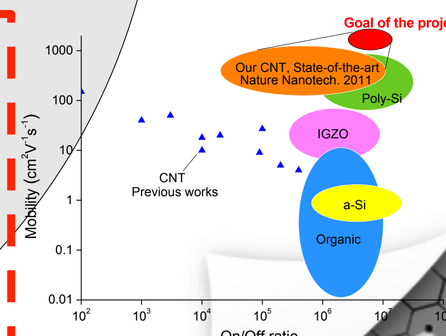


Technical University of Denmark
Dr. J. B. Wagner



CNRS, France
Dr. C. Bischara

Nagoya University



NanoMaterials Group, Aalto University School of Science

Department of Applied Physics

OPEN POSITIONS ! **OPEN POSITIONS !**

CANATU

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* Aalto MIDE and AEF programs

Prof. Y. Ohno, Nagoya University, Japan

IRENA
Indium Replacement by Single-Walled Carbon Nanotube Thin Films