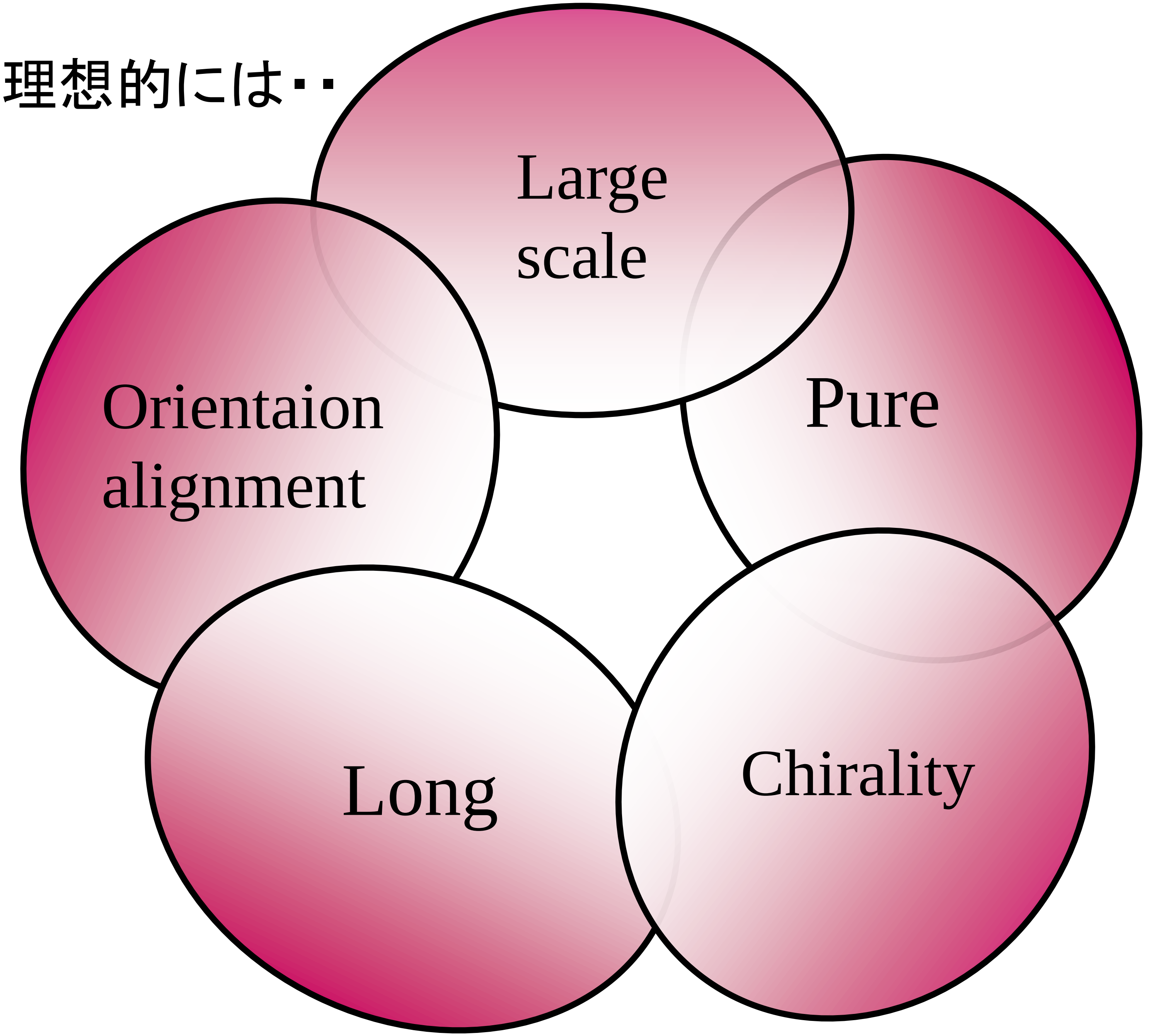
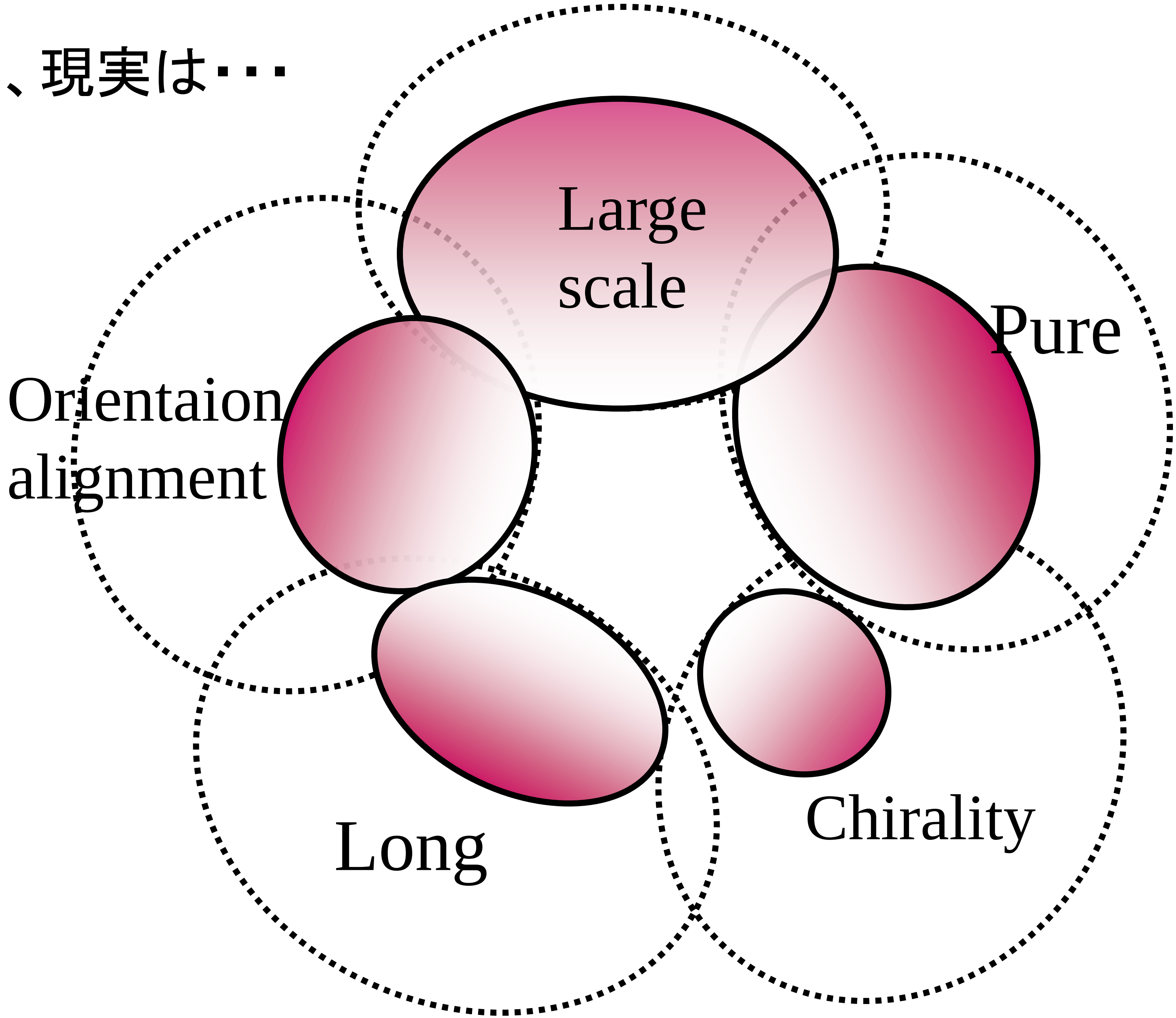
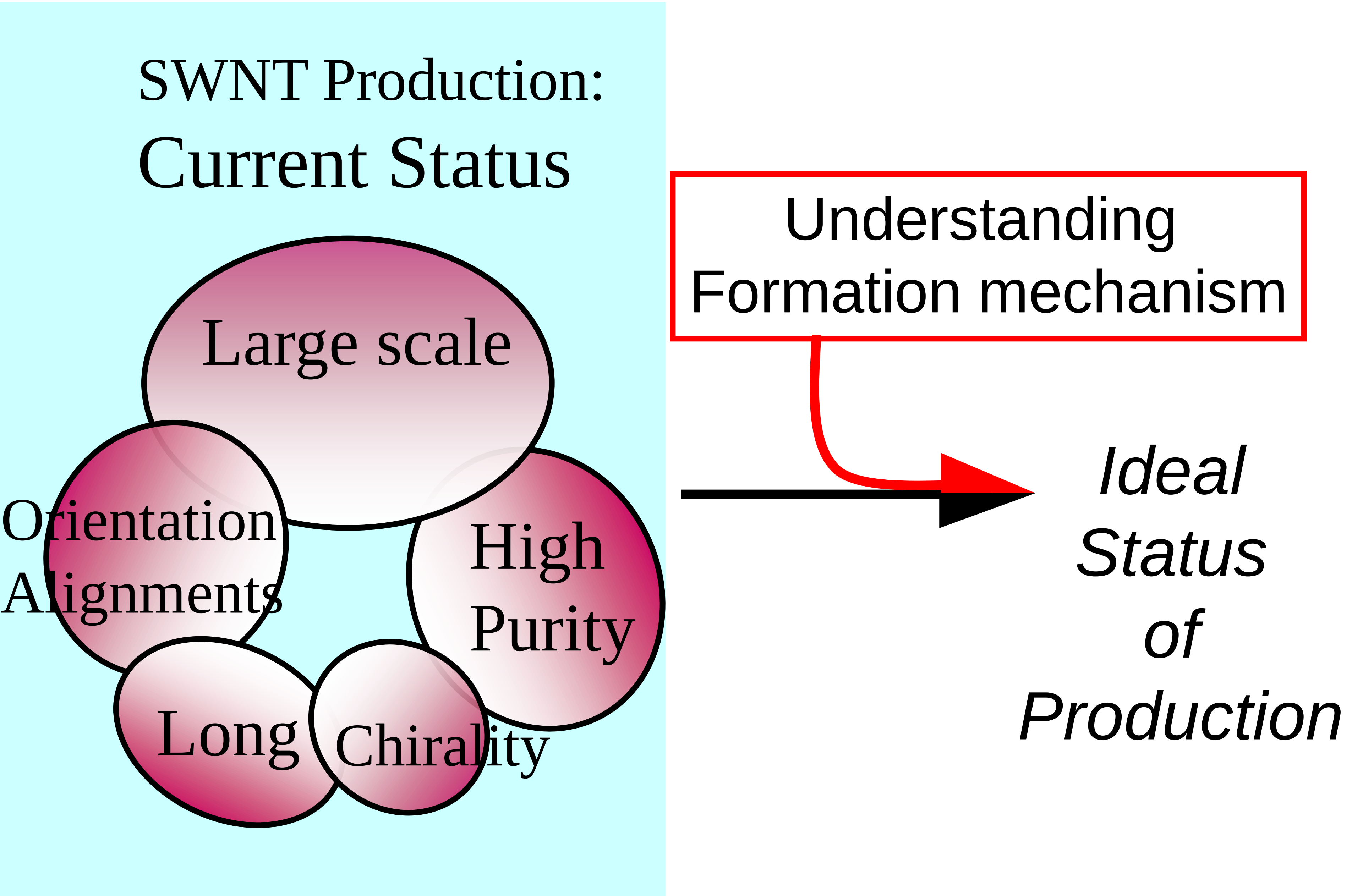
SWNT: 理想的には‥

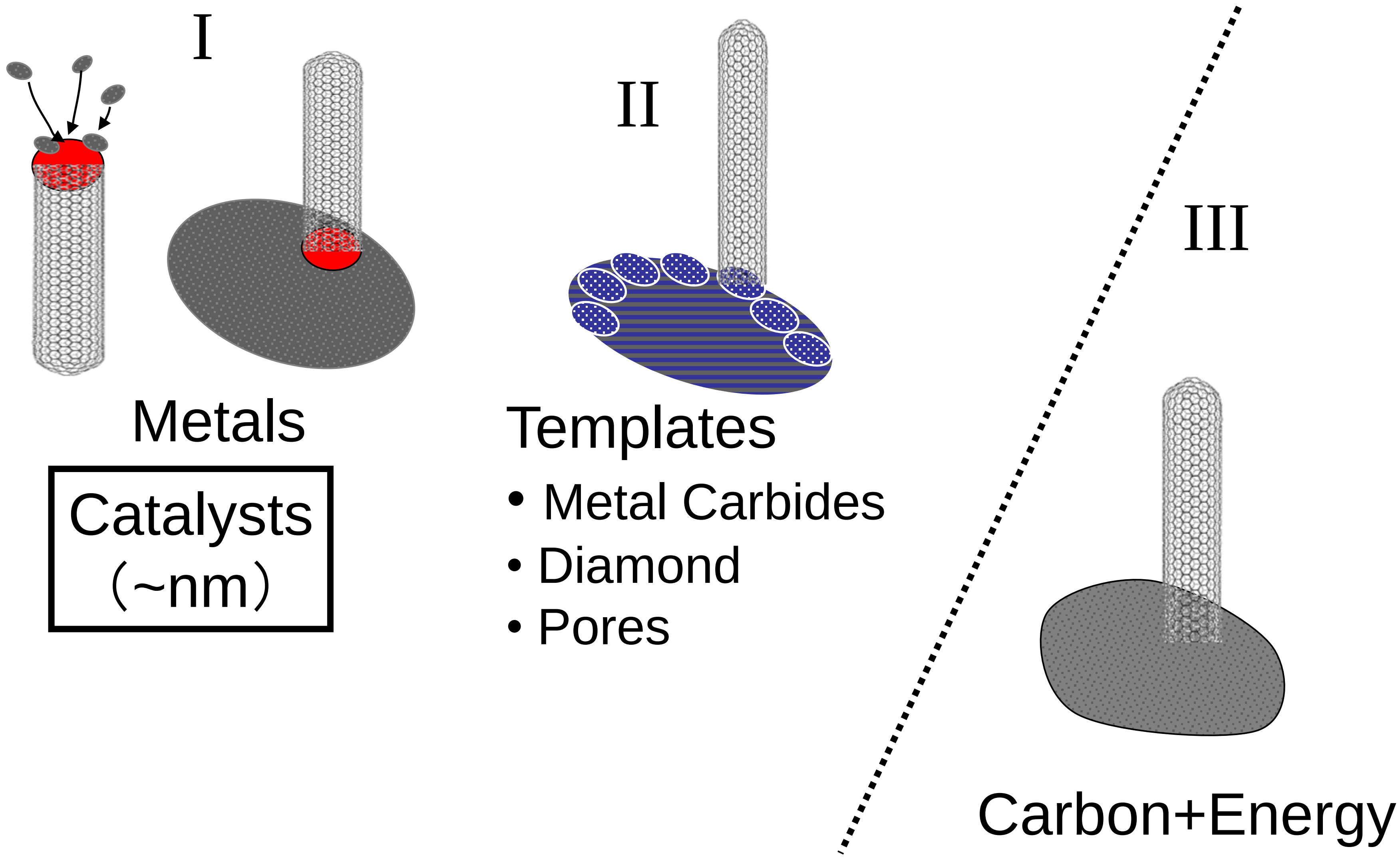


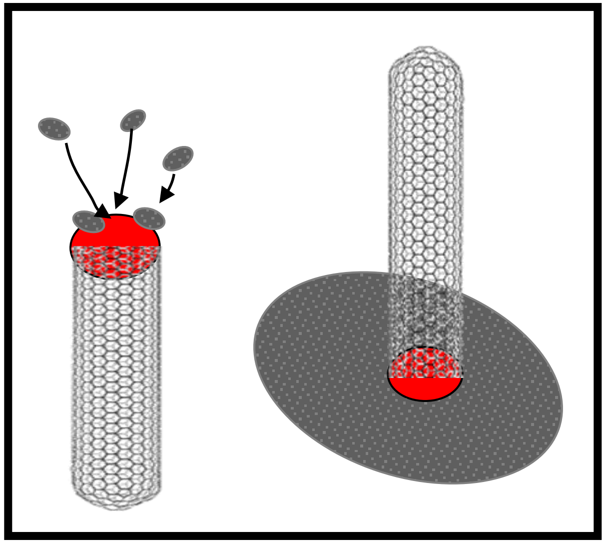
しかし、現実は・・・

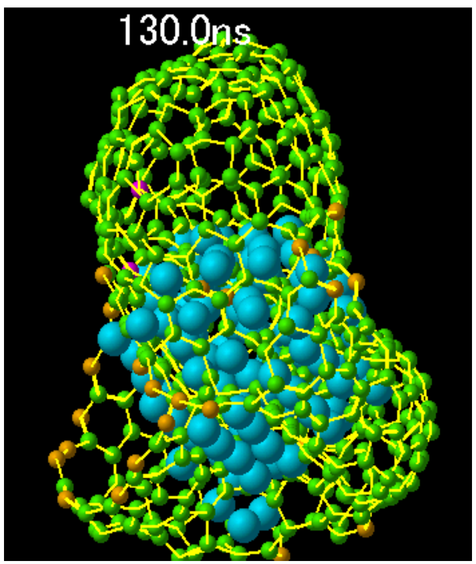



SWNT Production:
Current Status
Large scale
Orientation
Alignments
High
Purity
Long
Chirality
Understanding
Formation mechanism
Ideal
Status
of
Production

Growth Mechanism of SWNTs

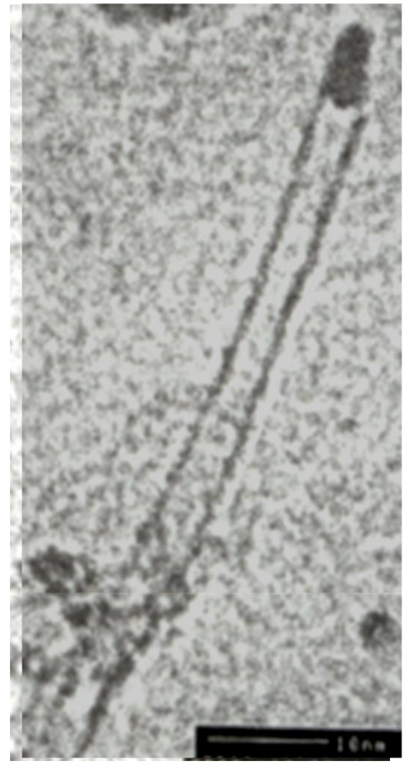






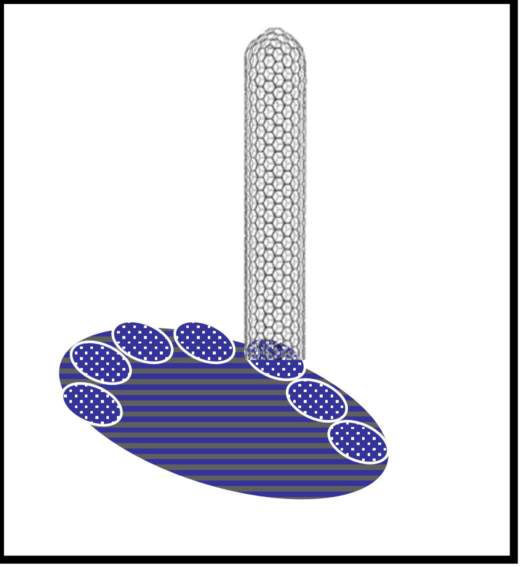
Shibuta, Maruyama (2002)

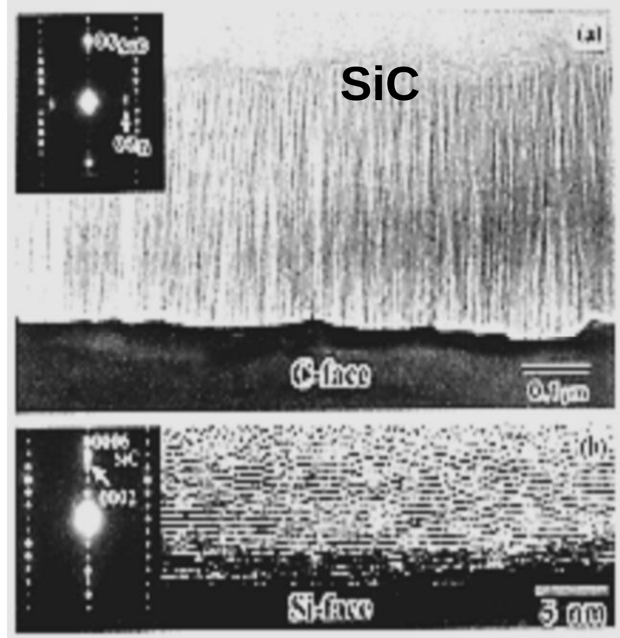
500 Carbon
&
Ni_{108} : 2500K



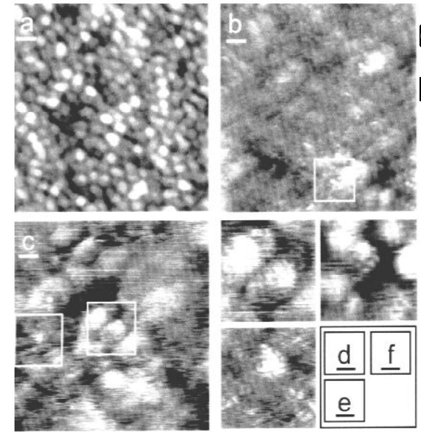
H.Dai et al.
Chem. Phys. Lett.
(1996).

Yudasaka et al.
JPC B 1998.





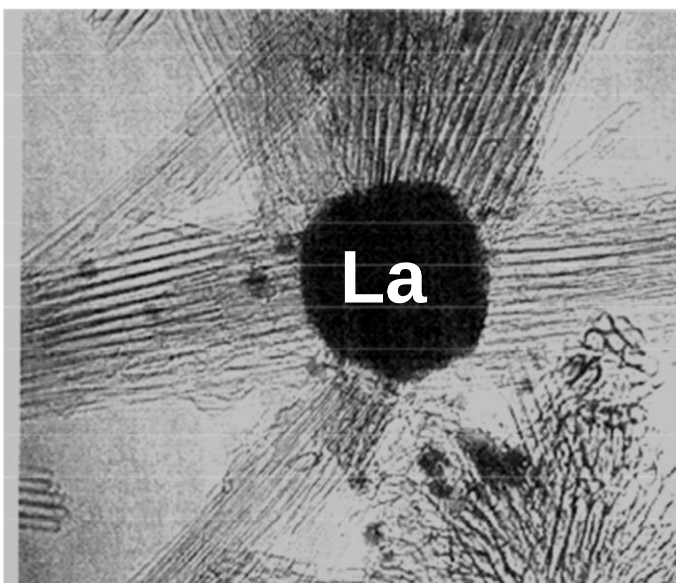
M. Kusunoki et al. Physica B (2002).



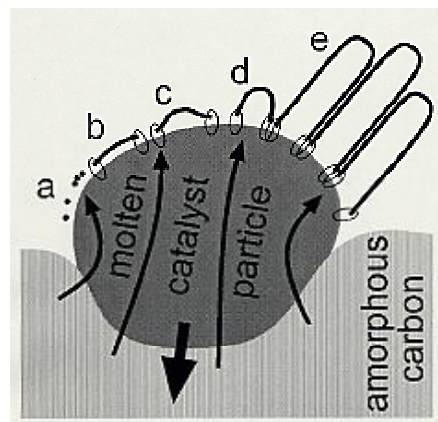
C –precipita-
tion at 800°C.

Tsui et al.
PRL (2002)

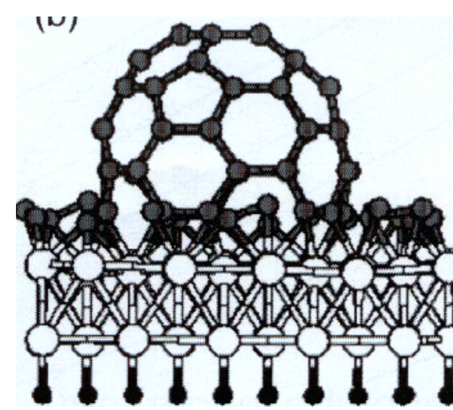
1 nm



Y. Saito et al. Chem. Phys. Lett. (1995).



Gorbunov et al, Carbon (2002).



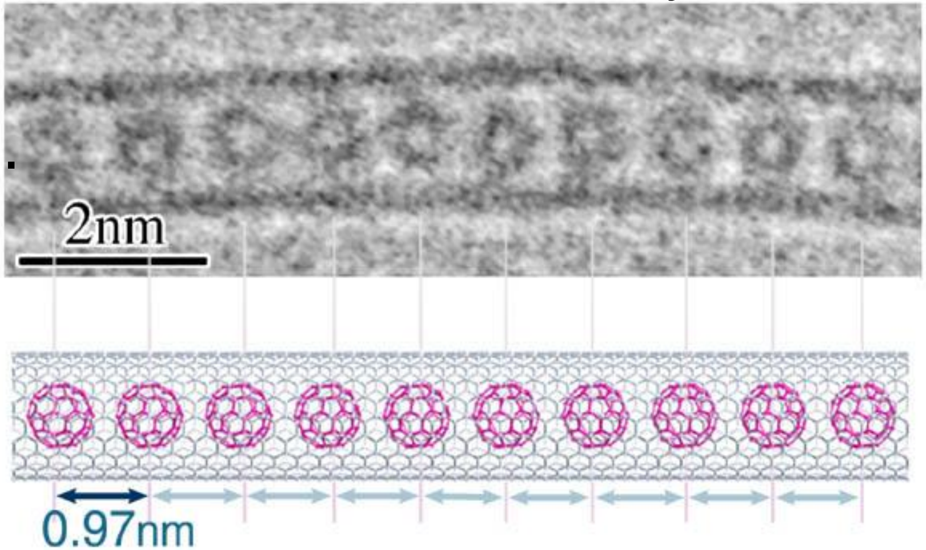
J. Gavillet et al.
Carbon (2002).

Growth Mechanism

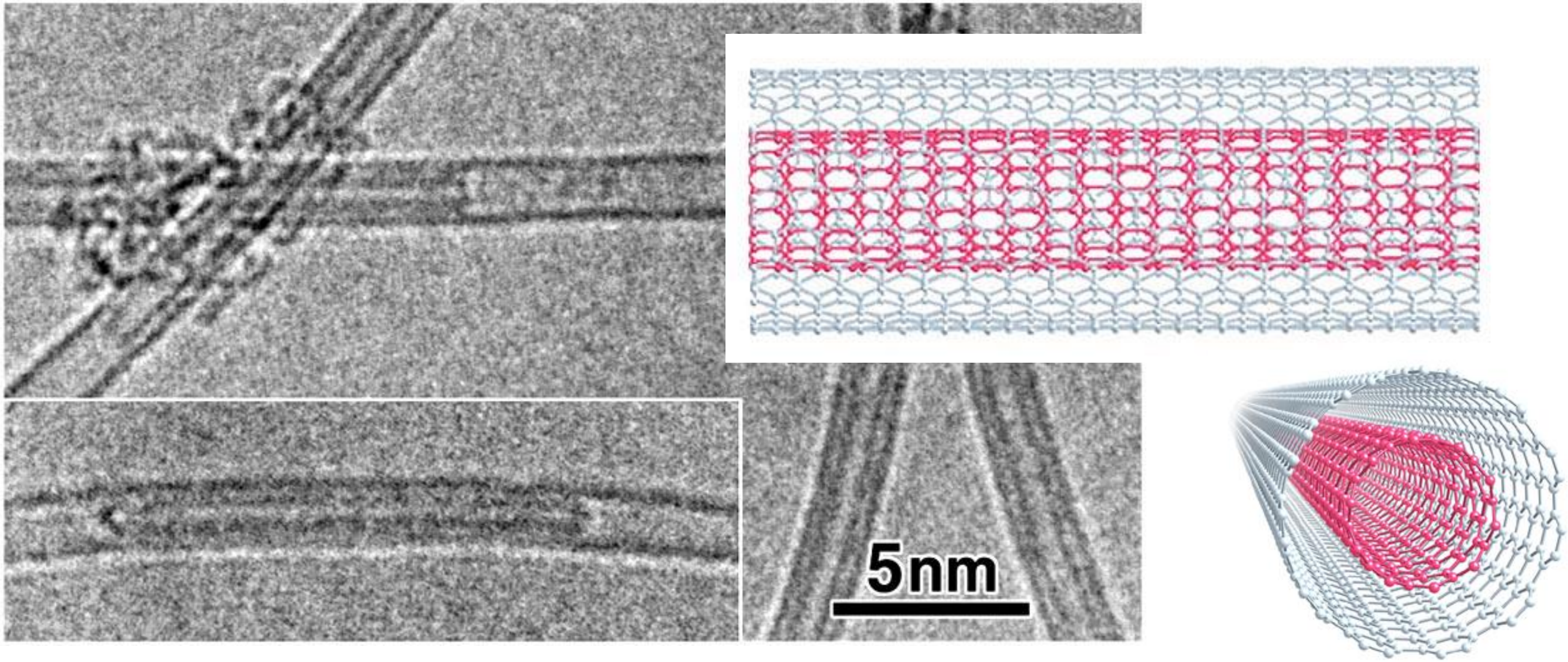
Bandow et al. Chem. Phys. Lett. 2001

Evidence of Template Growth.

- *Phase diagram?*
- *Catalyst?*
- *New type?*



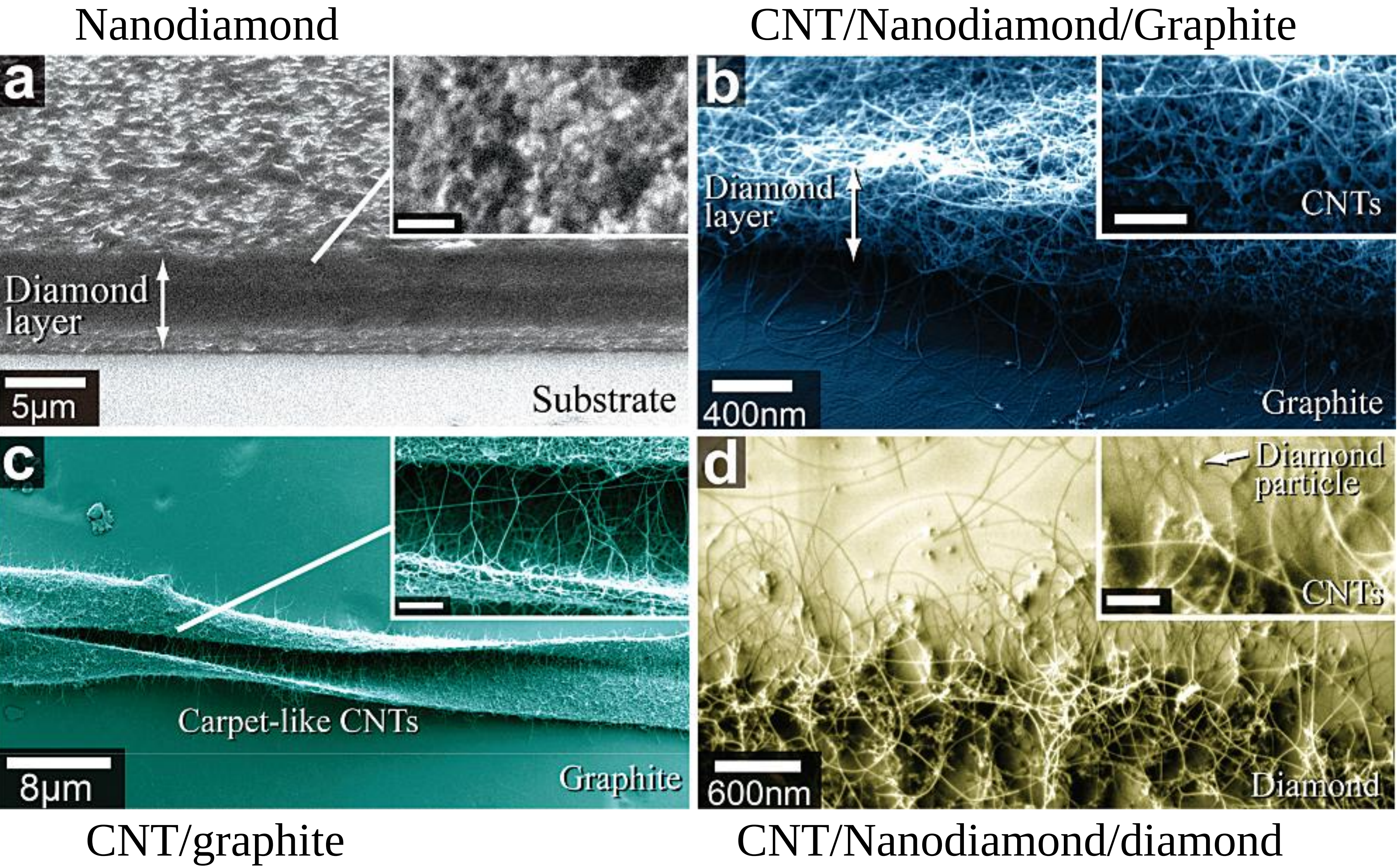
HT 1200ºC

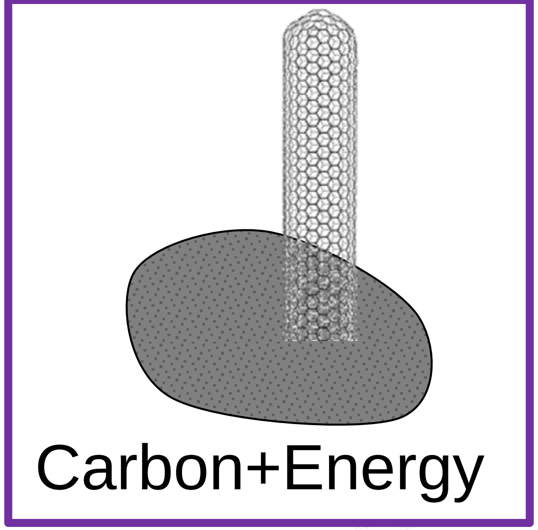


Carbon Nanotube Growth from Diamond

Takagi, Kobayashi, Homma, JACS 2009

EtOH CVD 850ºC



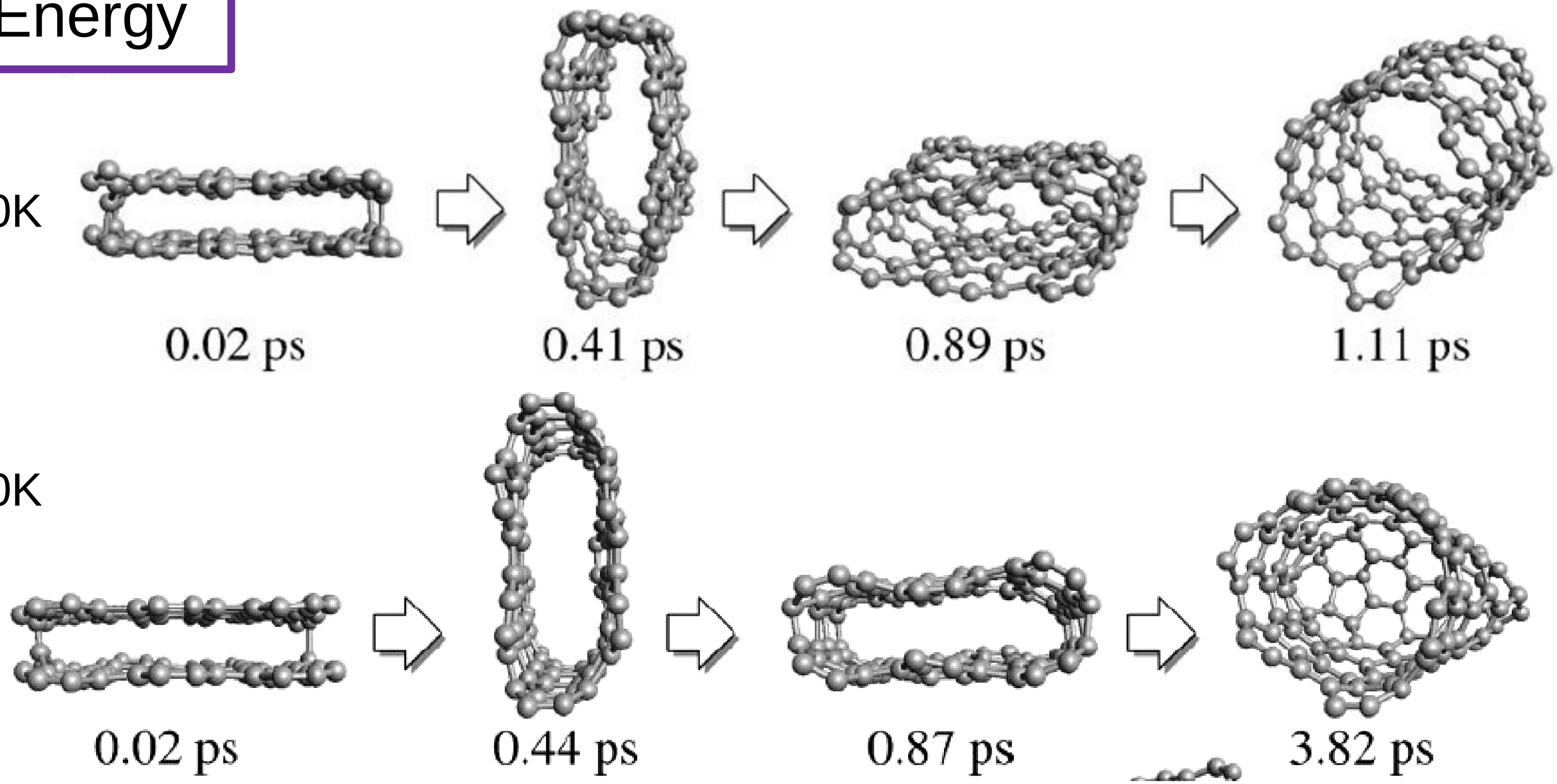


Nucleation of SWNT Growth Without Metal Catalysts and Templates.

Kawai et al. *Phys. Rev. B* **66**(2002)033404

0.21 nm, 2000K

0.21 nm, 1000K



Cap formation probability is about 50% at 1000K.
It decreases at higher temperature.

* Zhang &Crespi *PRB* **45**(1992)12227

SWNTを製造するためには,

- 炭素(源)を供給する。
- 反応エネルギーを与える。

・ 金属触媒の粒子を作る(溶解・析出）

SWNT　直径1~2 nm, (MWNT;　直径3~20 nm)

・ 鋳型を使う（表面同士の相互作用）

Channels in $AlPO_4$-5　(Z.K. Tang et al, Nature 408(2000)50 Appl. Phys. Lett. 73(1998)2287.) *Metal free growth : Pyrolyzing tripropylamine in the channels of the zeolite crystals. 0.4-nm SWNTs are formed which show superconductivity.*

SiC, SWNT, Diamond, et al

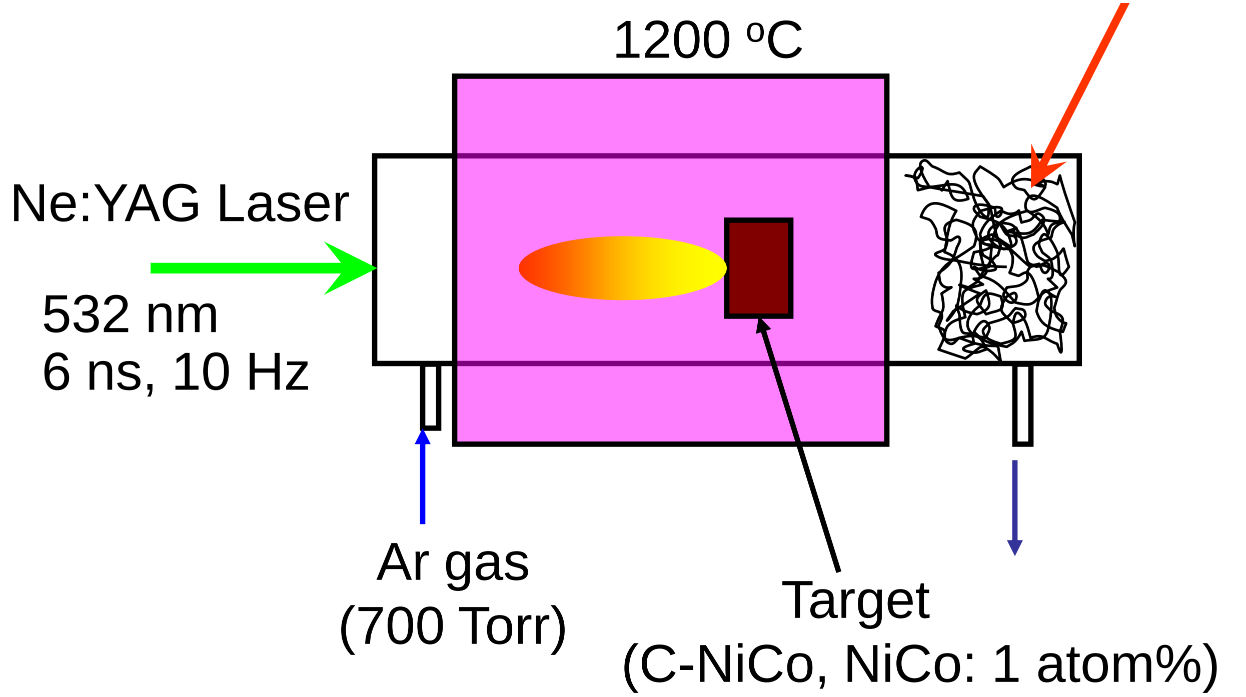
レーザーアブレーション法
アーク放電法
CVD法

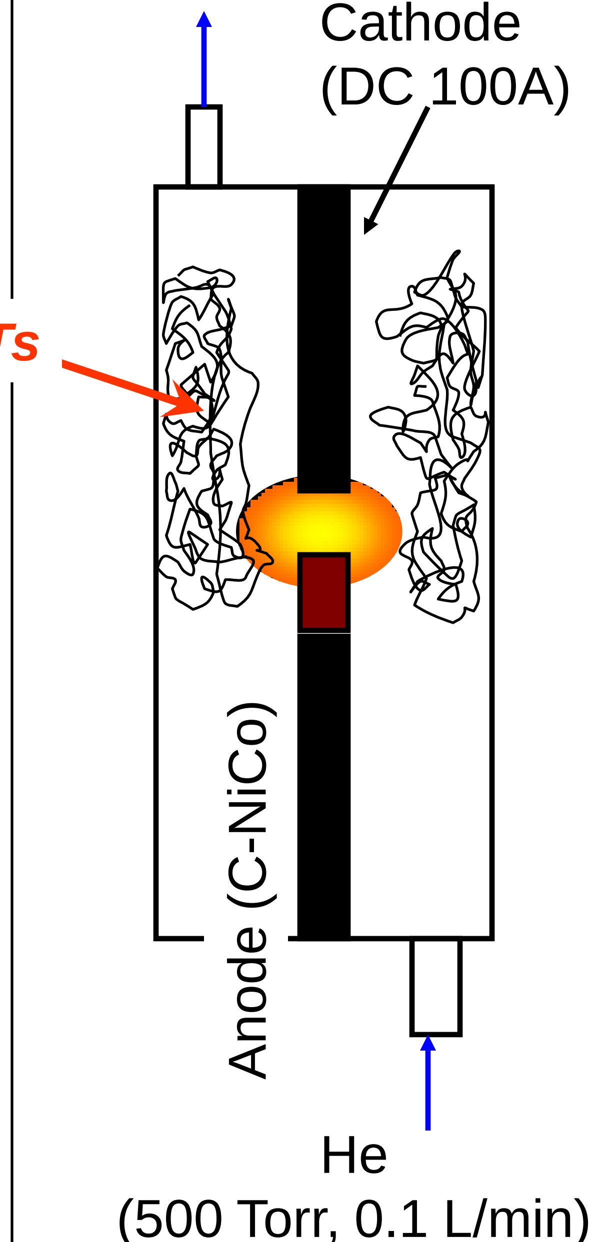
Formation of Single-Wall Carbon Nanotubes by Laser Ablation and Arc Discharge

Production rate: ~50 mg/h

Purity : 20~30%

Tube diameter : 1.2~1.5 nm





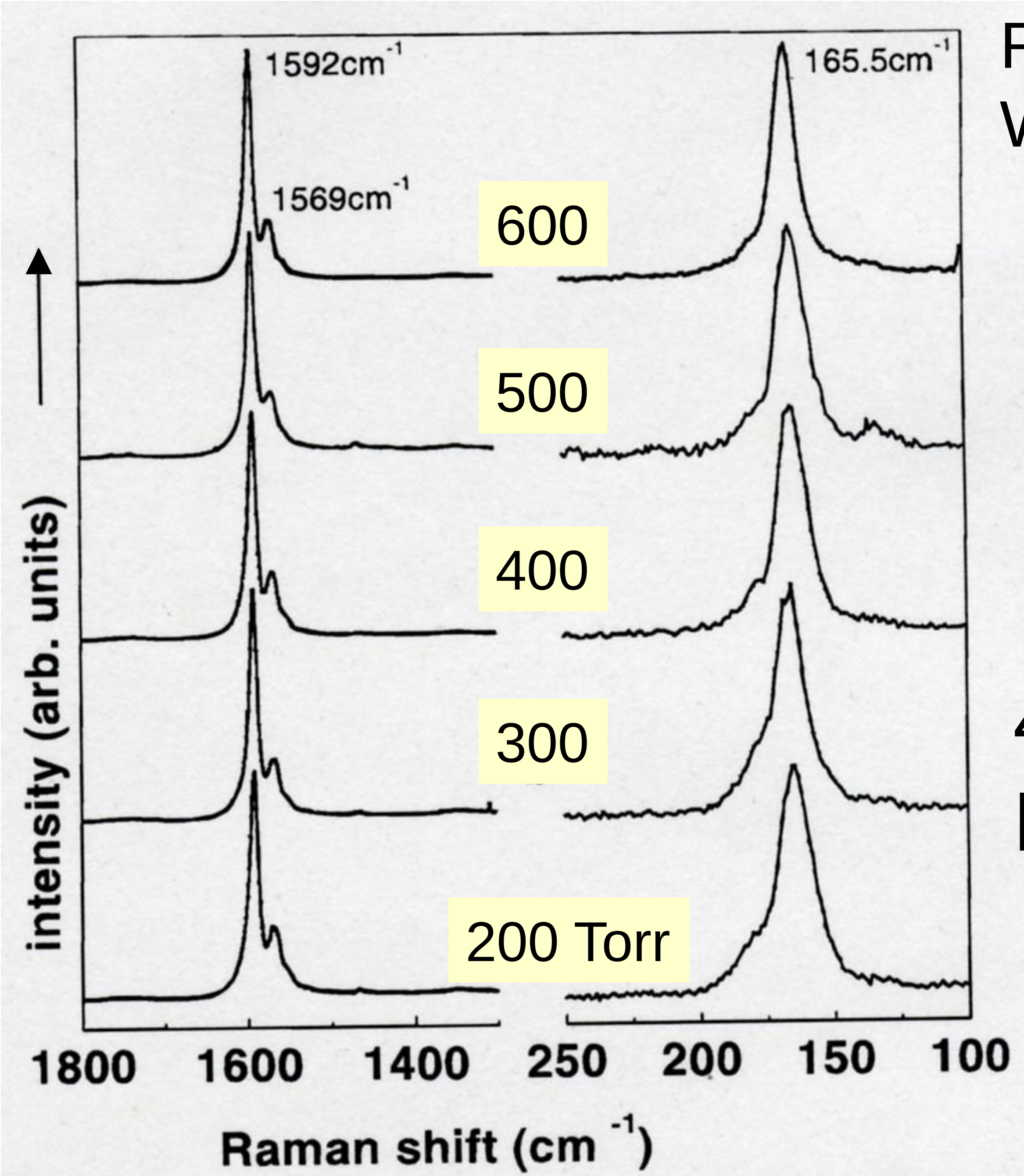
Guo et al. *Chem. Phys. Lett. 243*, 49, **1995.**

Thess et al. *Science 273*, 483, **1996**.

010614a

H.Dai et al.
Chem. Phys. Lett. 260(**1996**)471.

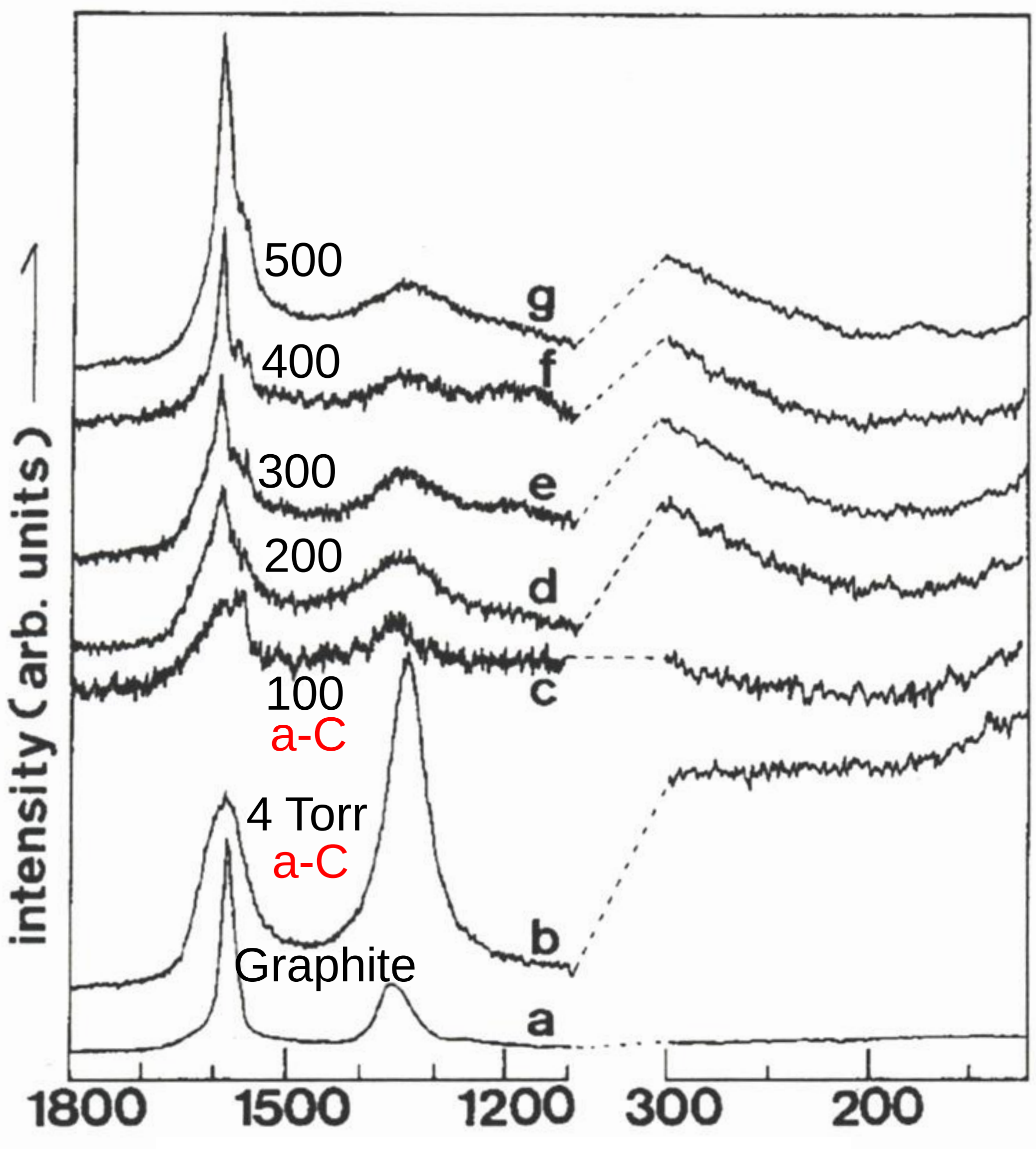
Raman spectra of Web-like deposits



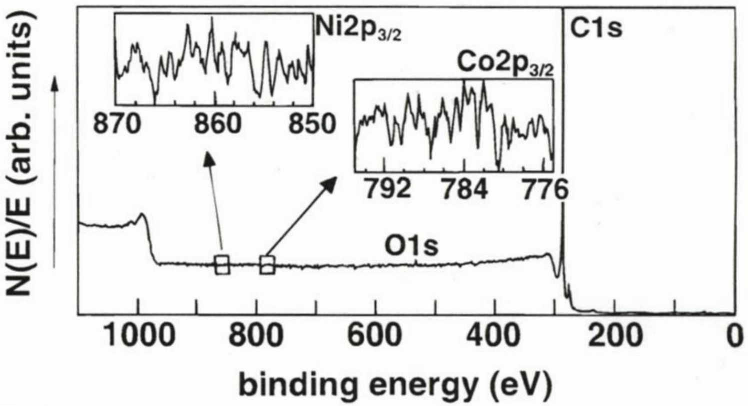
4 and100 Torr
No SWNTs.
?

Yudasaka et al JPCB 1998

Deposits in front of targets

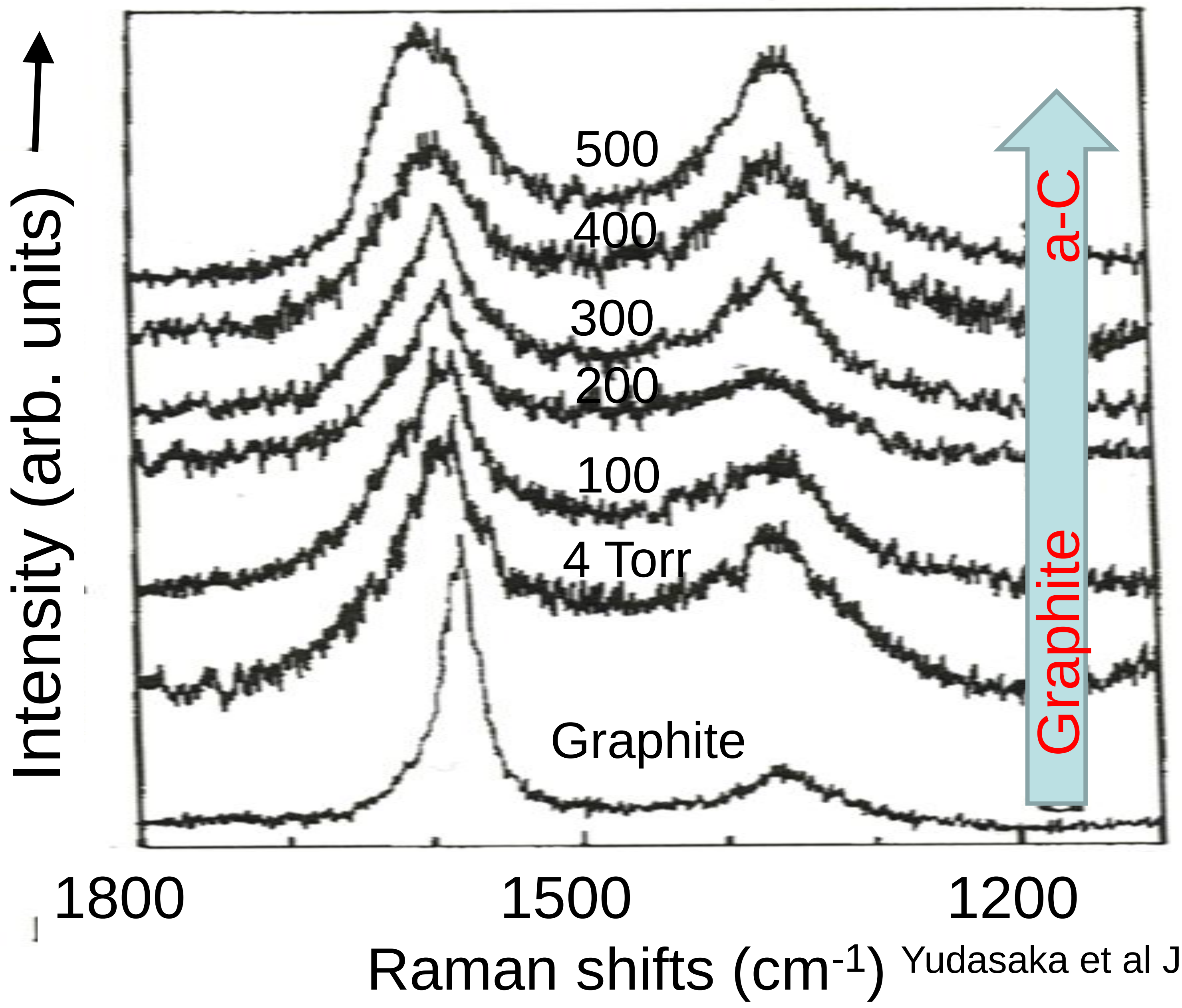


XPS: Ni, Co not exist on
Deposits at 4 Torr

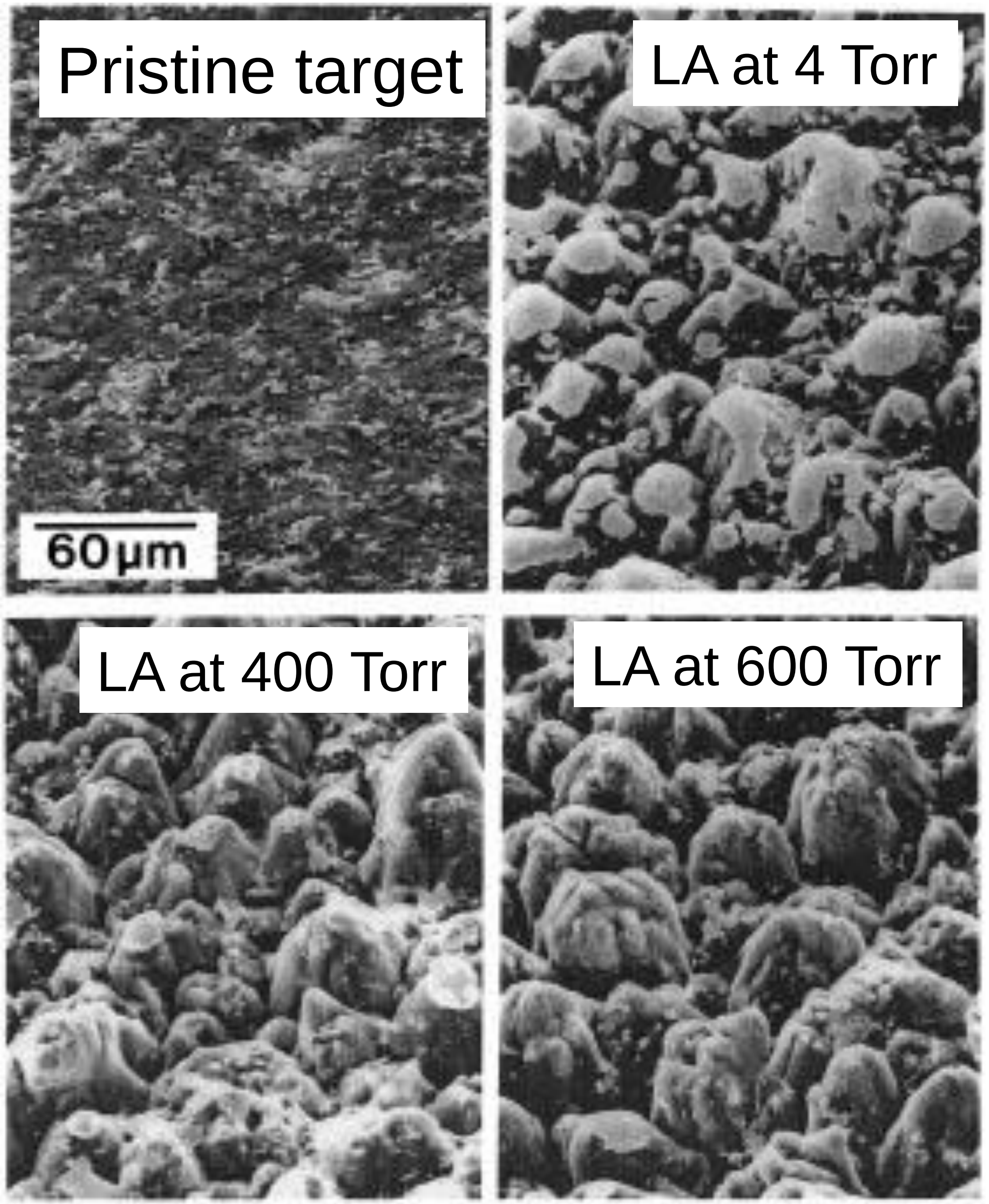


Yudasaka et al JPCB 1998

Raman spectra of graphite targets

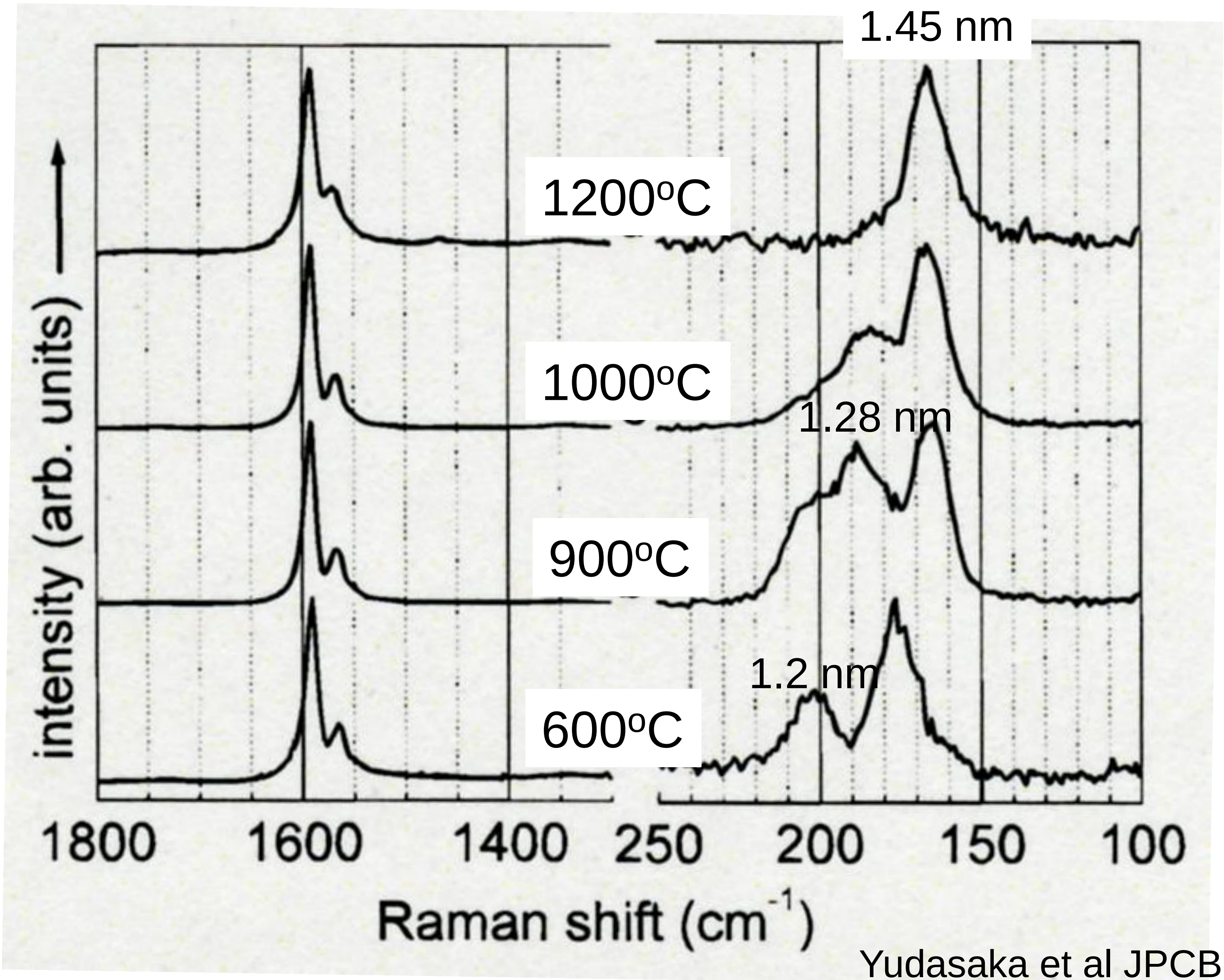


Yudasaka et al JPCB 1998

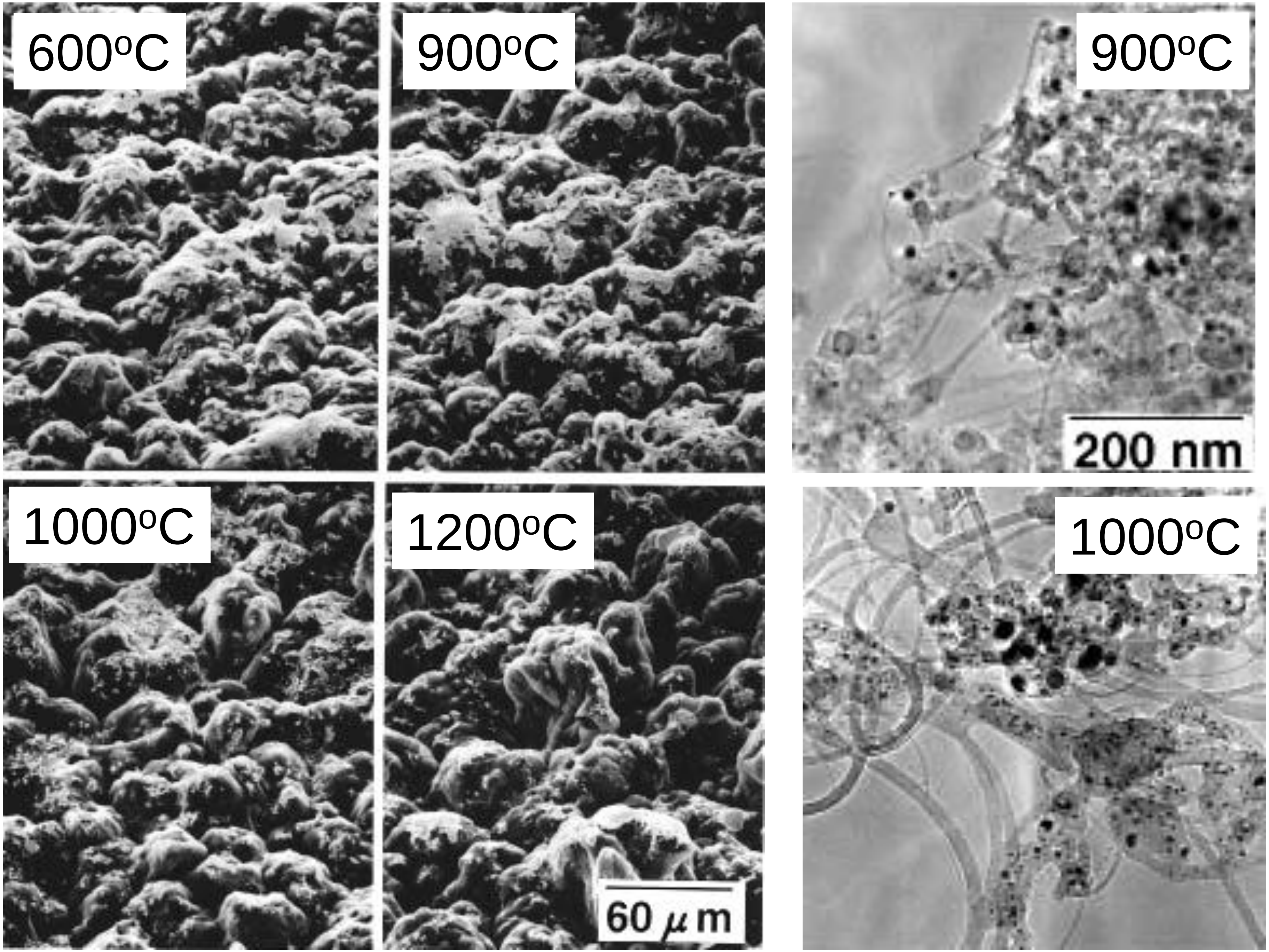


Yudasaka et al JPCB 1998

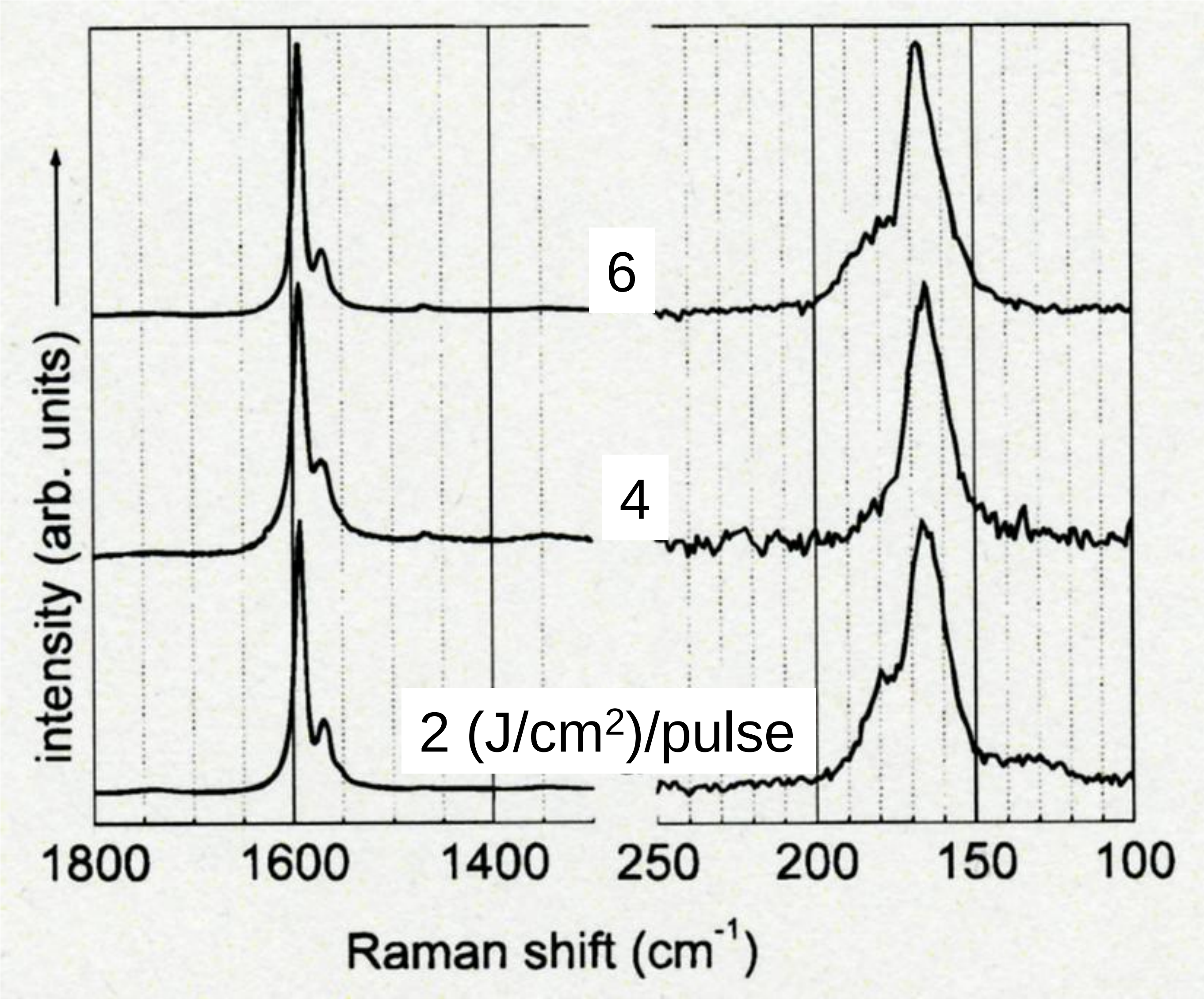
SWNT diameter decreased with ambient temperature.

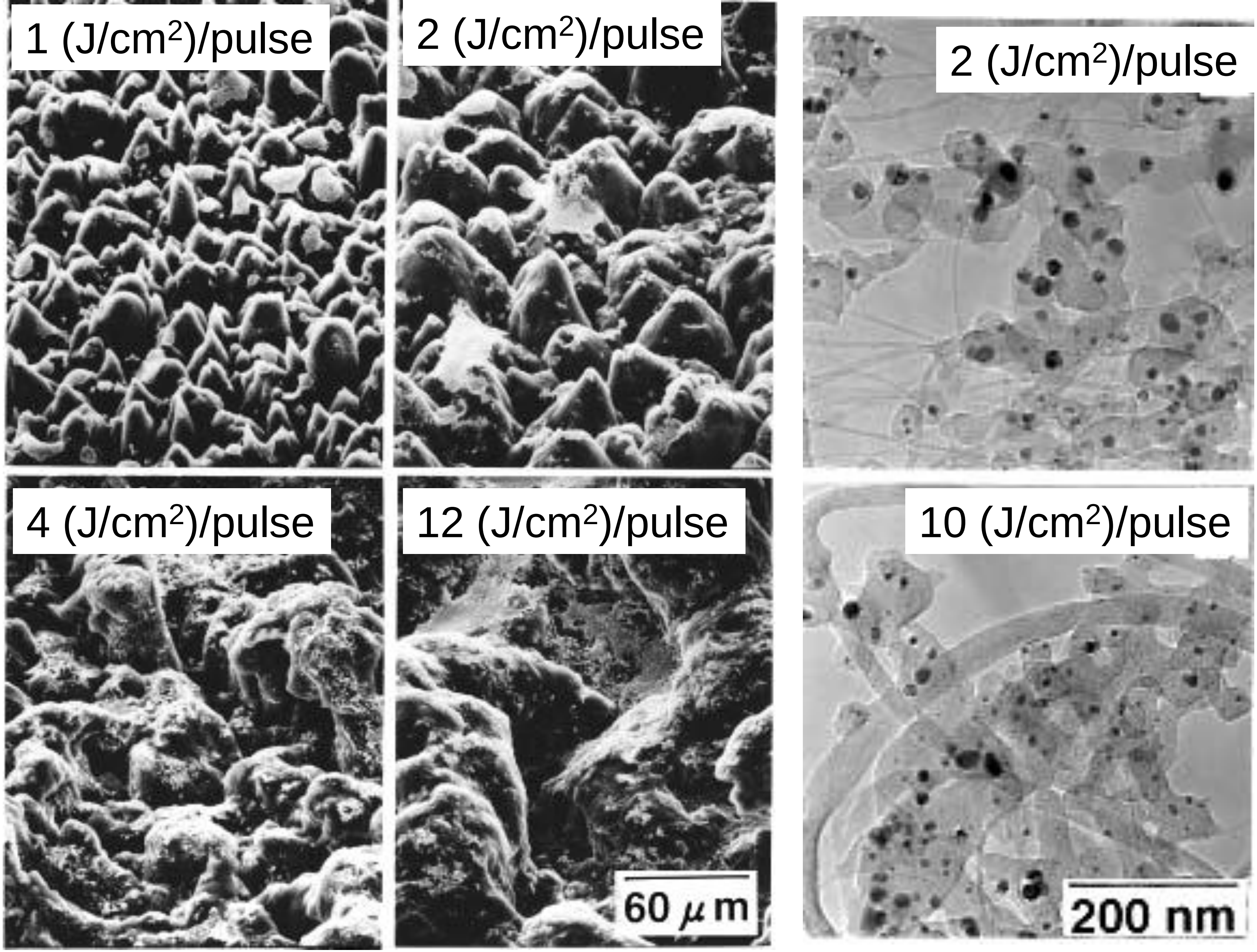


Yudasaka et al JPCB 1998


600oC
900oC
1000oC
1200oC
60 μm
900oC
200 nm
1000oC

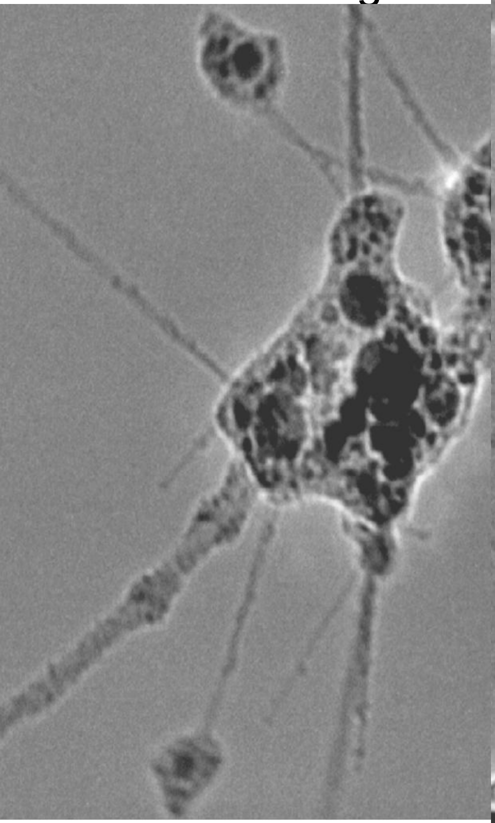
SWNT diameters did not depend on laser power intensity



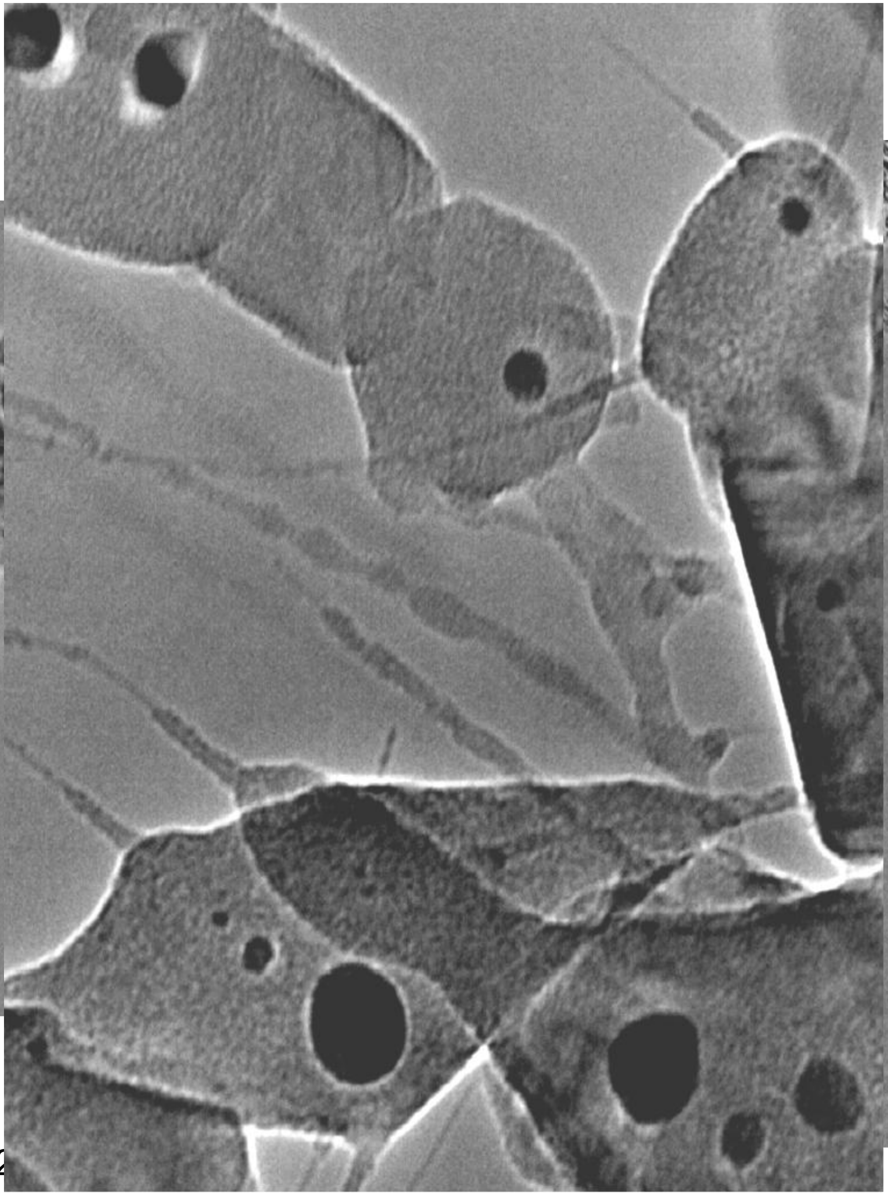

1 (J/cm2)/pulse
2 (J/cm2)/pulse
2 (J/cm2)/pulse
4 (J/cm2)/pulse
12 (J/cm2)/pulse
60 μm
10 (J/cm2)/pulse
200 nm

Nucleation and Growth of SWNTs
Individual SWNTs Start to Grow from a-C Having Metal Particles Inside

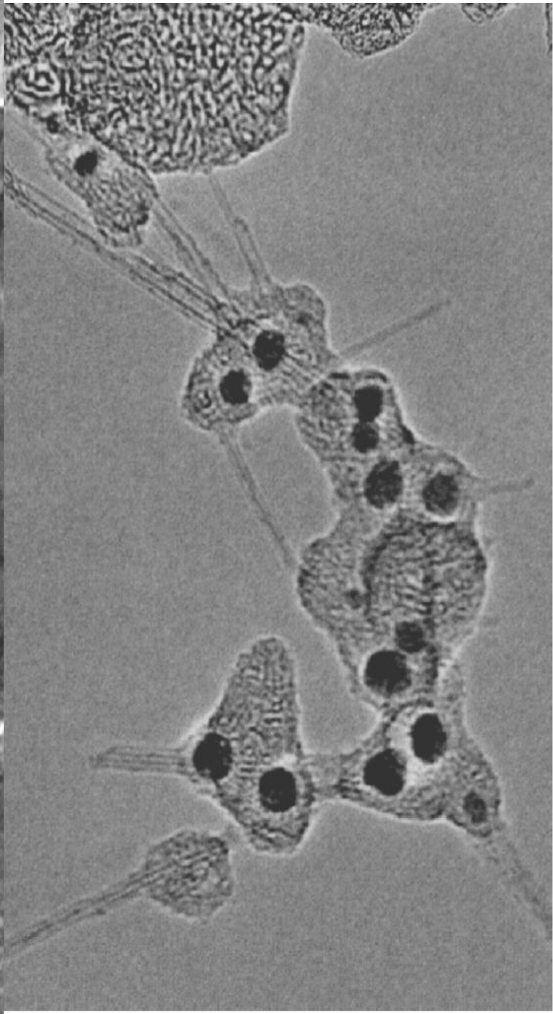
Arc discharge



Nd:YAG laser ablation

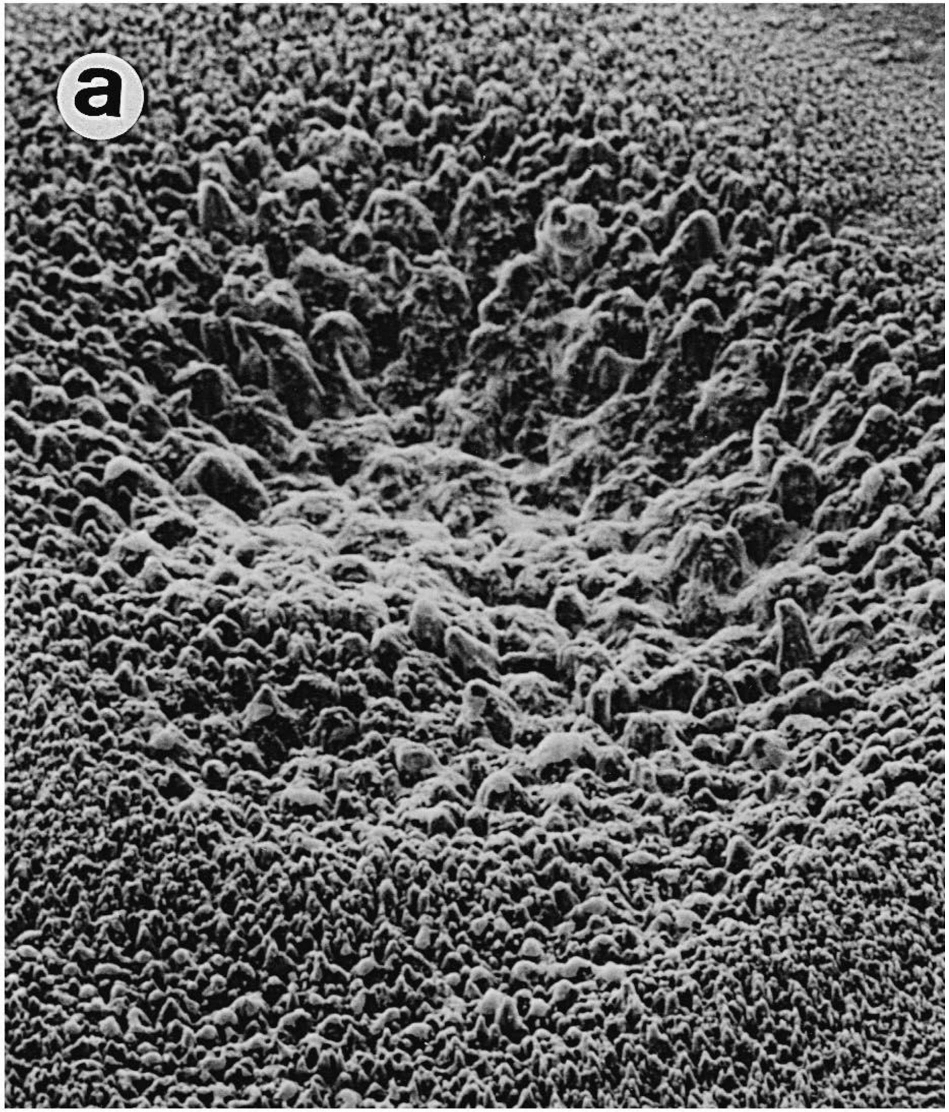


CO_2 laser ablation

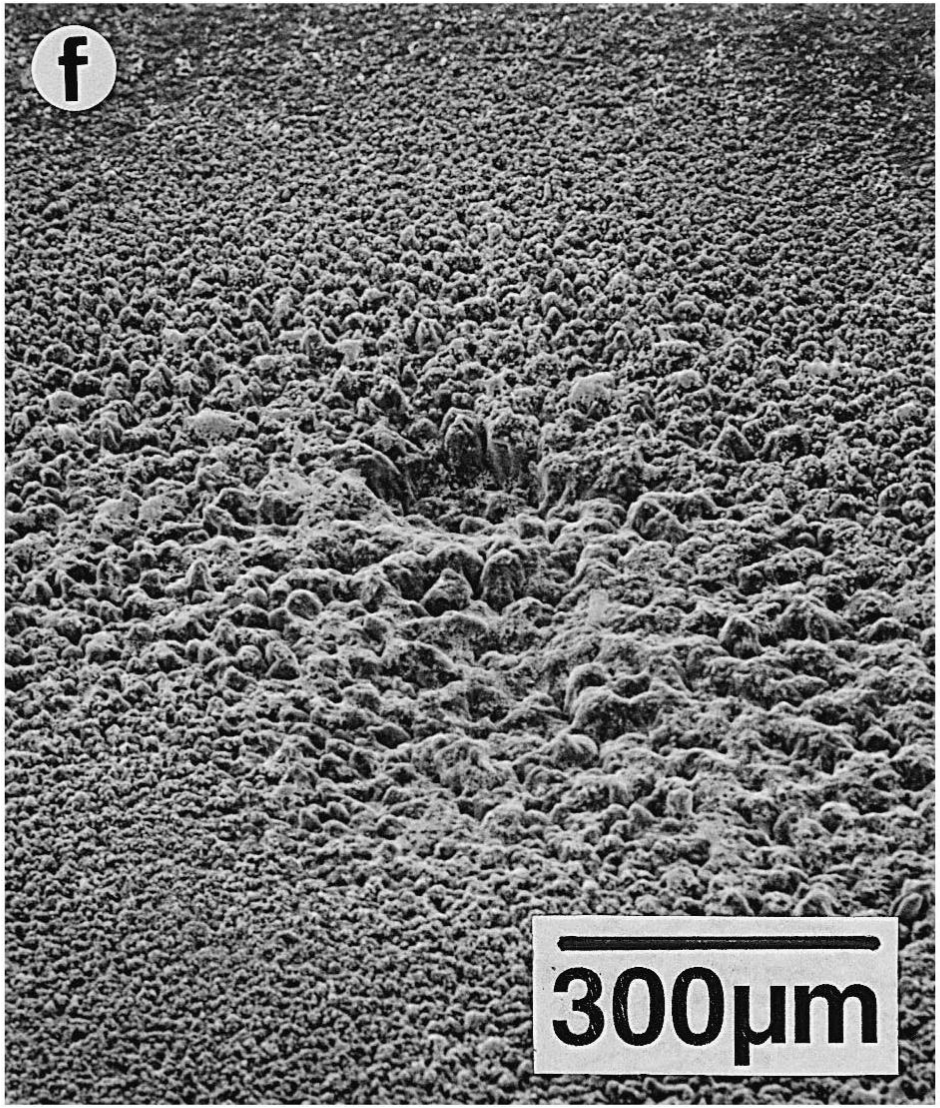


Pulse-pulse intervals (Total 150 pulses)

0.1 s

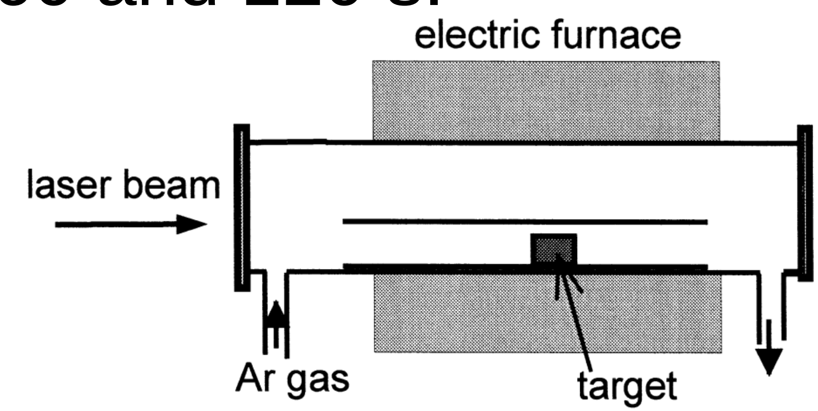


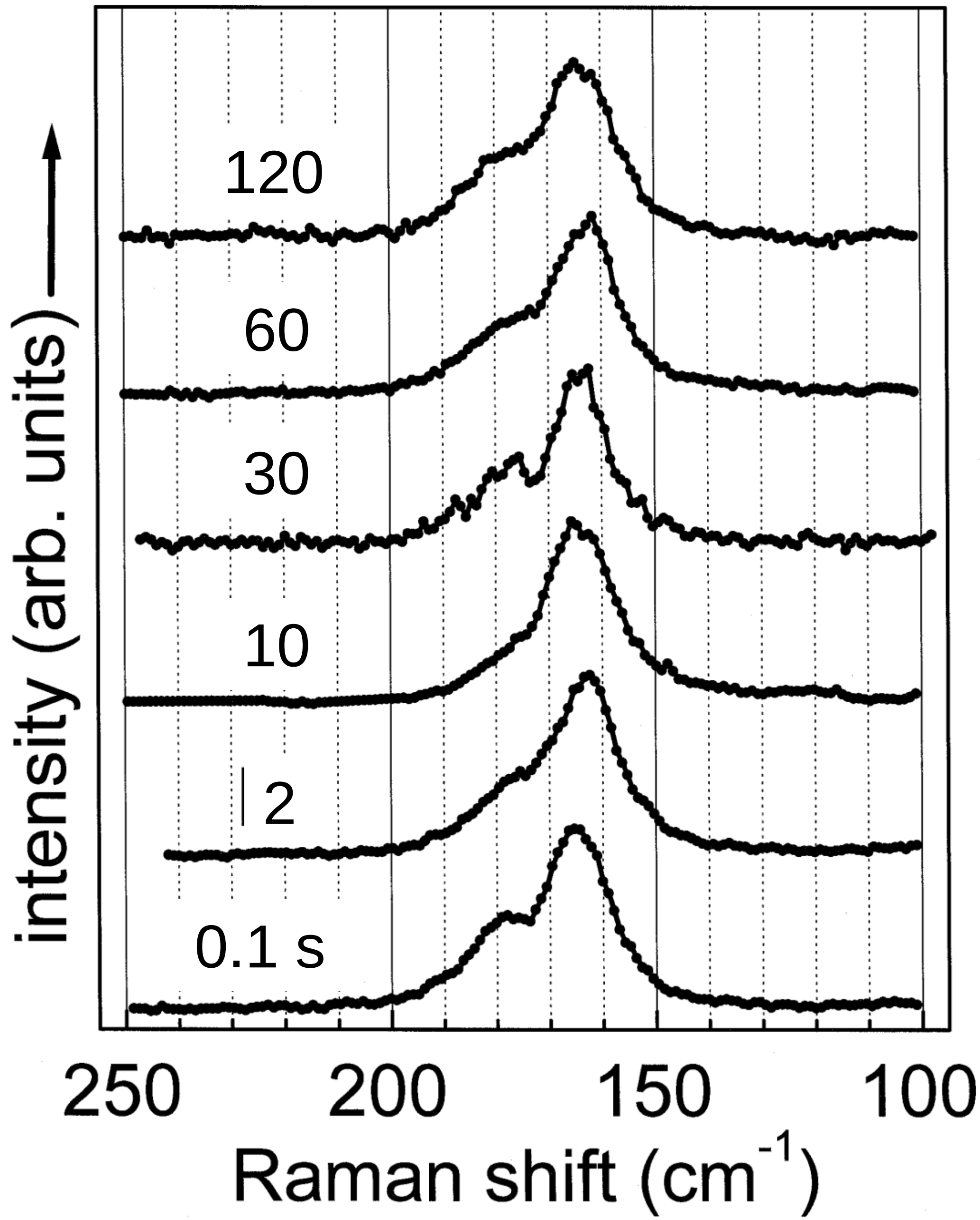
120 s



Nd:YAG laser
Wavelength 532 nm
Pulse width 6–7 ns
Frequency 10 Hz

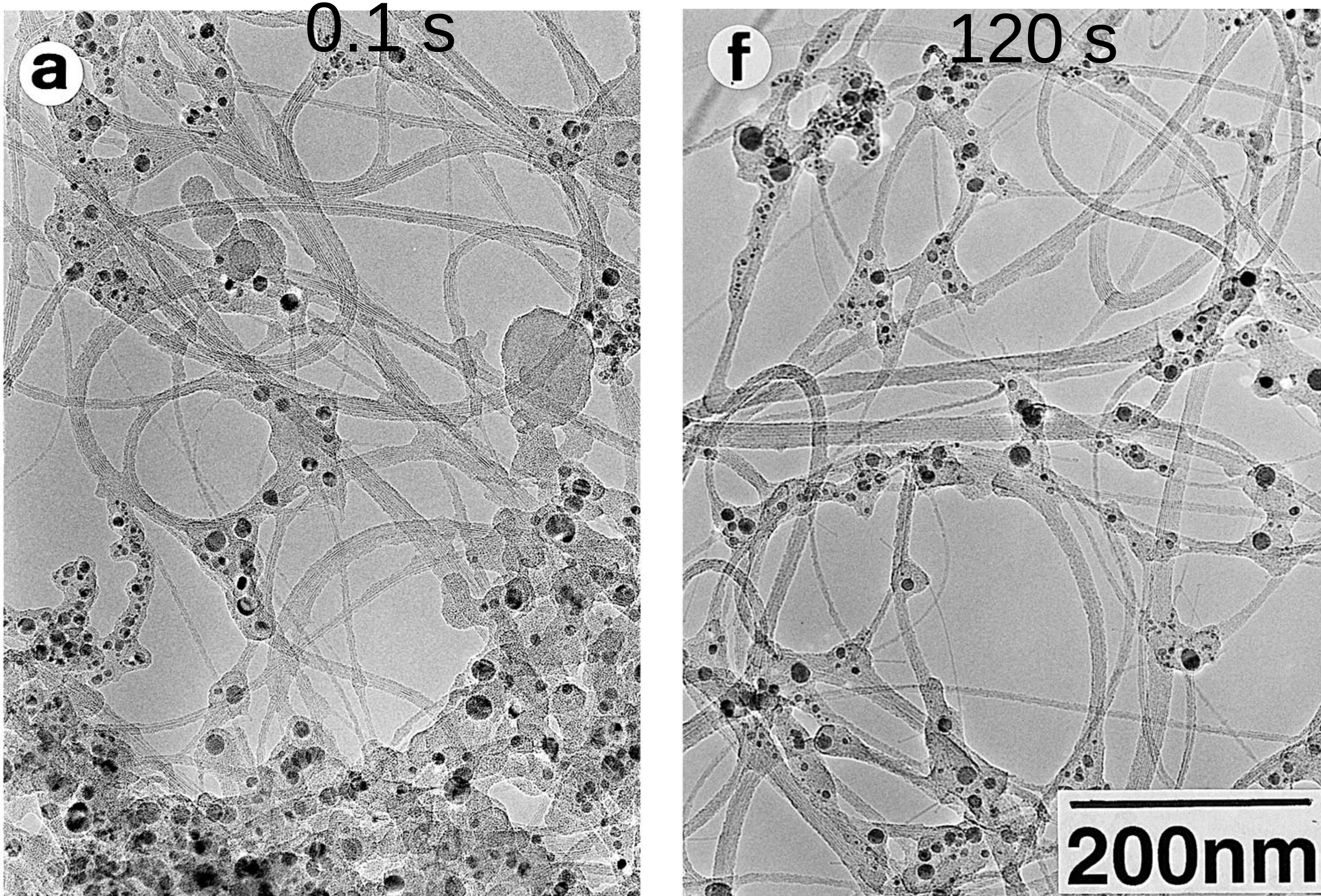
150 pulses
Pulse–pulse intervals
0.1, 2, 10, 30,
60 and 120 s.



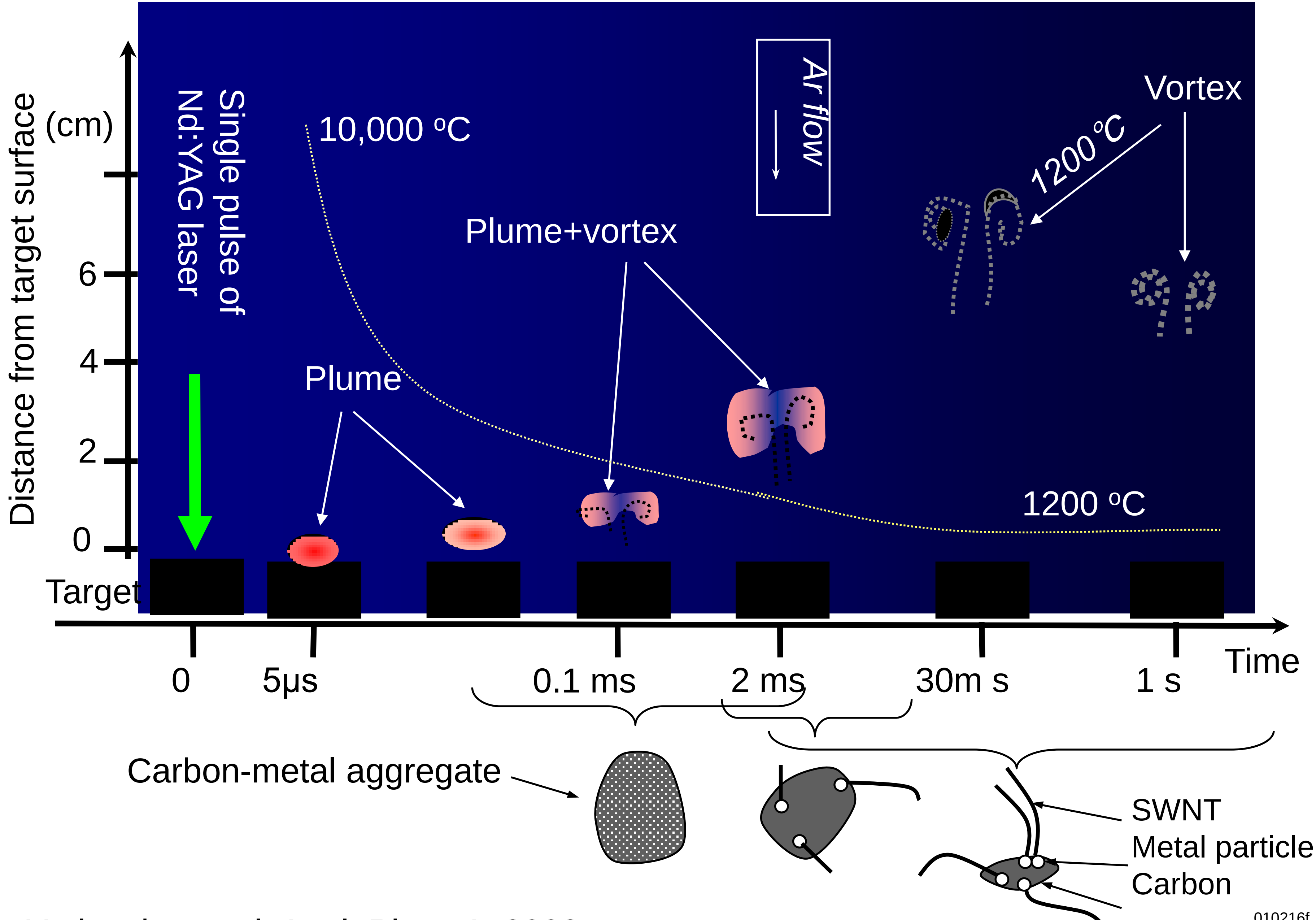


Yudasaka et al Chem. Phys Lett. 1999

Pulse-pulse intervals (Total 150 pulses)



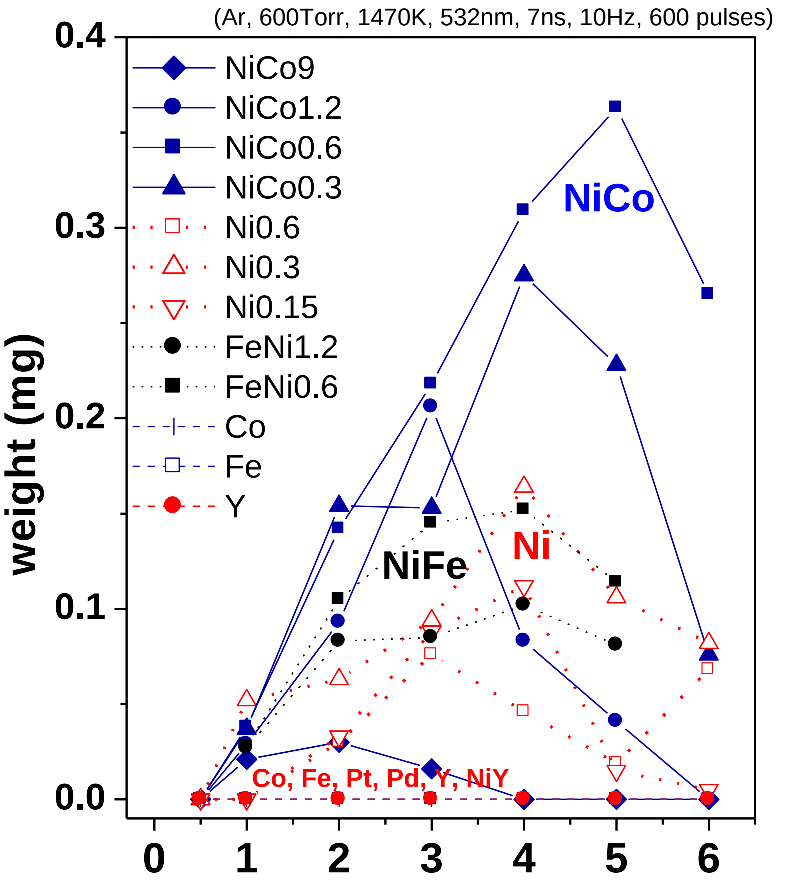
Nucleation and Growth of SWNTs by Single-Pulse of Nd:YAG Laser



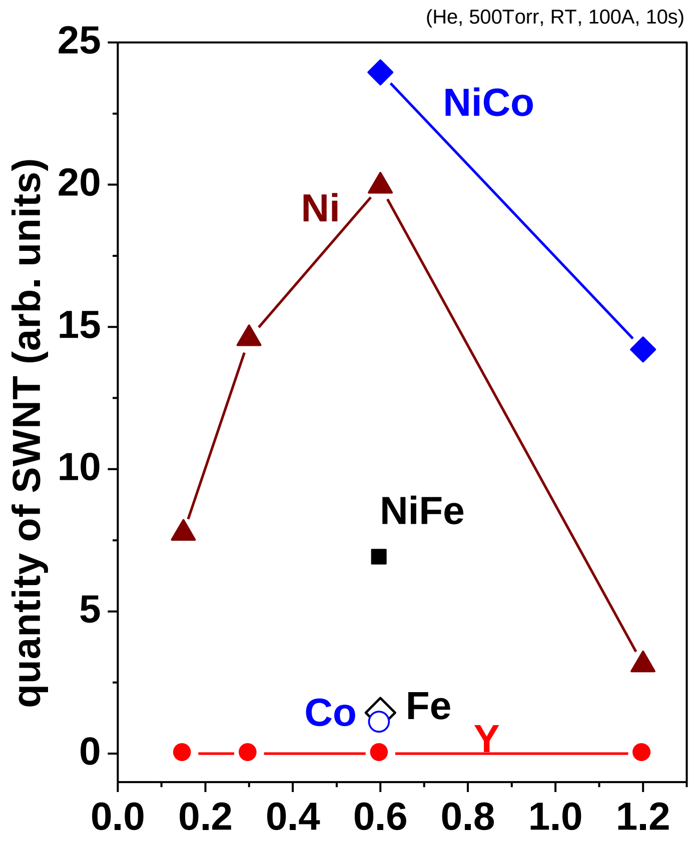
Yudasaka, et al. Appl. Phys. A 2002

NiCo, Ni, and NiFe Are Effective Catalysts. Co, Fe, and Pt Are Poor Catalysts.

Quantities of web-like deposits formed by Nd:YAG laser ablation



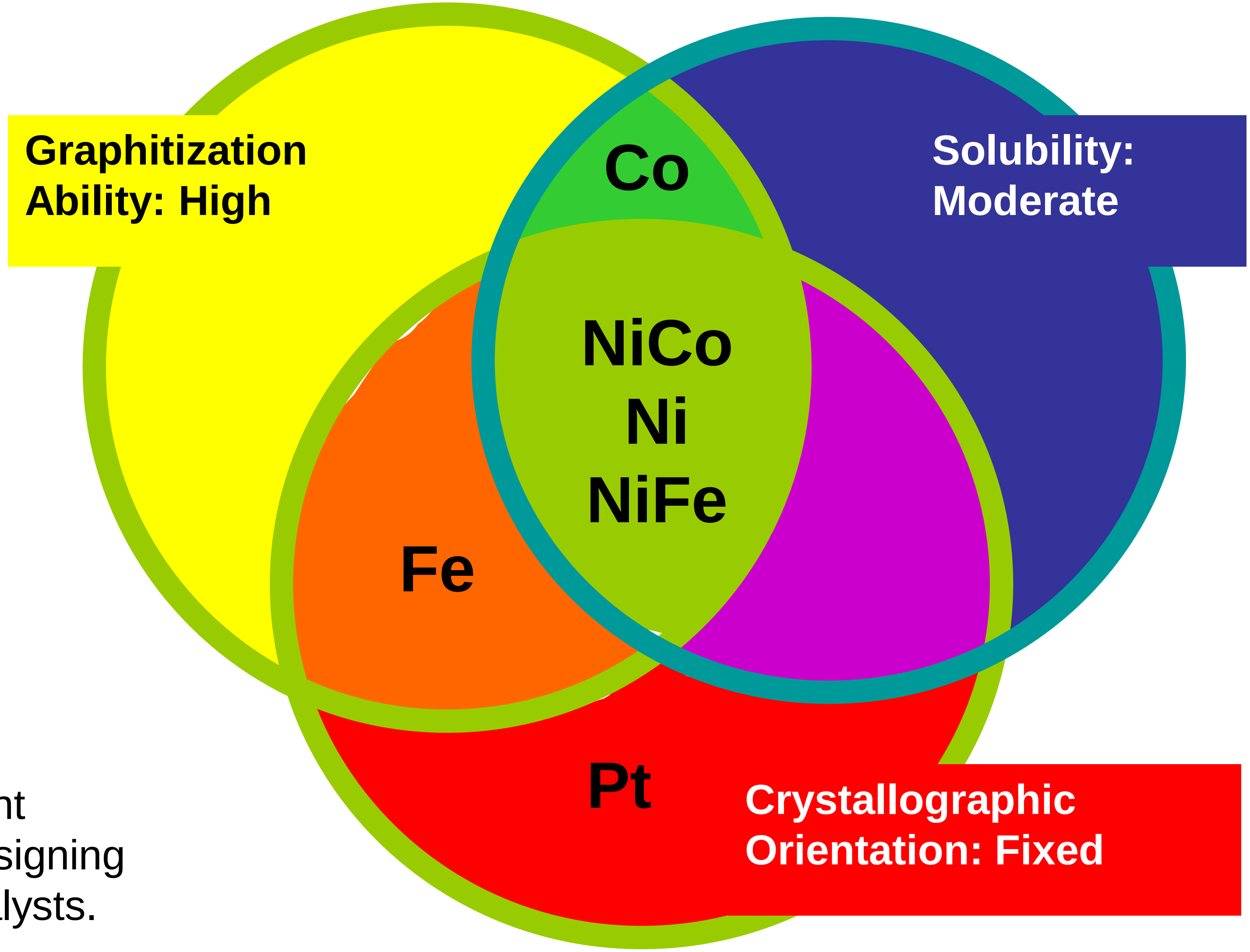
Quantities of soot containing SWNTs formed by DC arc discharge using $C_{100-x}M_x$ or $C_{100-2x}M_xN_x$ anodes



001208c

Yudasaka et al . J. Phys. Chem. B

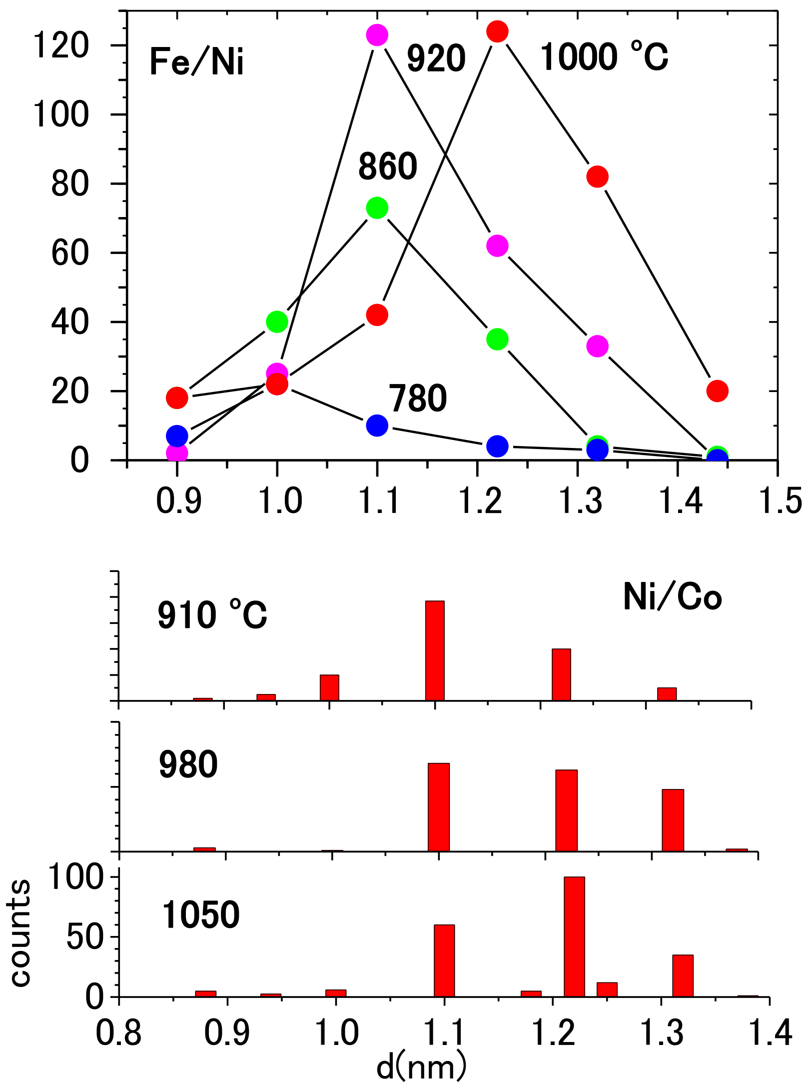
Yield of SWNTs Are Controlled by Three Factors of Metal-Carbon interactions



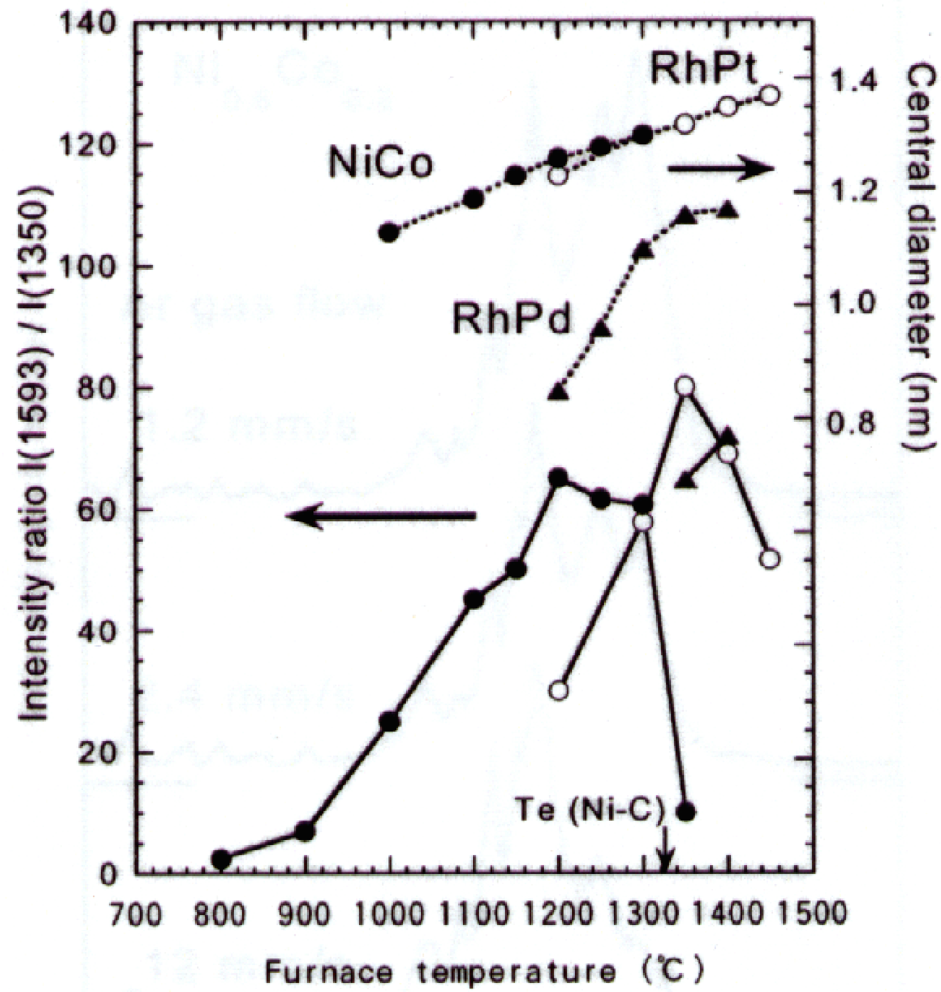
This study might be useful in designing new metal catalysts.

Diameter Control of SWNTs.
Possible by Choosing Formation Temperature or Metal Catalysts.

S. Bandow et al.
Phys. Rev. B 59 (1999) 2388.

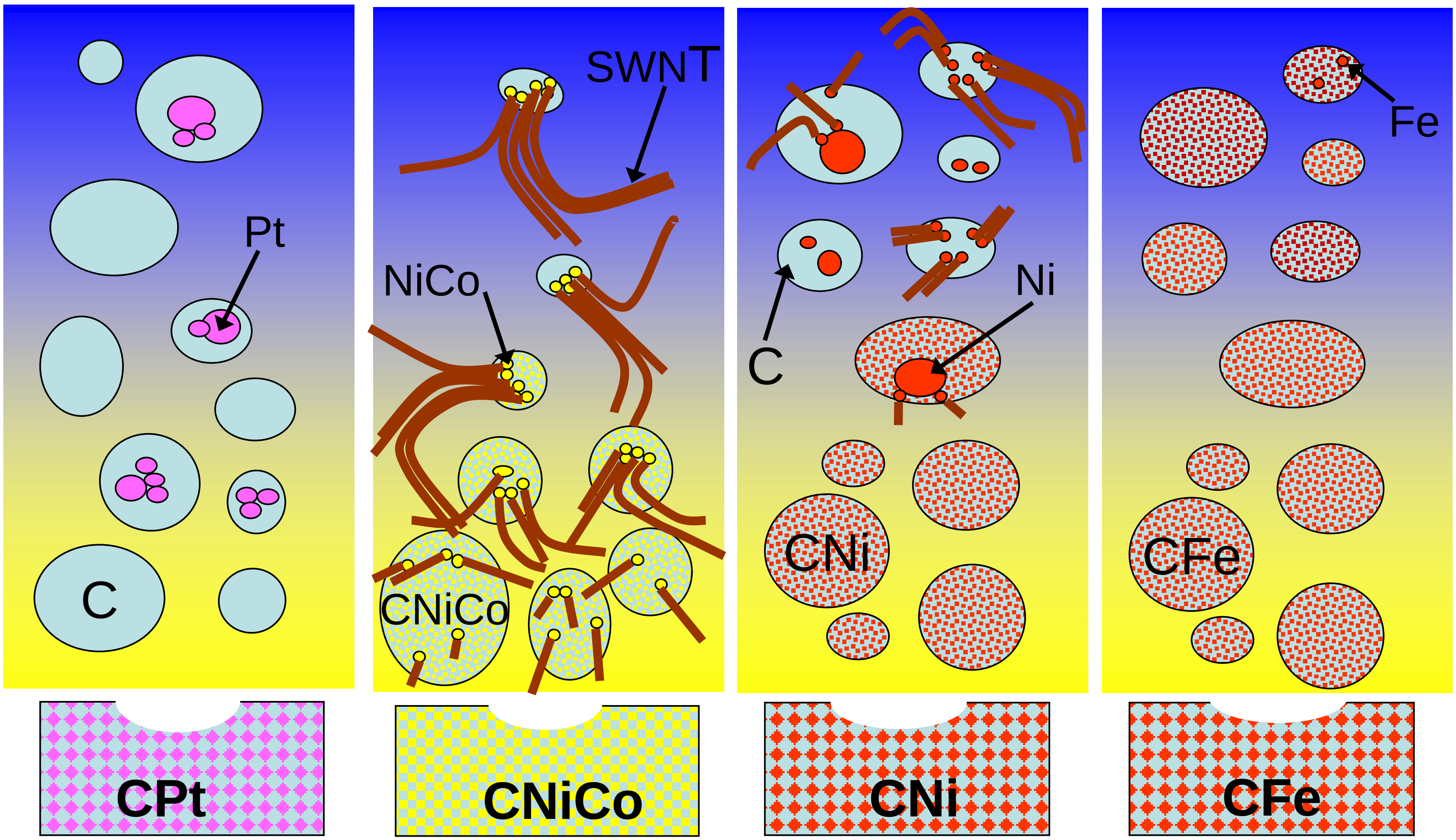


H. Kataura et al. Carbon 38(2000)1691.



010920 Ban Kataura Carbon

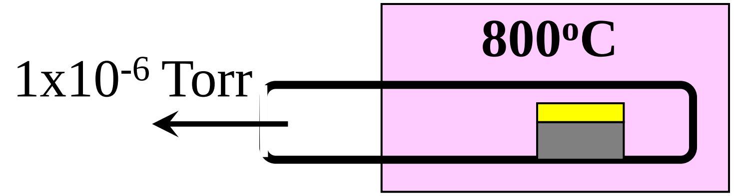
SWNT Growth Depending on Metal Catalysts



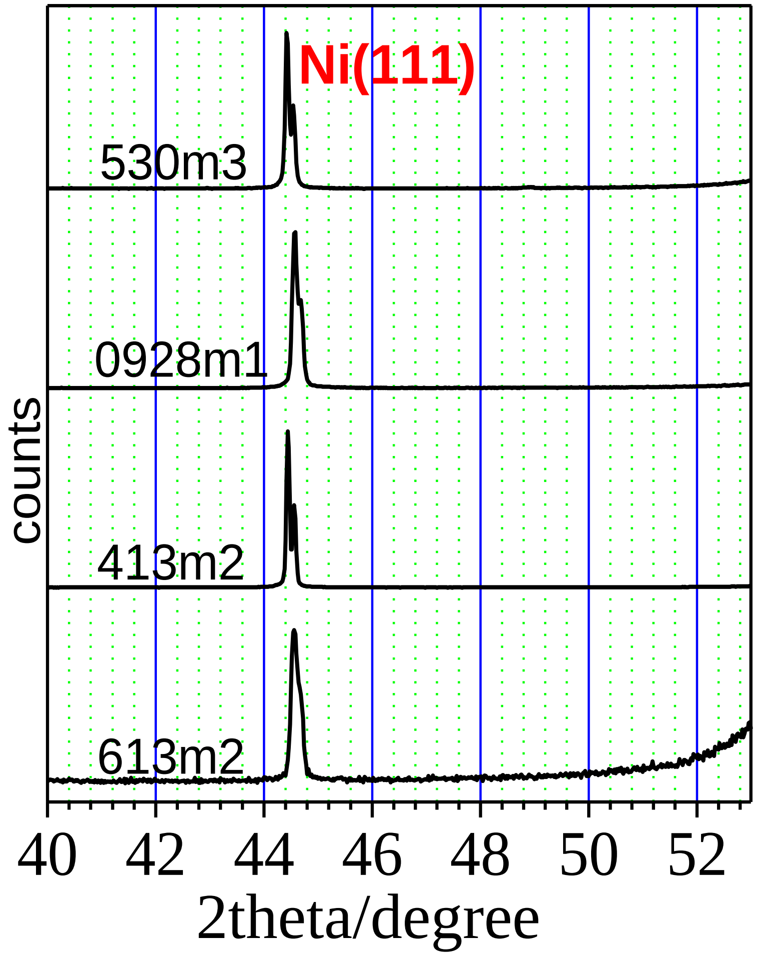
Yudasaka et al. J. Phys. Chem. B 1999

M. Yudasaka et al. Appl. Phys. A 74, 377(2002).

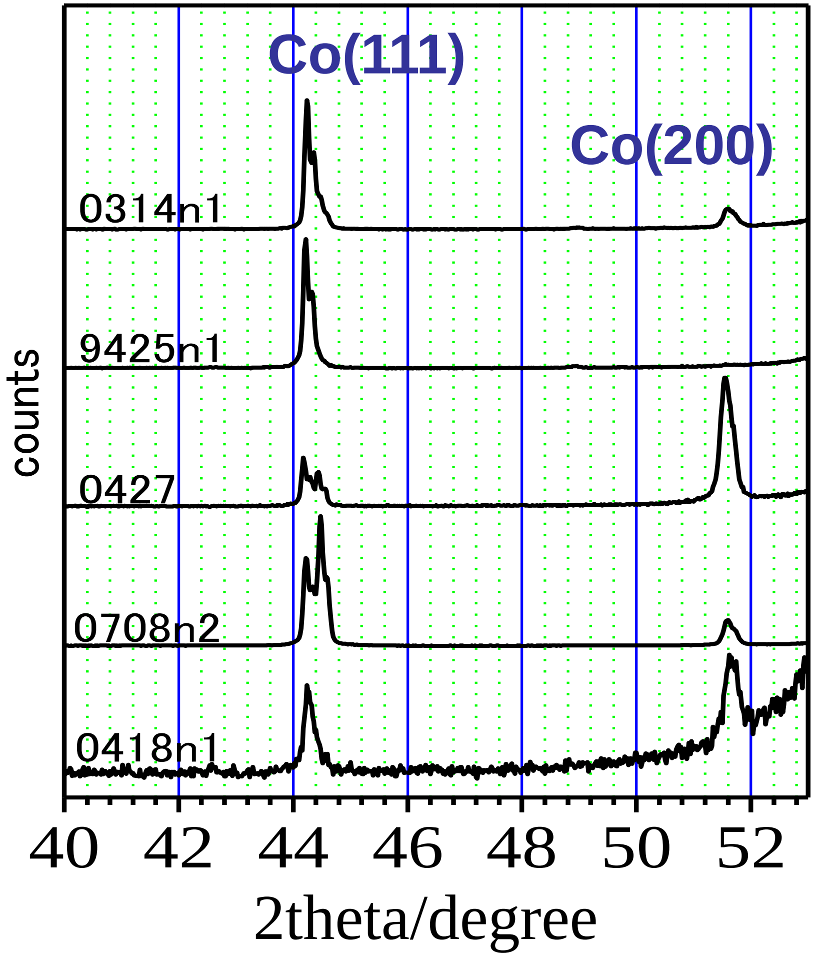
X-ray diffraction of Ni/Graphite and Co/Graphite



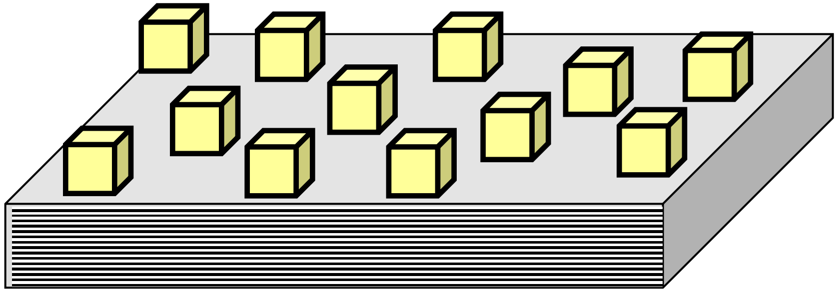
Heat treated at 800°C
REPRODUCEBLE



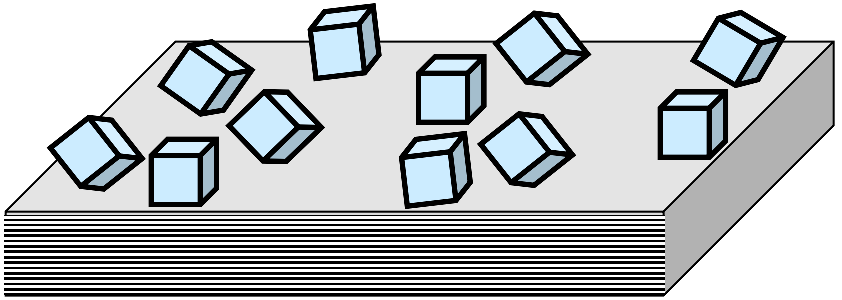
Heat treated at 800°C
***NOT** REPRODUCEBLE*



Crystallographic Orientations of Ni and Co on Graphite Surfaces.

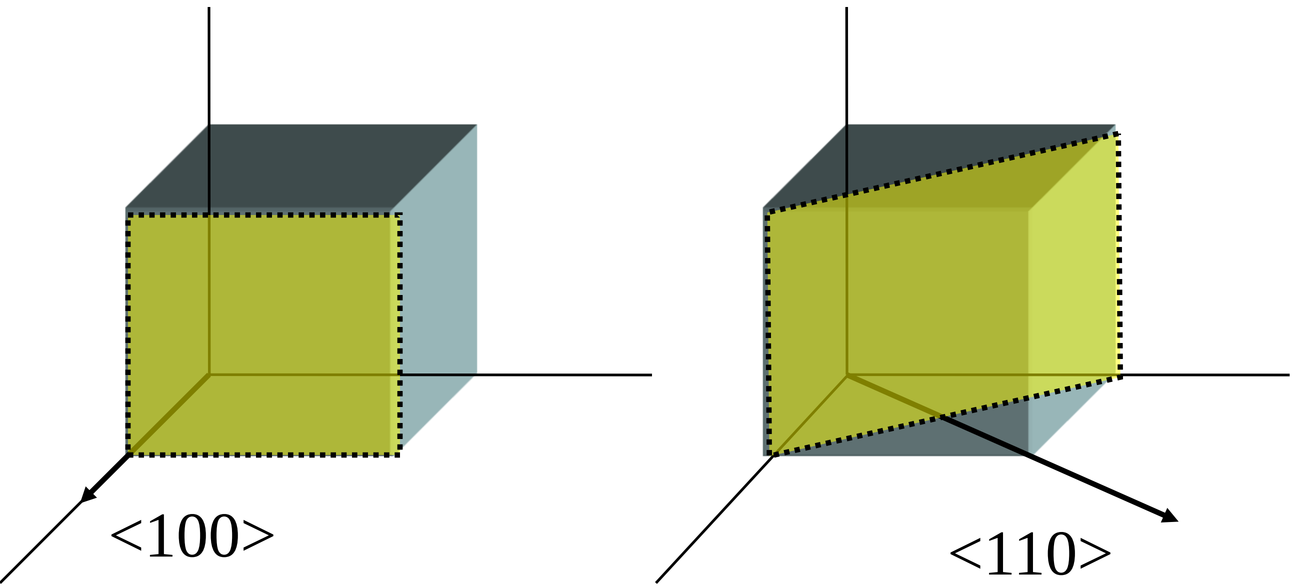


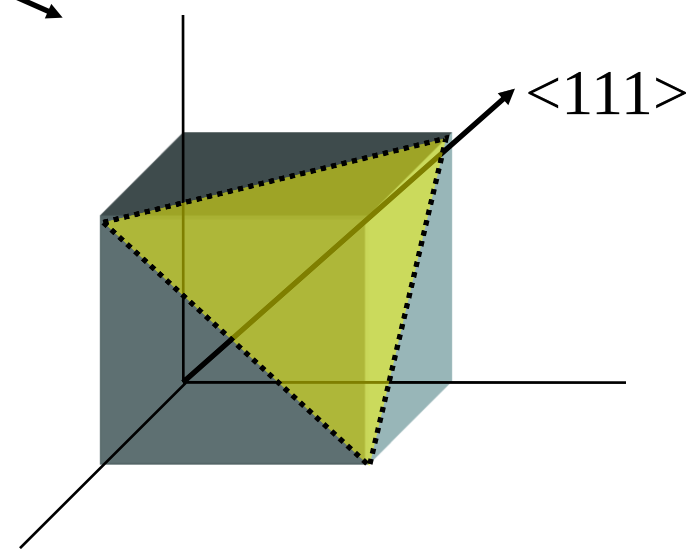
Ni/Graphite



Co/Graphite

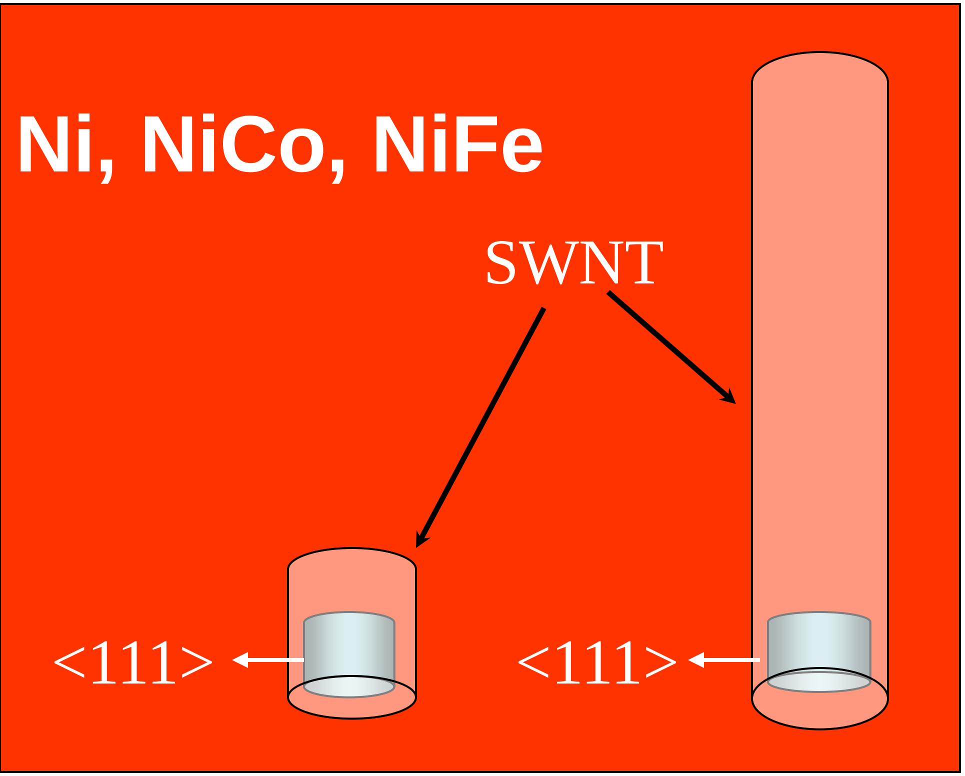
Graphitization Ability Depends on Crystallographic Faces of Metals

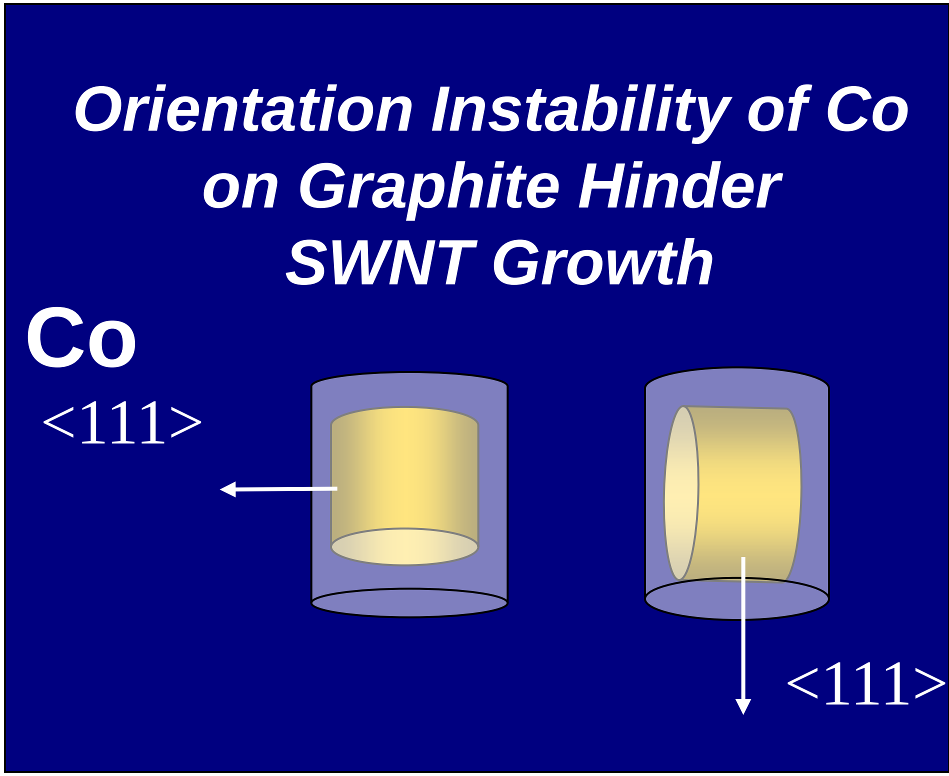




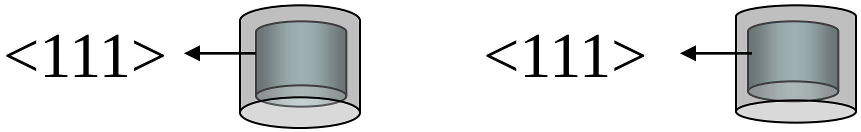
Not Clear Yet. But {100} or {110} may have the higher catalytic effect than {111}.

A. Presl and P. Walker, Carbon 1 (7) 1969.
M.Yudasaka et al. JVST A, 2463 (16) 1998.





Pt



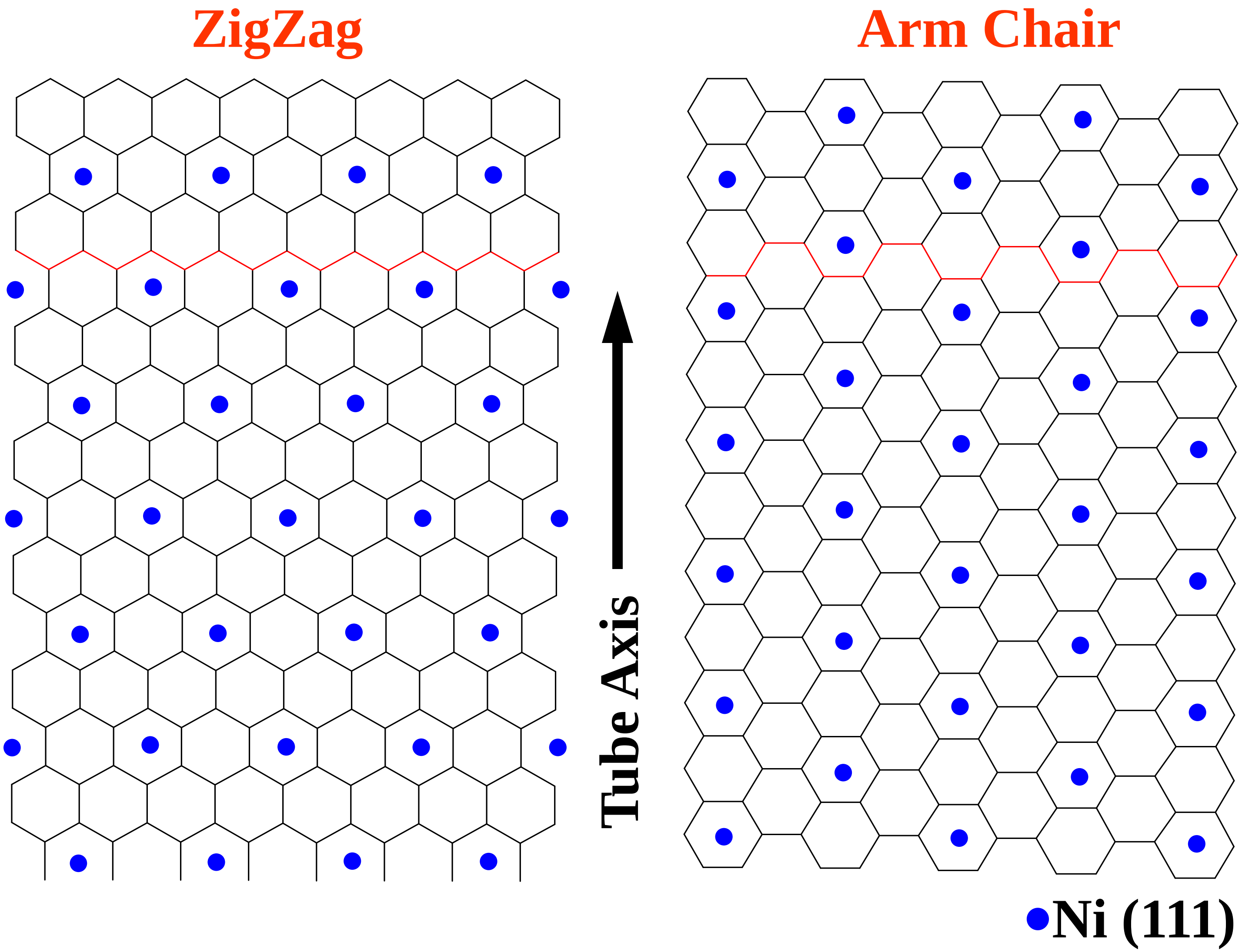
Poor graphitization-catalyst

Fe

High solubility in carbon

APS 2001 M. Yudasaka

SWNT Chirality Controlled by Lattice Matching of Graphite and Ni (111)



M. Yudasaka et al. Appl. Phys. A 74, 377(2002).

SWNT Formation by CVD

Catalysts: **Fe, FeCo, Co, Mo**

Controlling these metal particle sizes at 1- 2 nm

References of SWNT growth by CVD

1. H. Dai A.G. Rinzler, P. Nikolaev, A. Thess, d.T. Colbert, R.E. Smalley Chem. Phys. Lett., 260(1996)471. **NiCo, Mo**
2. Fonseca, A, K. Hernadi, P. Piedigrosso, L.P. Biro, S. Lazarescu, Ph. Lambin,P.A. Thiry, D. Bernaerts, J.B. Nagy ., *Proc. of Fullerenes : Chemistry of Physics and New Directions IX;* The Electrochemistry Society Inc.: Montreal, 1997.
3. Fonseca A., K.Hernadi, P. Piedigrosso, J.-F. Colomer, K. Mukhopadhyay, R. Doome, S. Lazarescu, L.P. Biro, Ph. Lambin,P.A. Thiry, D. Bernaerts, J.B. Nagy, Appl.Phys. A, 67(1998)11. (silica, zeolite) **Co > Cu, Fe**
4. J. Kong, H.T Soh, A.M. Casell, C.F. Quate, H. Dai, Nature 395(1998)878. **Fe, Mo** (Al)
5. J. Kong, A.M. Casell, H. Dai, Chem. Phys. Lett. 292(1998)567. $\mathbf{Fe_2O_3/Al_2O_3}$
6. Z.K. Tang, H.D. Sun, J. Wang, J. Chen, G. Li, Appl. Phys. Lett., 73(1998)2287. (microporous aluminophosphate AlPo4-5 diameter=1.01 nm, tripropylamine, 500-800^{O}C)
7. H.M. Chen, F. Li, G. Su, H.Y. Pan, L. L. He, X. Sun, M.S. Dresselhaus, Appl. Phys. Lett., 72(1998)3282. **Fe** (S, H)
8. H.M. Chen, F. Li, X. Sun, S.D.M. Brown, M.A. Pimenta, A. Marucci, G. Dresselhaus, M.S. Dresselhaus, Chem. Phys. Lett. 289(1998)602. **Fe** (S, H) 1100-1200ºC
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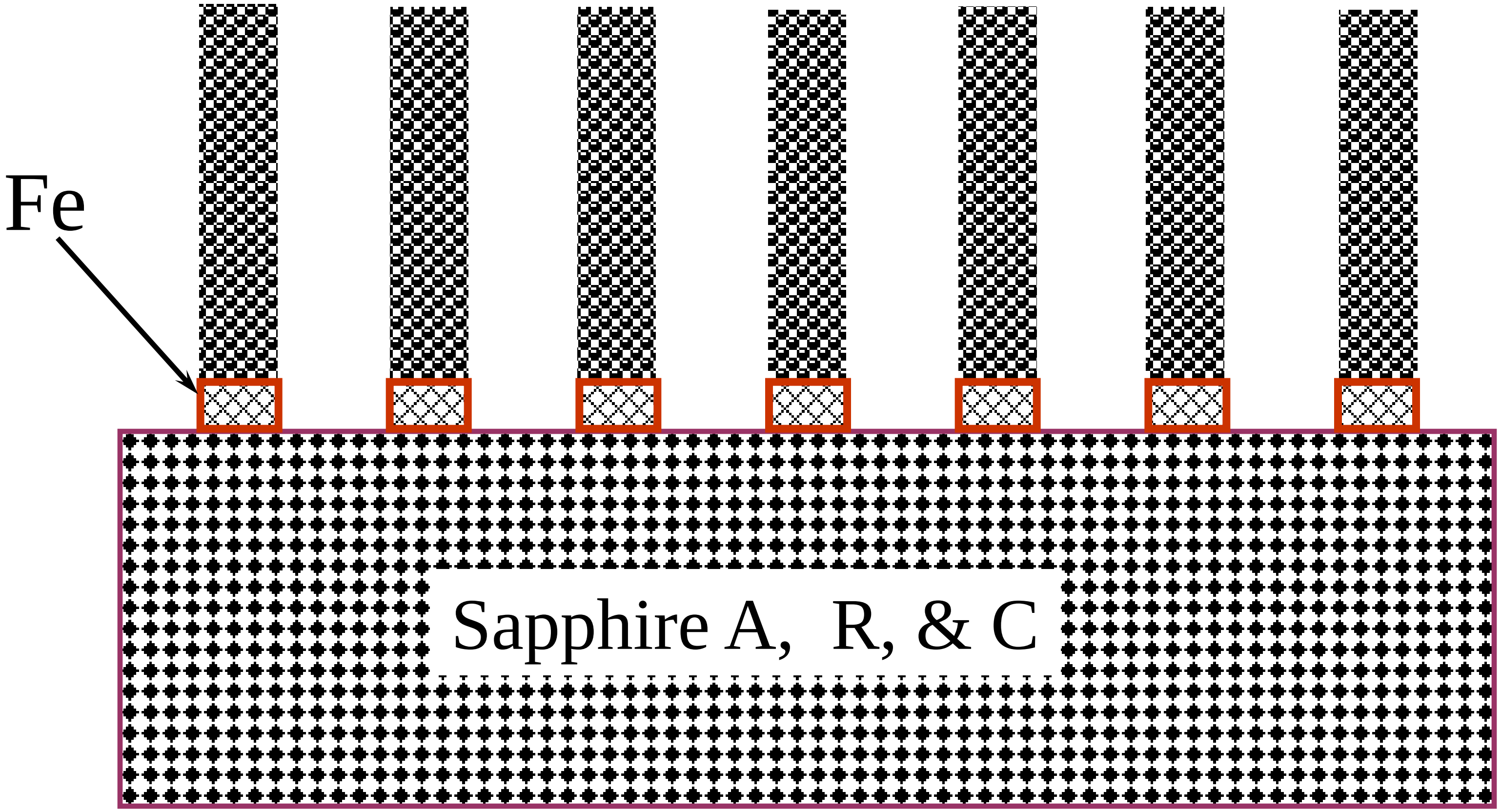
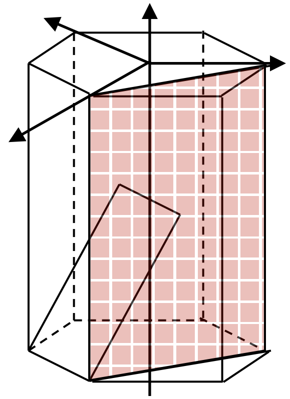
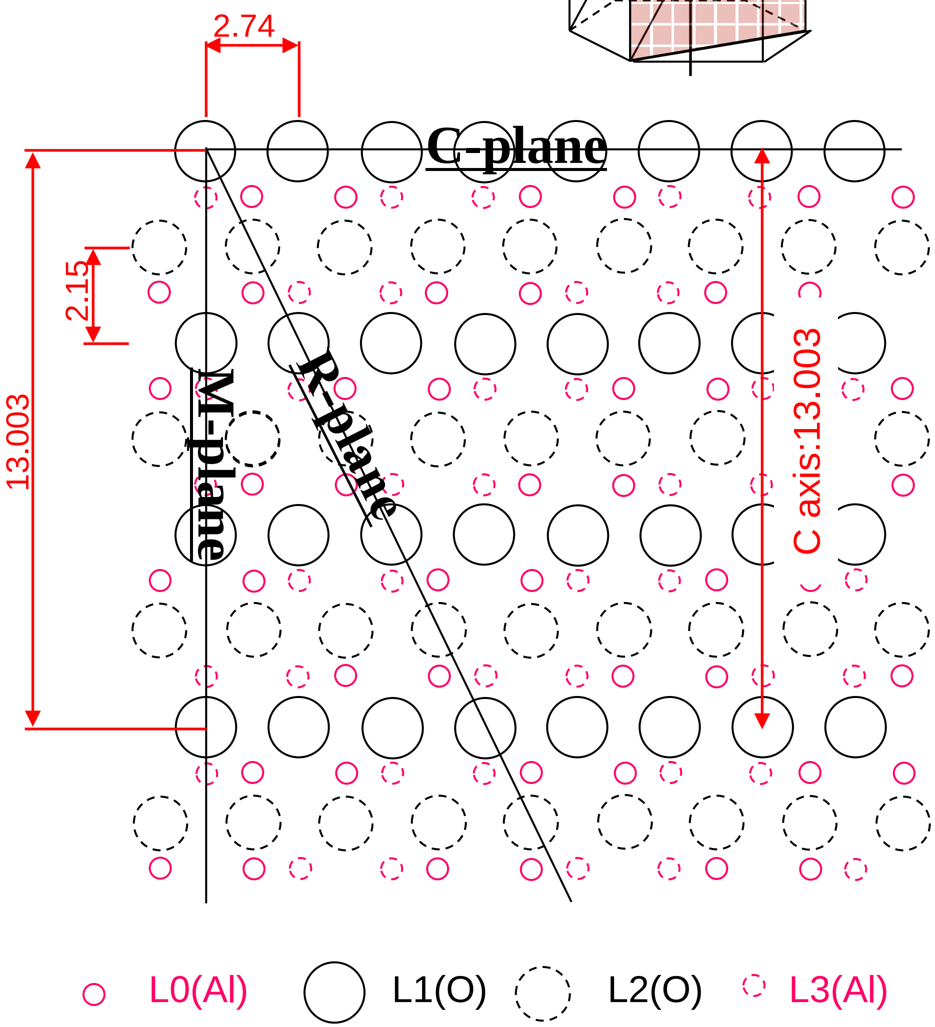
12. P. Nikolaev, M. J. Bronikowski, R. K. Bradley, F. Rohmund, D. T. Colbert, K. A. Smith, R.E. Smalley Chem. Phys. Lett., 313(1999)91. **Fe**
13. J.–F. Colomer, C. Stephan, S. Lefrant, G. V. Tendeloo, U. Eiliams, Z. Konya, A. Fonseca, Ch. Laurent, J.B. Nagy Chem Phys. Lett., 317(2000) 83. **CoFe, Fe, Co** (**Mg**O)
14. I. Wilems, Z. Konya, J. –F. Colomer, V. Tendeloo, N. Nagaraju, A. Fonseca, J. B. Nagy, Chem.Phys. Lett., 312(2000)71. **CoMo, CoV**
15. M. Su, B. Zheng, J. Liu, Chem. Phys. Lett., 322(2000)321. (low density in aerogel) **Fe, Mo**

One Idea of Controlling the Chirallities of SWNTs.

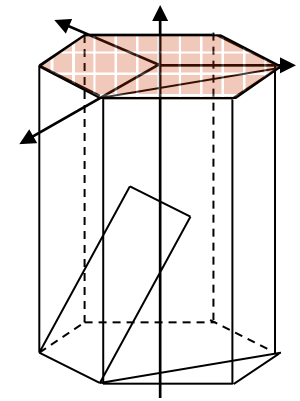


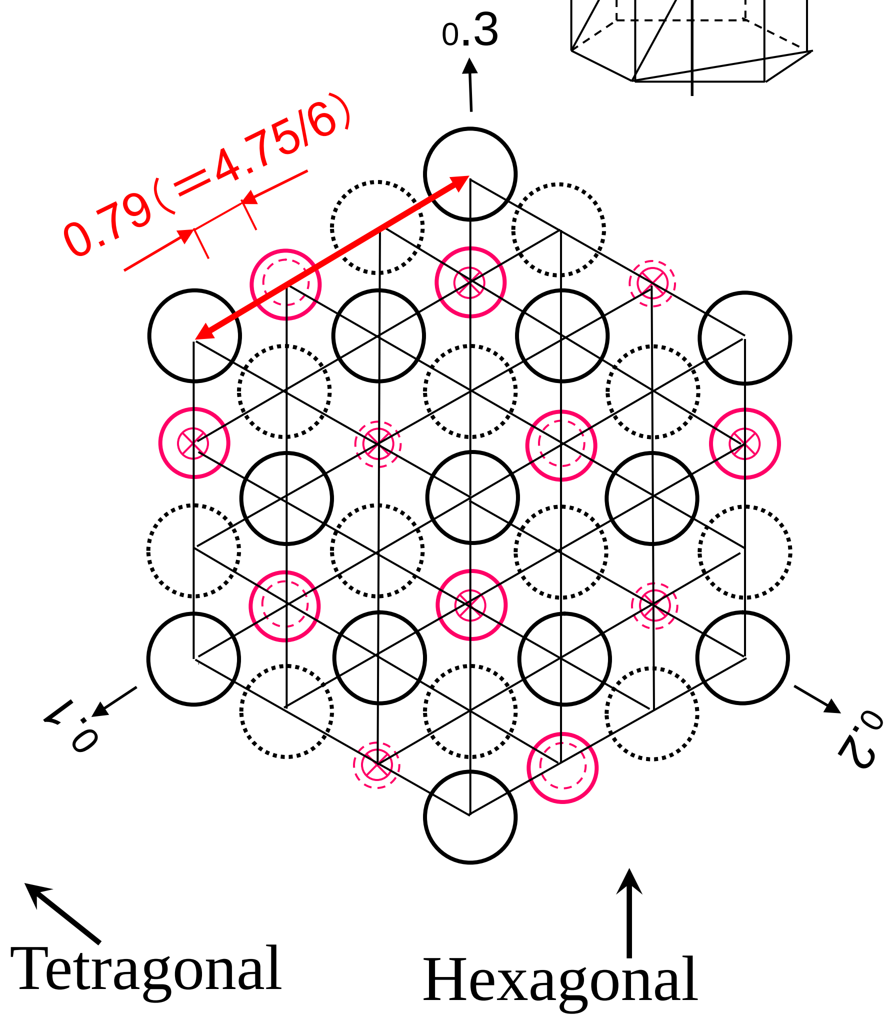
A face (11$\bar{2}$0)



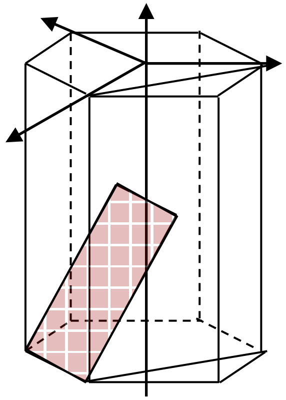


C face (0001)

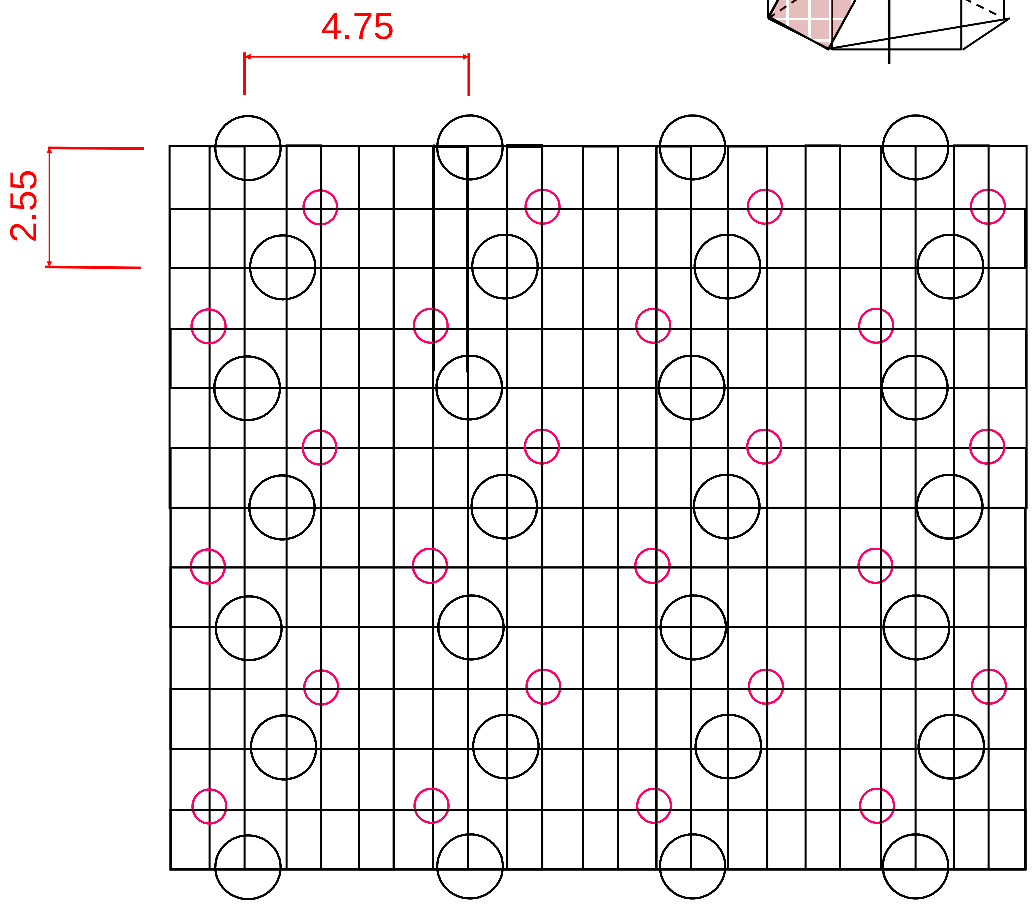




R face (1$10\overline{2}$)



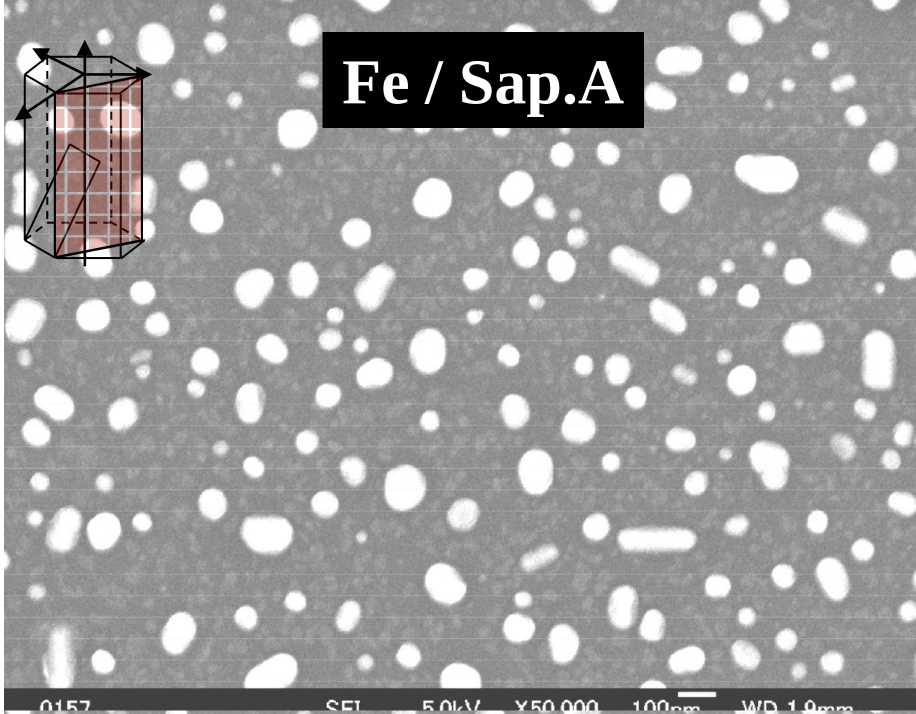
Fe:Cubic

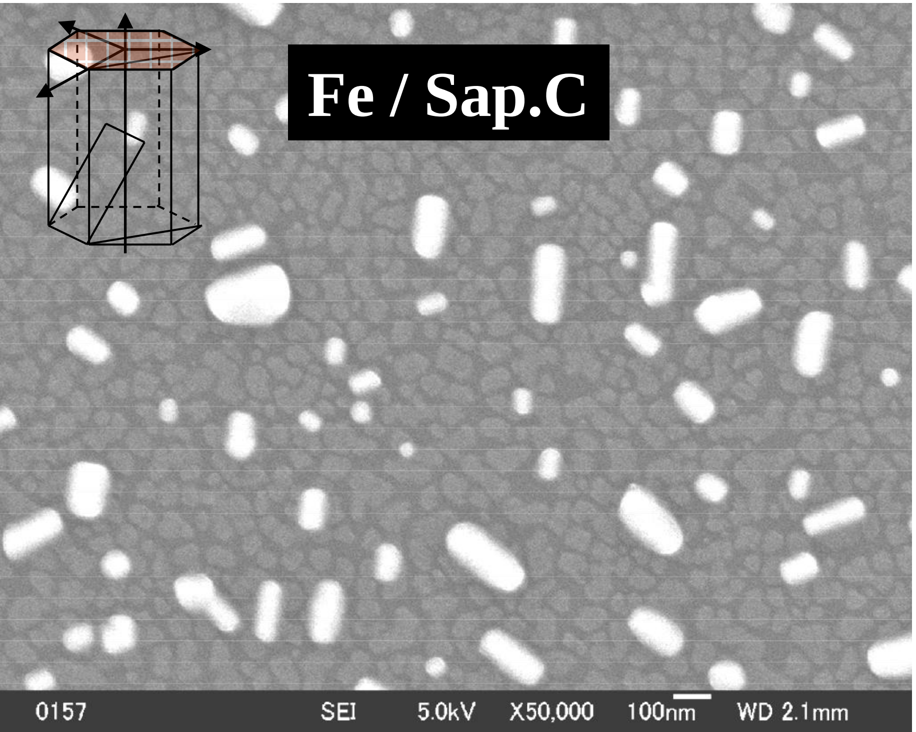


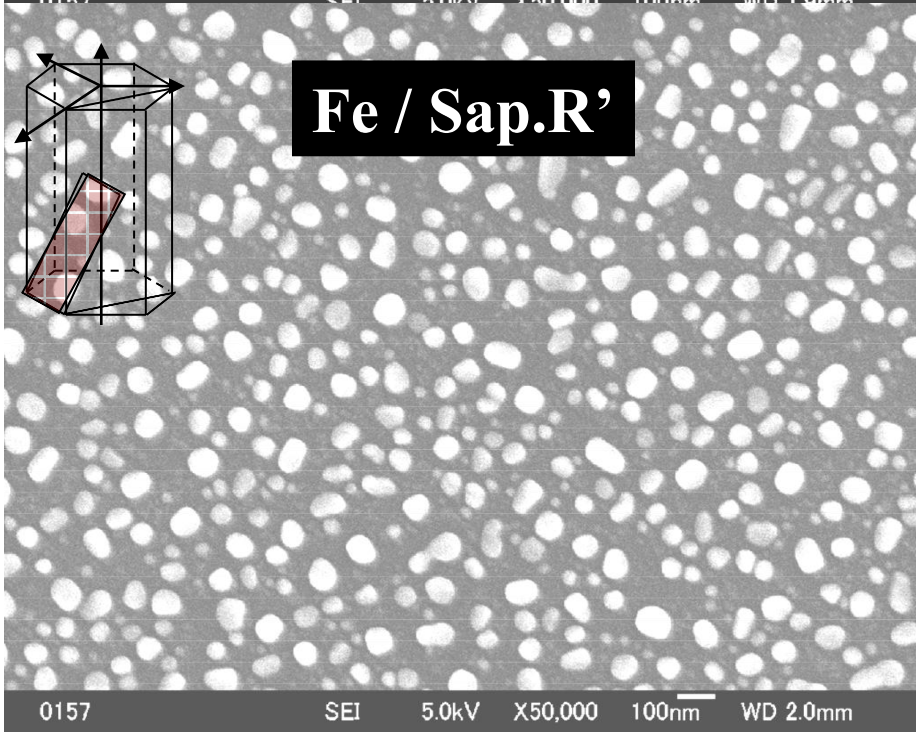
Tetragonal-like

SEM Images of Fe(5nm)/Sapphires Heat Treated at 600^{o}C. Size and Shape of Crystallites Depend on Sapphire Faces.

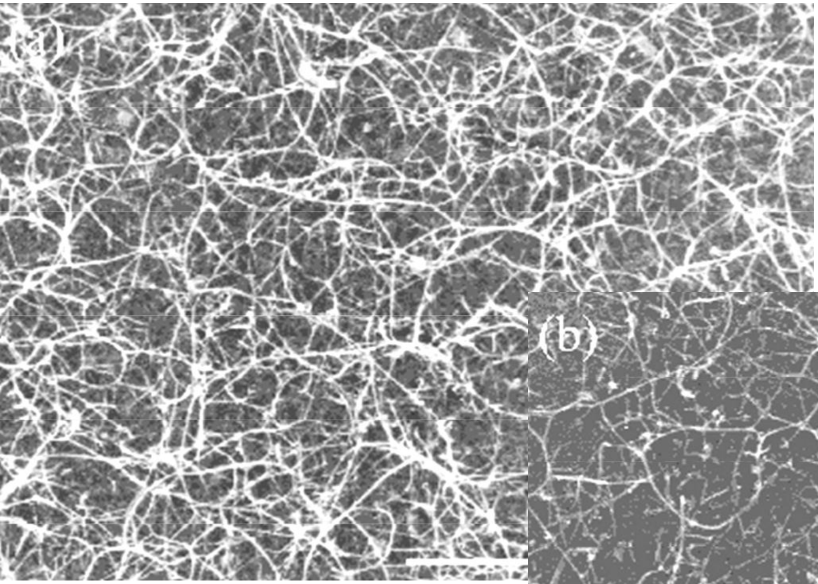
M. Yudasaka, *J. Nanoscience and Nanotechnology, in press.*



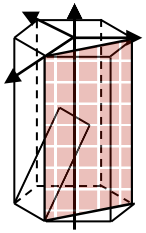




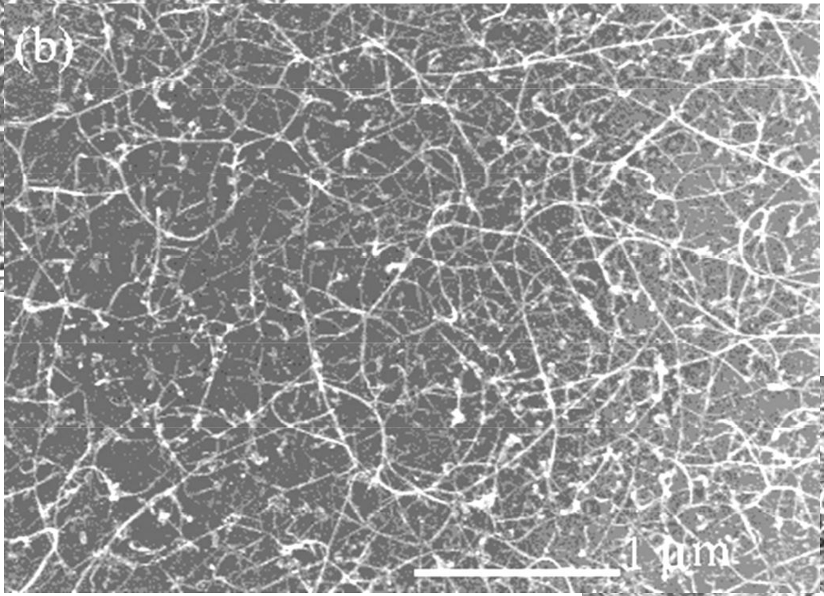
SEM Images of Deposits Obtained by CVD : Fe (2 nm) /Sapphire, 800ºC, CH_4 (0.6L/min)



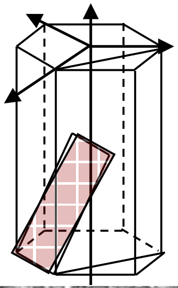
a-face

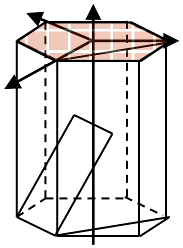


- *Many SWNTs*
- *Bundles*
- *Less MWNTs*

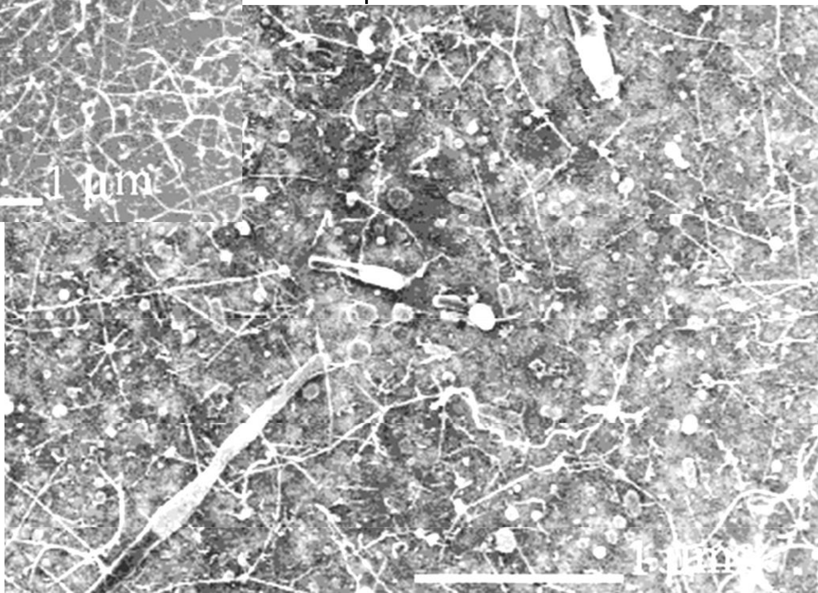


r-face





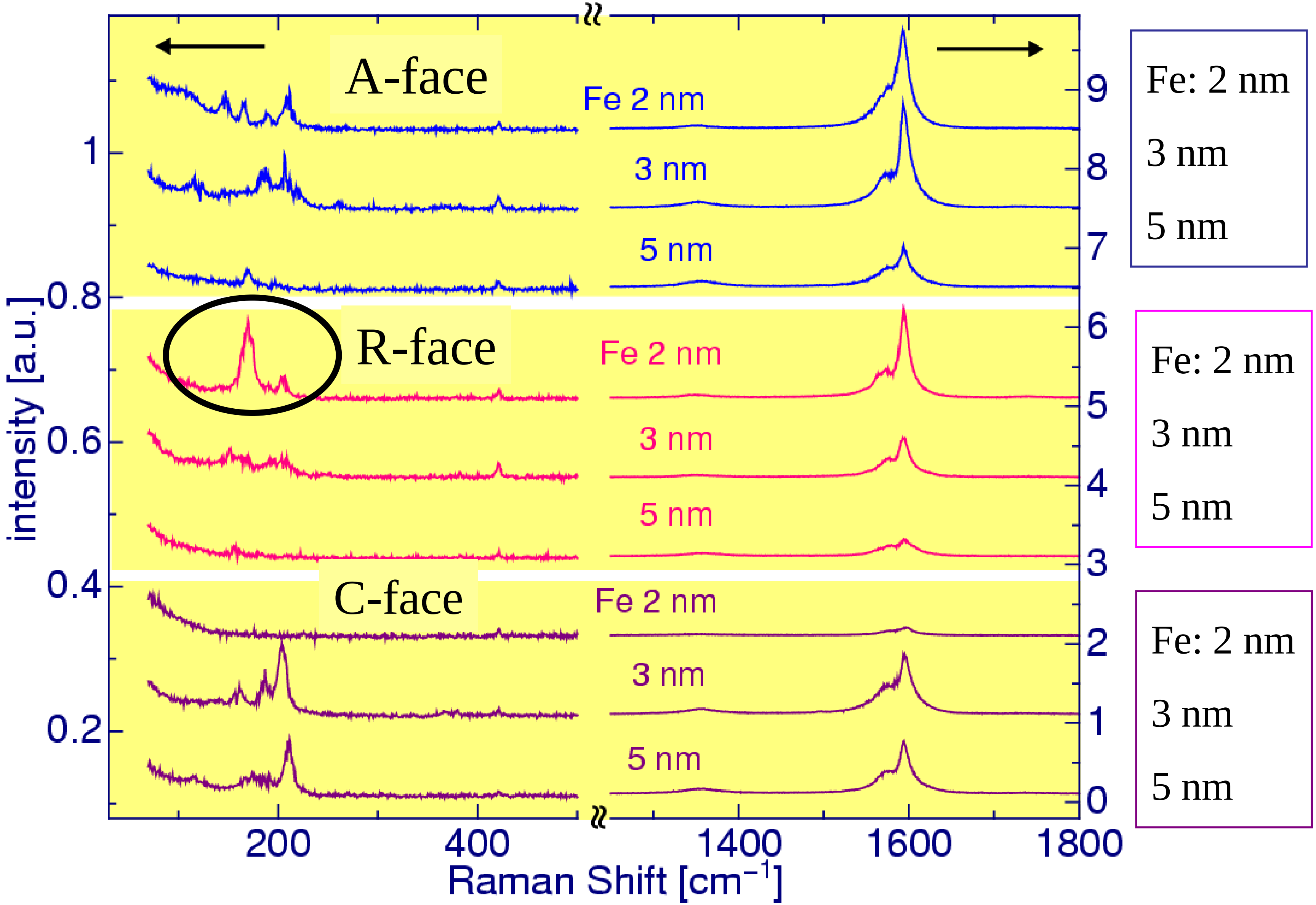
c-face



Hongo, Yudasaka, Ichihashi, Nihey, Iijima
Chem. Phys. Lett. 361(2002)349.

Hongo, Yudasaka, Ichihashi, Nihey, Iijima. *Chem. Phys. Lett.* 361(2002)349.

Raman spectra (488 nm)

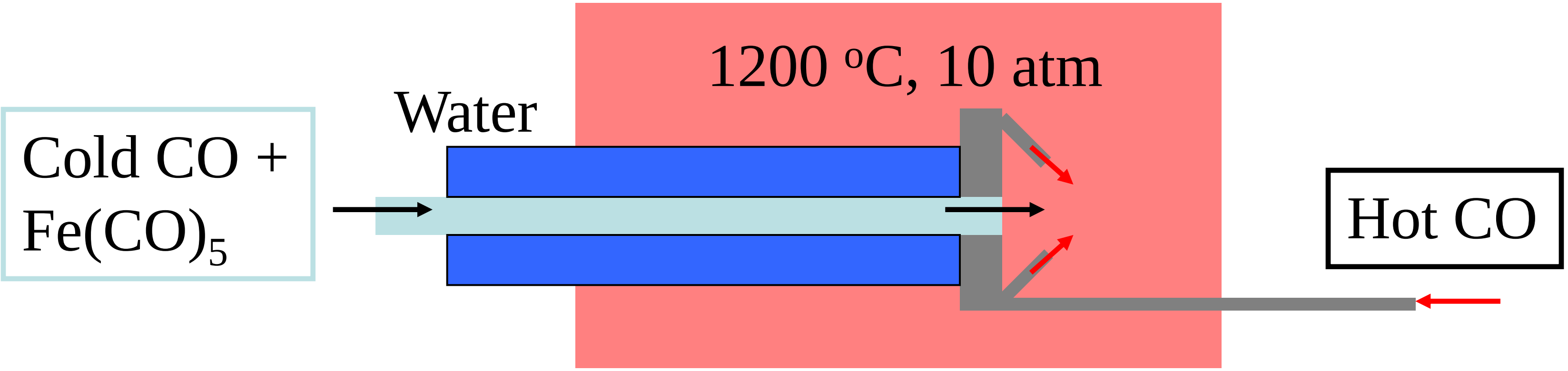


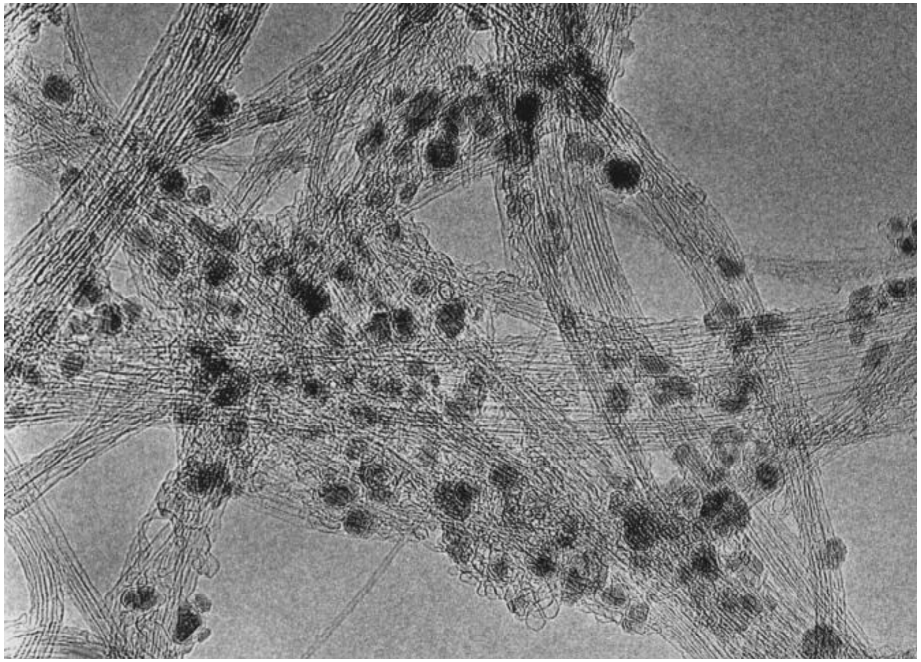
SWNT growth by CVD

Large scale
Site selective
Orientation
Long

1999: Large Scale Production of SWNTs by High Pressure Gas Phase Reaction (Smalley Group)

(P. Nikolaev et al. Chem. Phys. Lett. 313(1999)91.)





Production rate: ~1 g/h

Purity : 70%

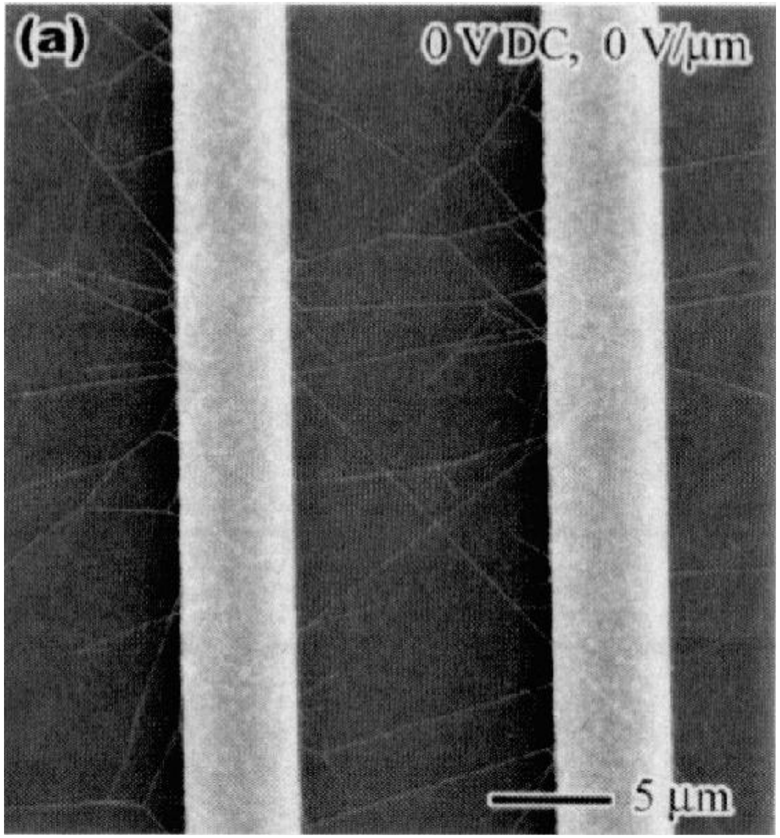
Tube diameter : 0.7~1.0 nm

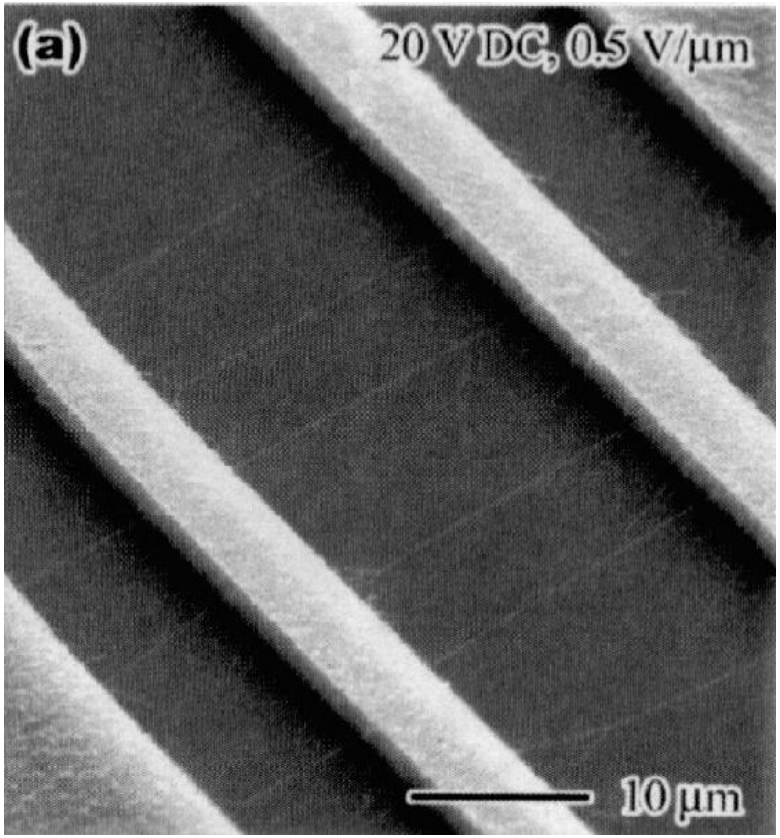
Price: 500 $/g (CNI)

Complete removal of Fe is difficult.

図8　電場印加CVDにより配向をそろえて成長したSWCNT

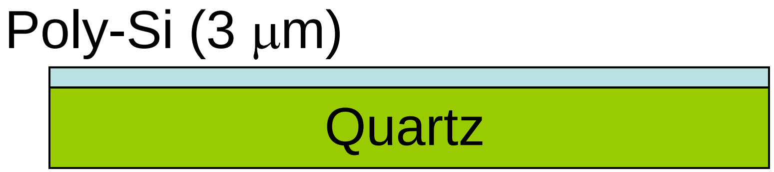
Y. Zhang et al, Appl. Phys. Lett. , 79（3083）2001

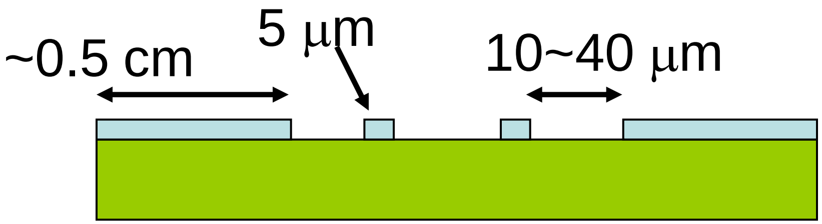




印加電圧ゼロの時にはSWCNTがいろいろな方向に成長している（左）が、0.5 V/μmかけるとSWCNTが向きをそろえて成長する（右）。

Y. Zhang et al.
Appl. Phys. Lett. 79(2001)3155.

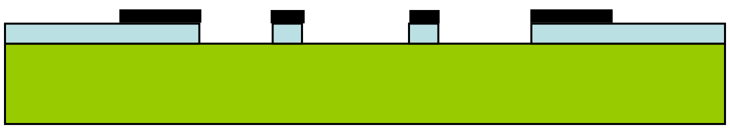




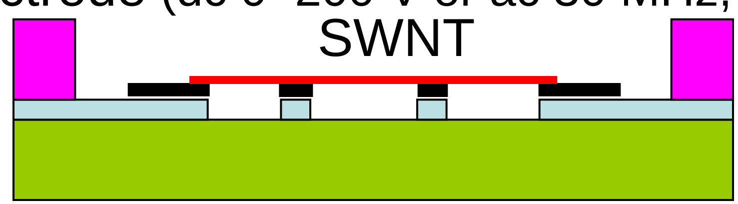
Photolithography and plasma etching.

A liquid phase catalyst precursor film (AlCl$_3$, SiCl$_4$, FeCl$_3$, MoO$_2$Cl$_2$, EtOH, MeOH, P103 block copolymer) was transferred onto the top of the poly-Si pattern by contact printing using a poly(dimethylsiloxane) elastomer tamp.Calcination at 300^{o}C for 12h in air to Remove organic materials.

Catalyst (Fe oxide and Mo oxide nanoparrtilces supported on mesoporous alumina/silica frames on the elevated poly-Si structures.)



Electrode (dc 0~200 V or ac 30 MHz, 10V)

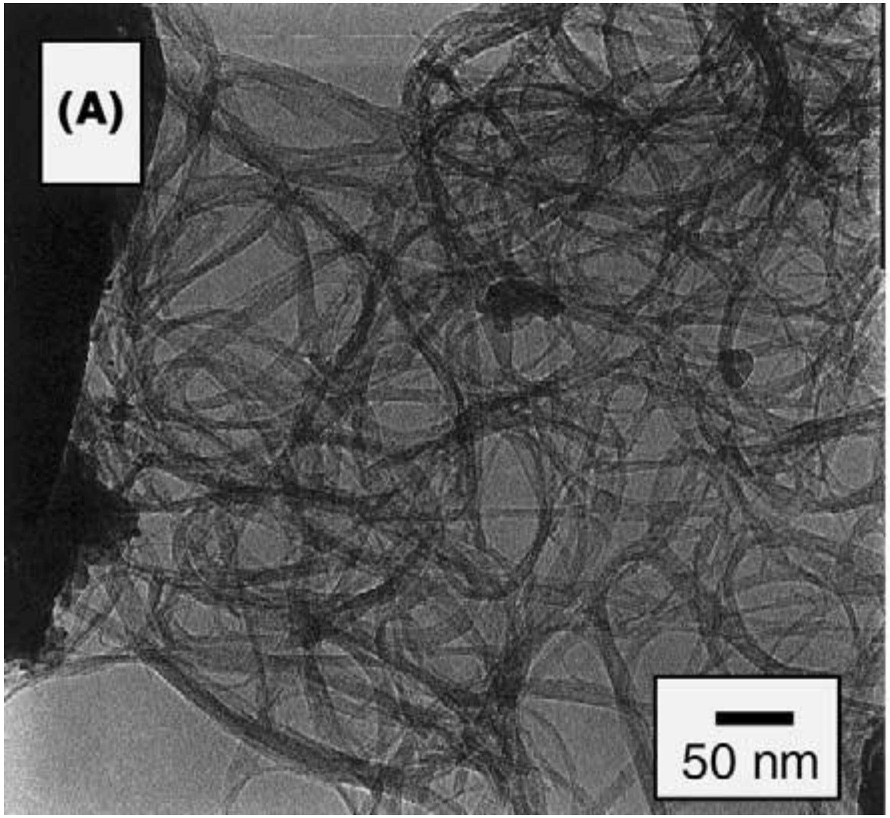


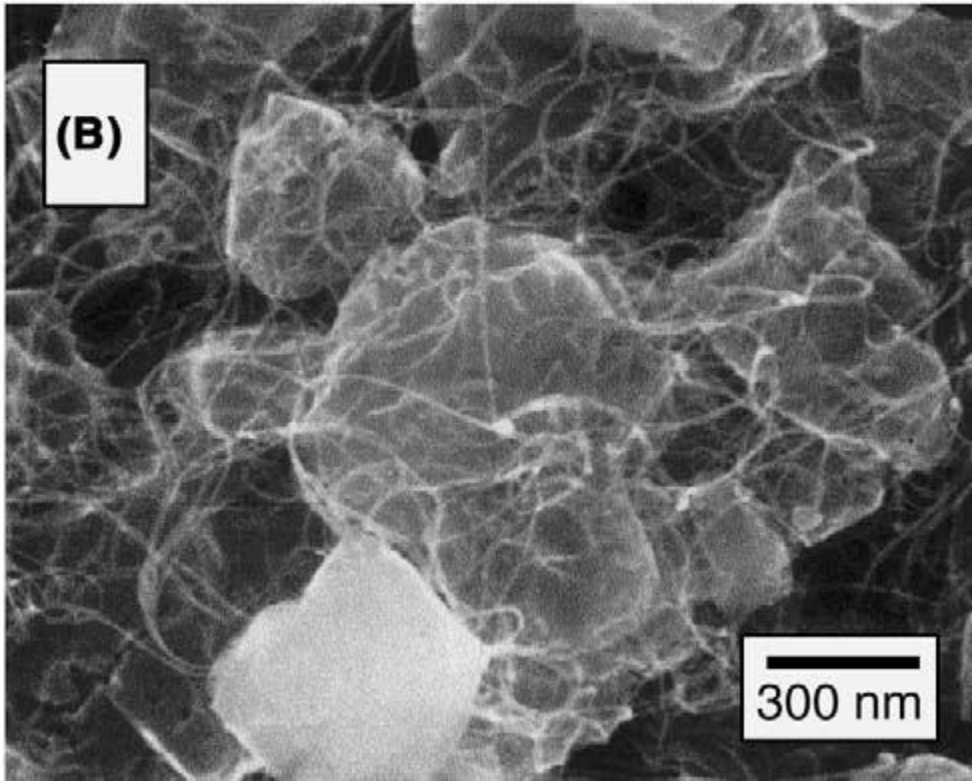
CVD: 900^{o}C, CH_4(500 sccm), H_2(200sccm), 4 min, 1 in. tube furnace.

011202a

Alcohol CVD

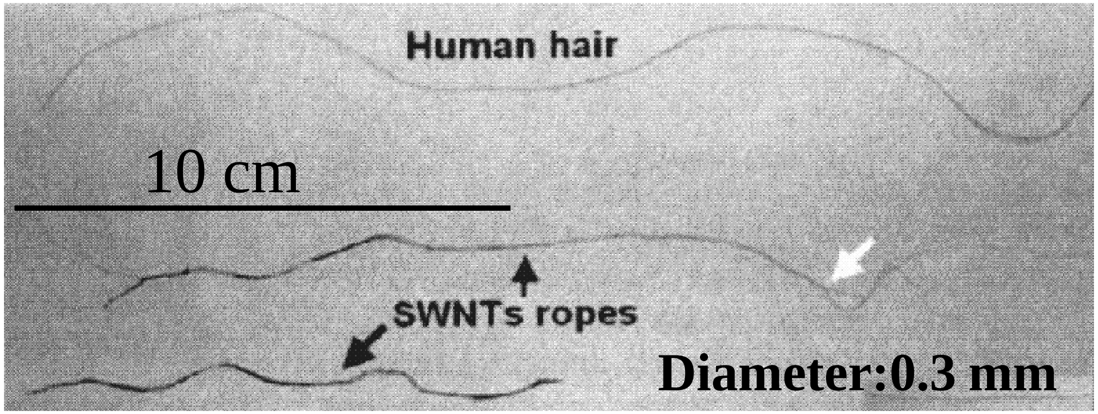
Maruyama et al 2002

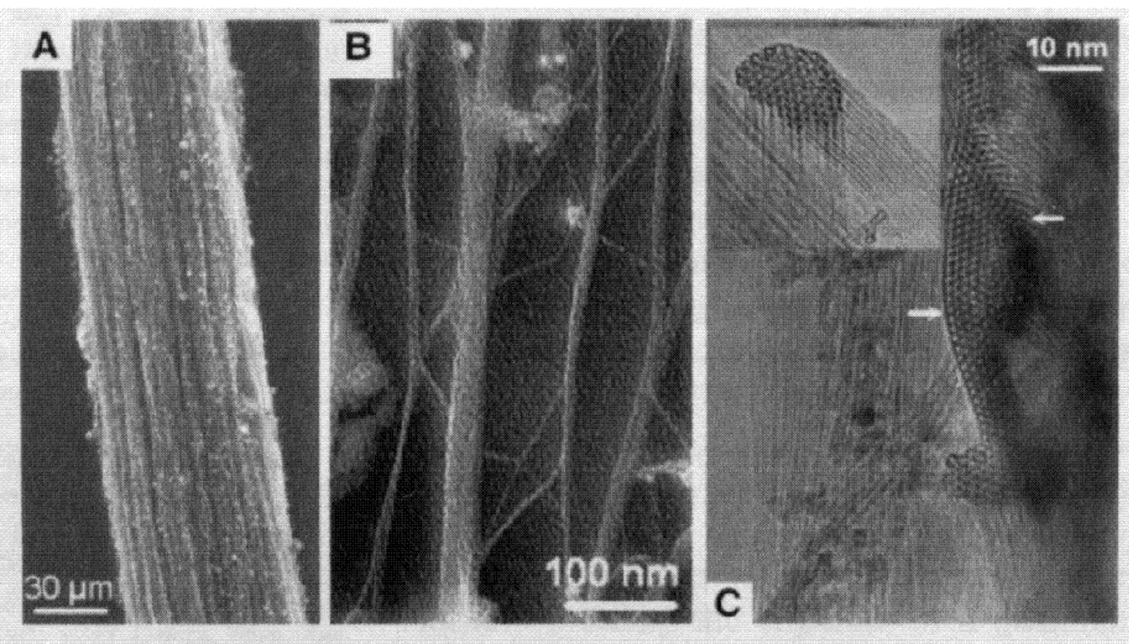




Long SWNT Strands.

H. W. Zhu et al. Science **296**(2002)884.





Catalytic CVD (Floating catalyst method) in a vertical furnace.

n-Hexane solution of ferrocene (0.018 g/ml) + Thiohene (Sulfur additive, 0.4 weight %): 0.5 ml/min.

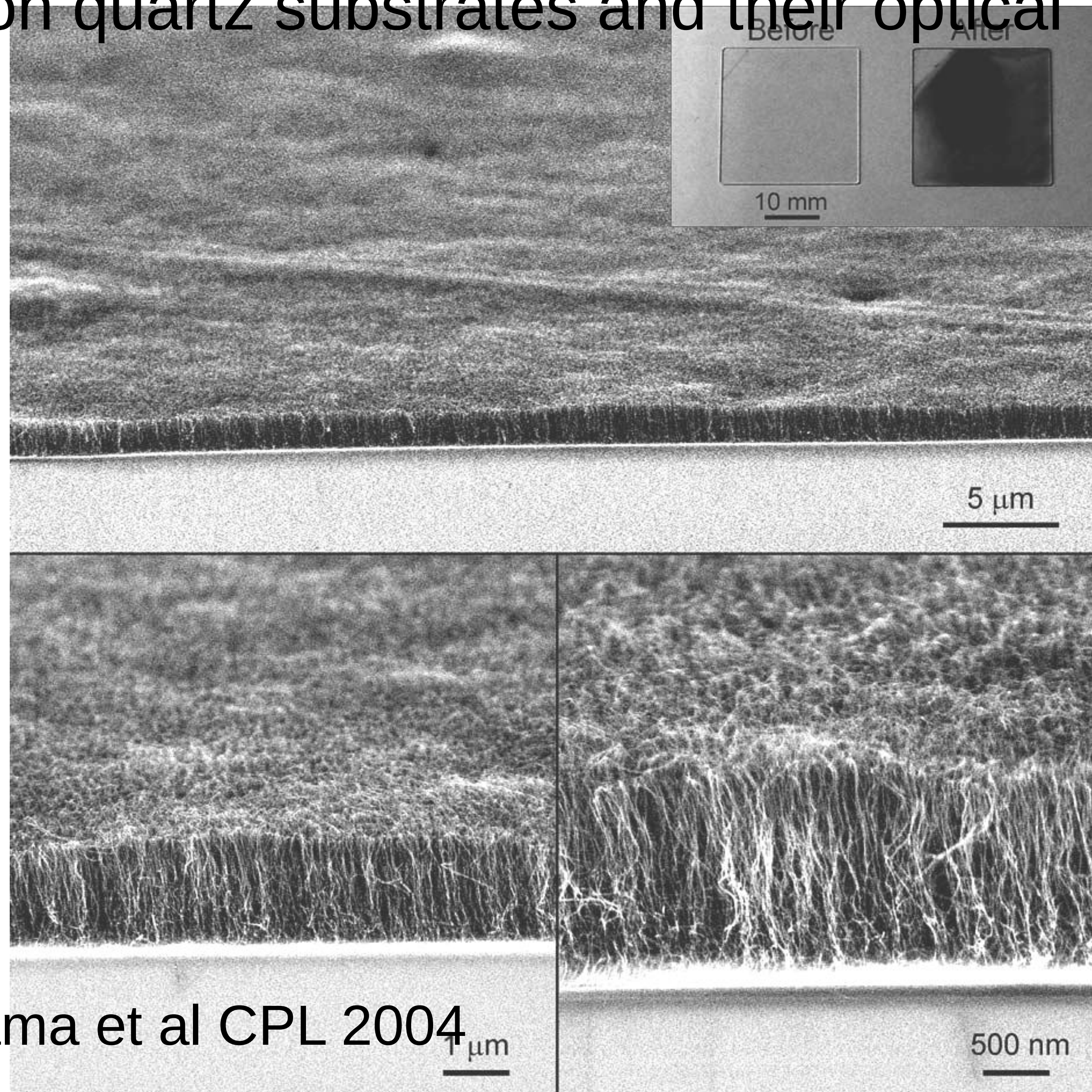
Carrier gas(H_2): 250 ml/min.
1200^{o}C

SWNTs: ~0.5 g/h
Impurity(Fe, a-C): ~5 wt%)

Young's modulus: 77 GPa

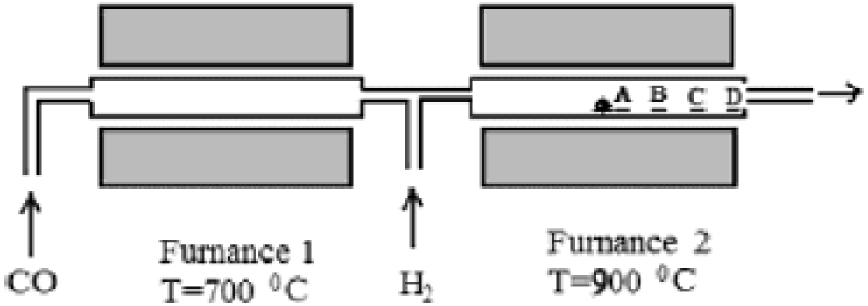
020617

Growth of vertically aligned single-walled carbon nanotube films on quartz substrates and their optical anisotropy

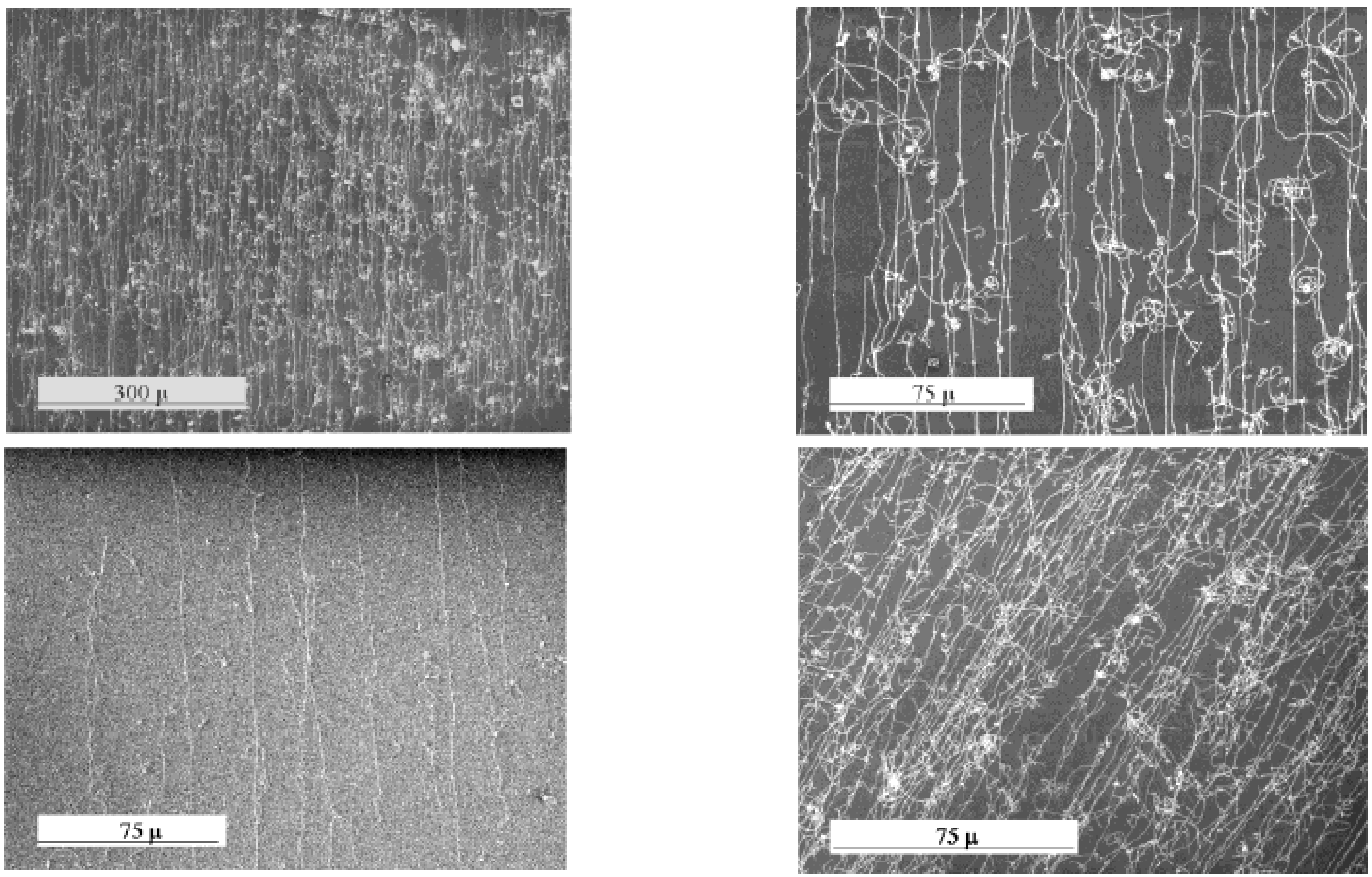


Murakami, Maruyama et al CPL 2004

Long Ropes of SWNTs for Elevators to Moon.

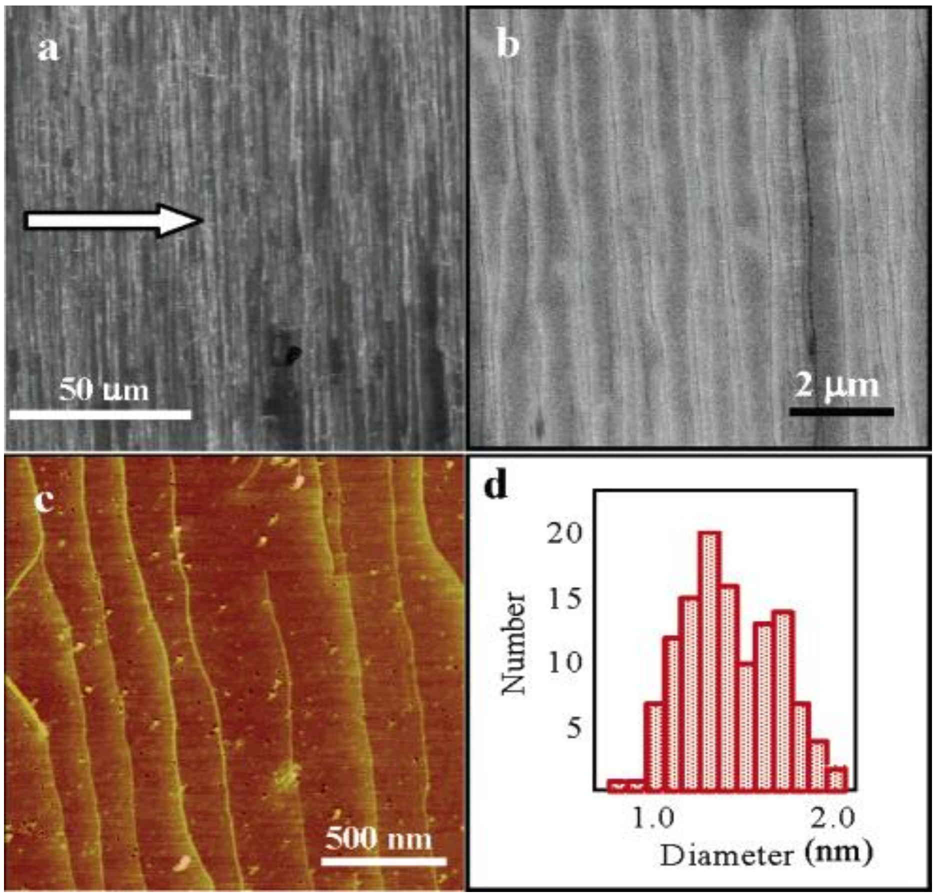


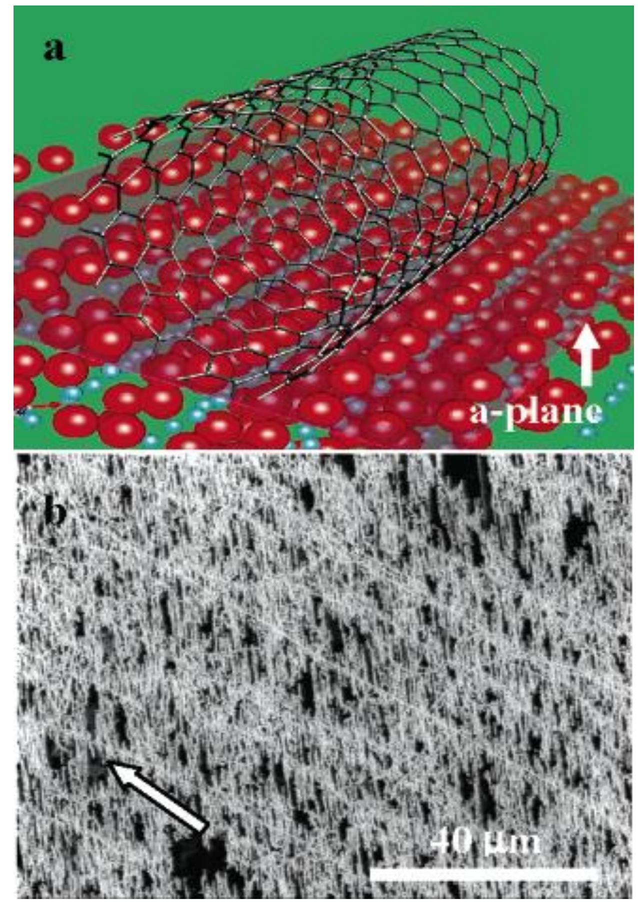
S. Huang et al.
J. Chem. Phys. B
jp0364708



Template-Free Directional Growth of Single-Walled Carbon Nanotubes on a- and r-Plane Sapphire

Song Han, Xiaolei Liu, and Chongwu Zhou

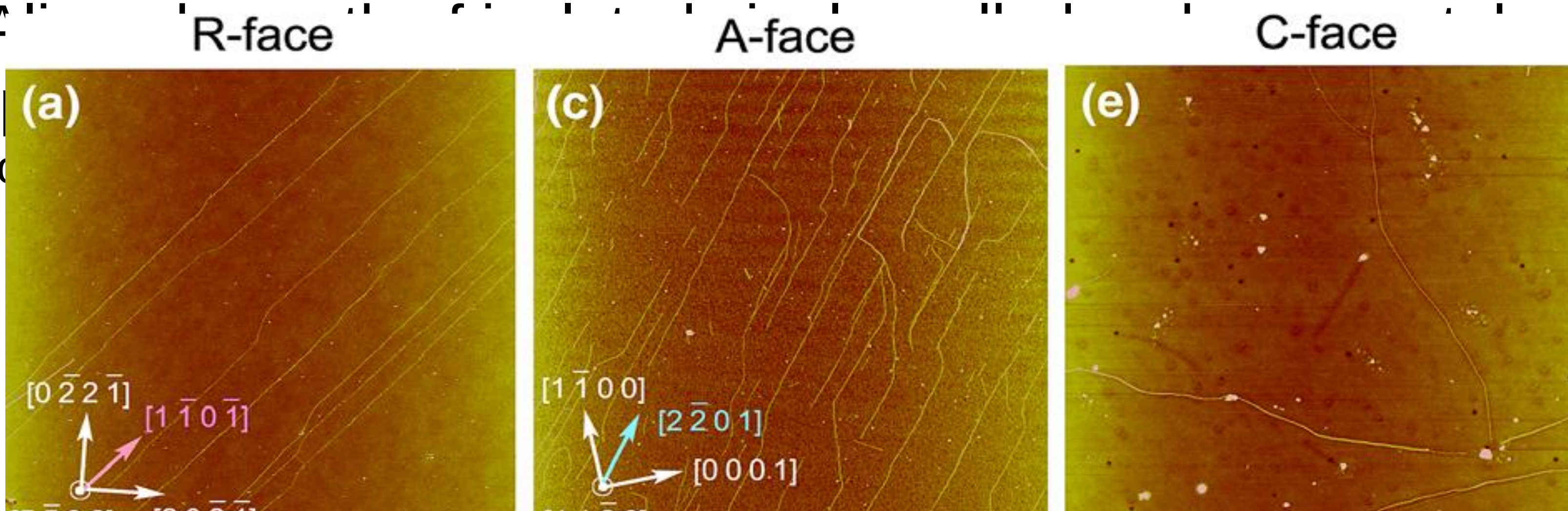




JACS **2005**, 127, 5294-5295

A … s

Hiro … mi,



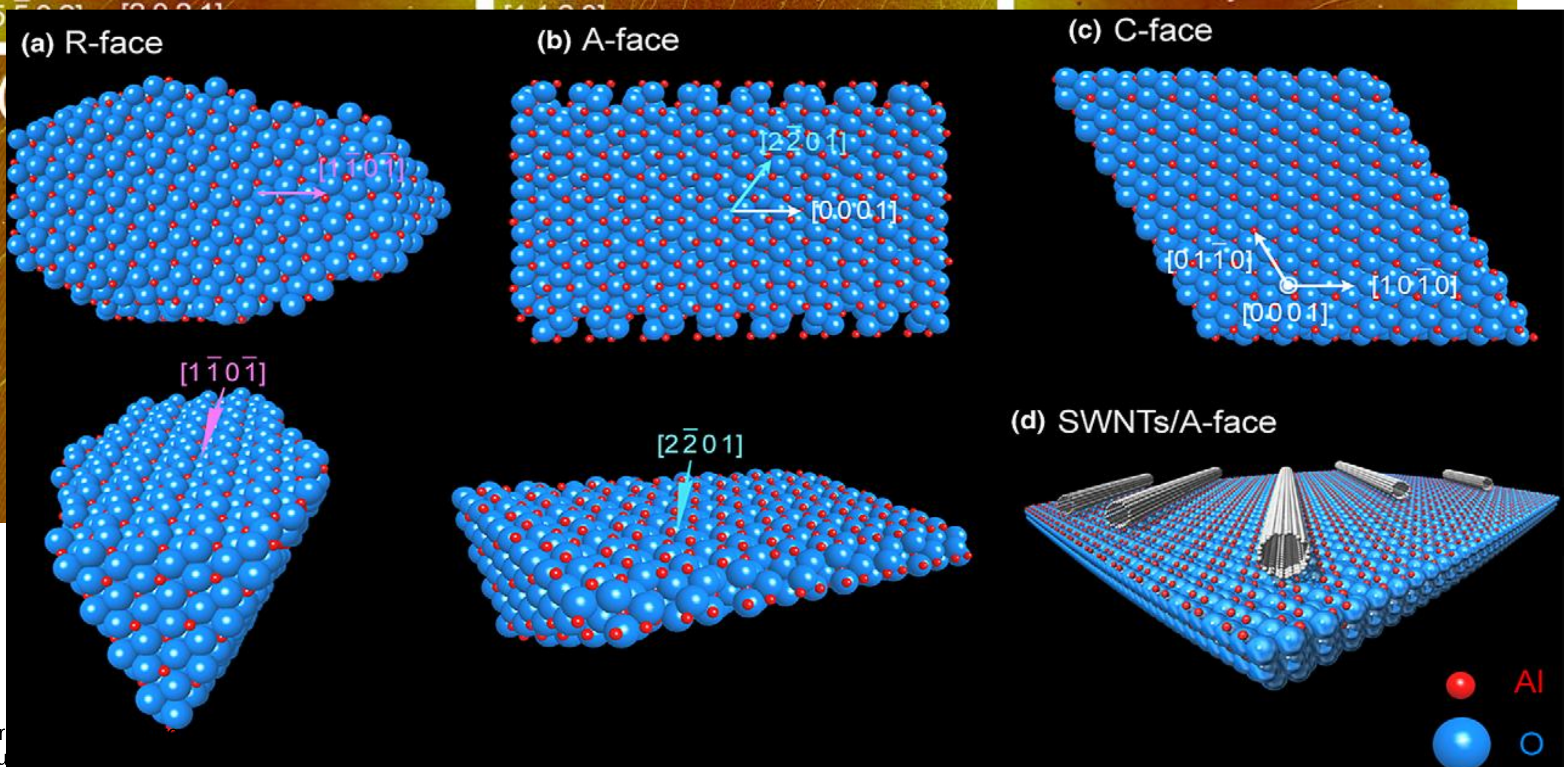
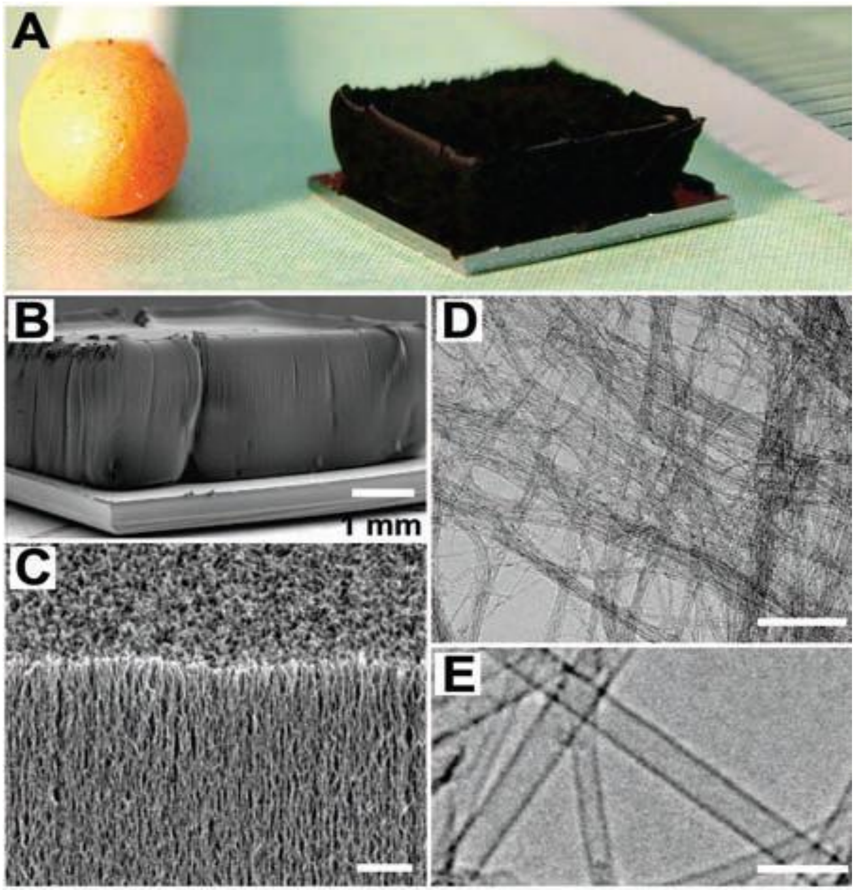
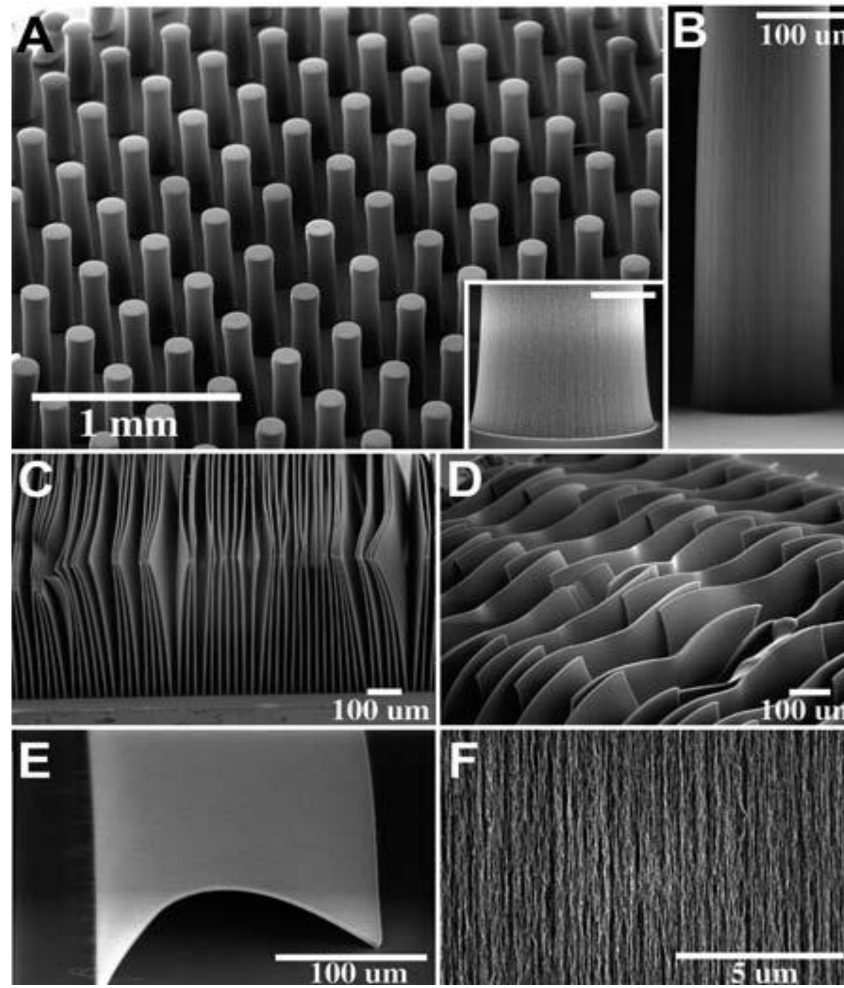


Fig. 5. Surface str…
Two lower left figu…
pink and light blue arrows for the R and A faces, respectively. A schematic diagram of SWNTs grown on the A-face substrate is shown in (d). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Water-Assisted Highly Efficient Synthesis of Impurity-Free Single-Walled Carbon Nanotubes

Kenji Hata,*. Don N. Futaba,* Kohei Mizuno, Tatsunori Namai,
Motoo Yumura, Sumio Iijima





Science *306*(**2004**) 1362.