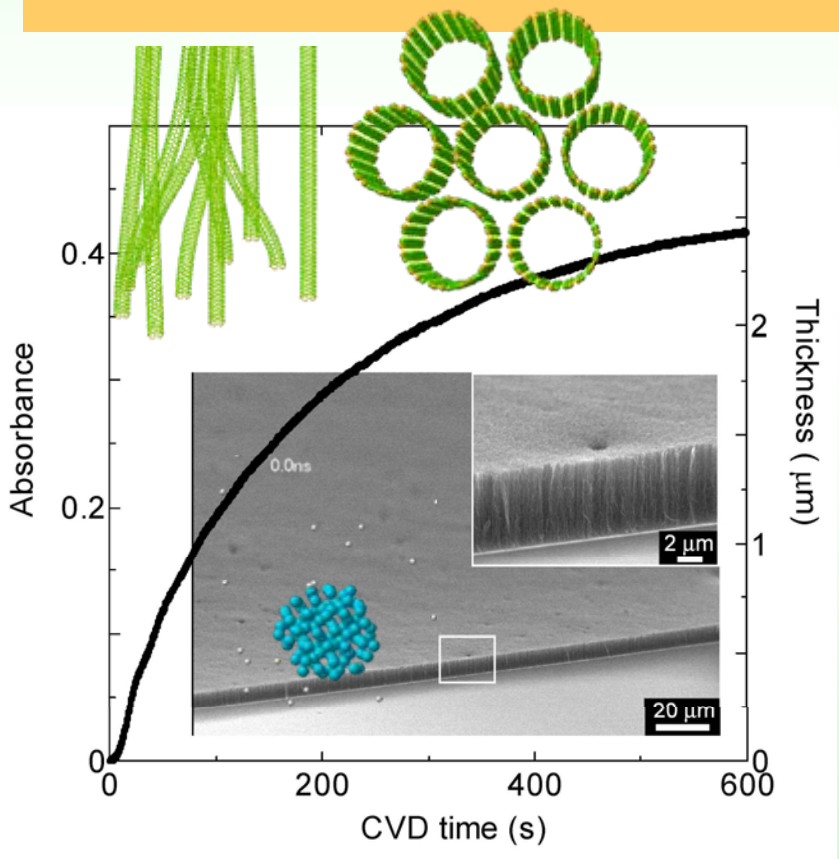
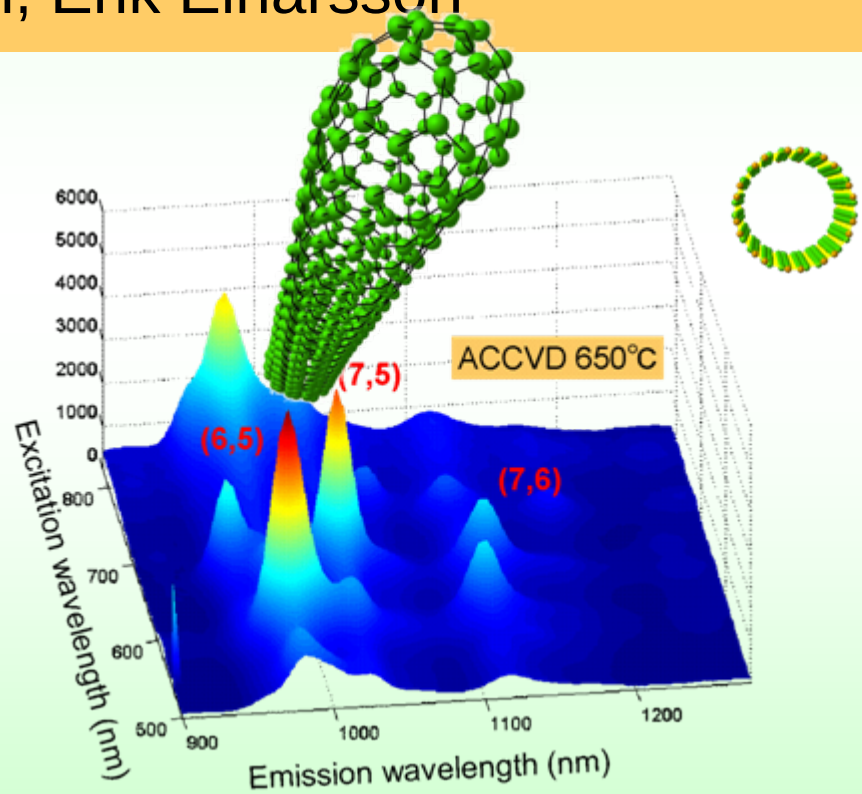
CVD Growth Mechanism of Single-Walled Carbon Nanotubes from Alcohol

Shigeo Maruyama, Yuhei Miyauchi, Yoichi Murakami,
Shohei Chiashi, Erik Einarsson

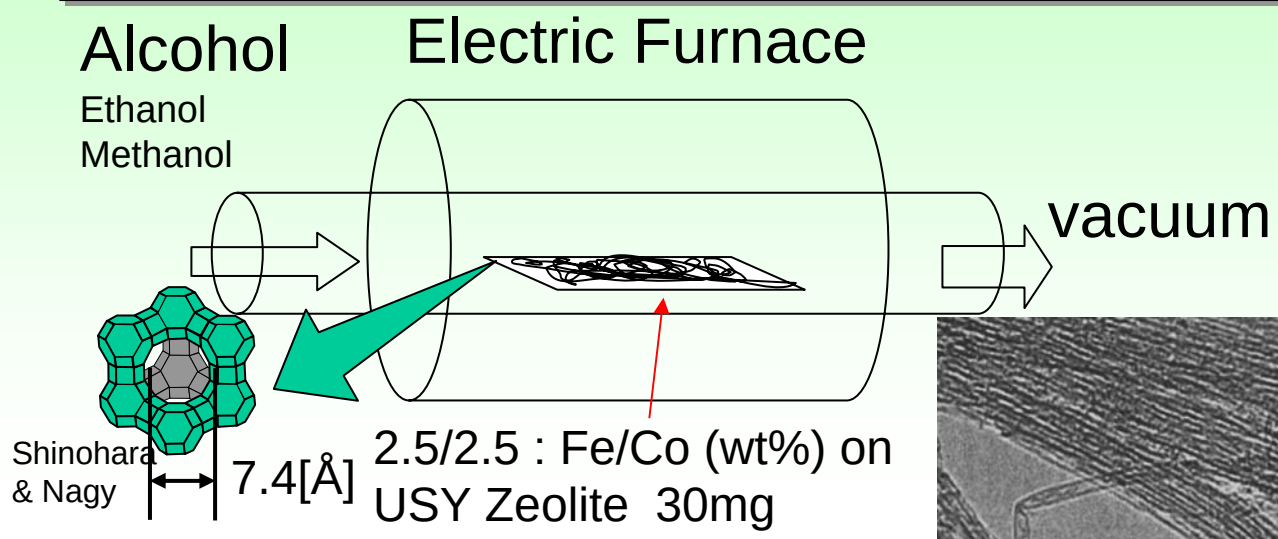




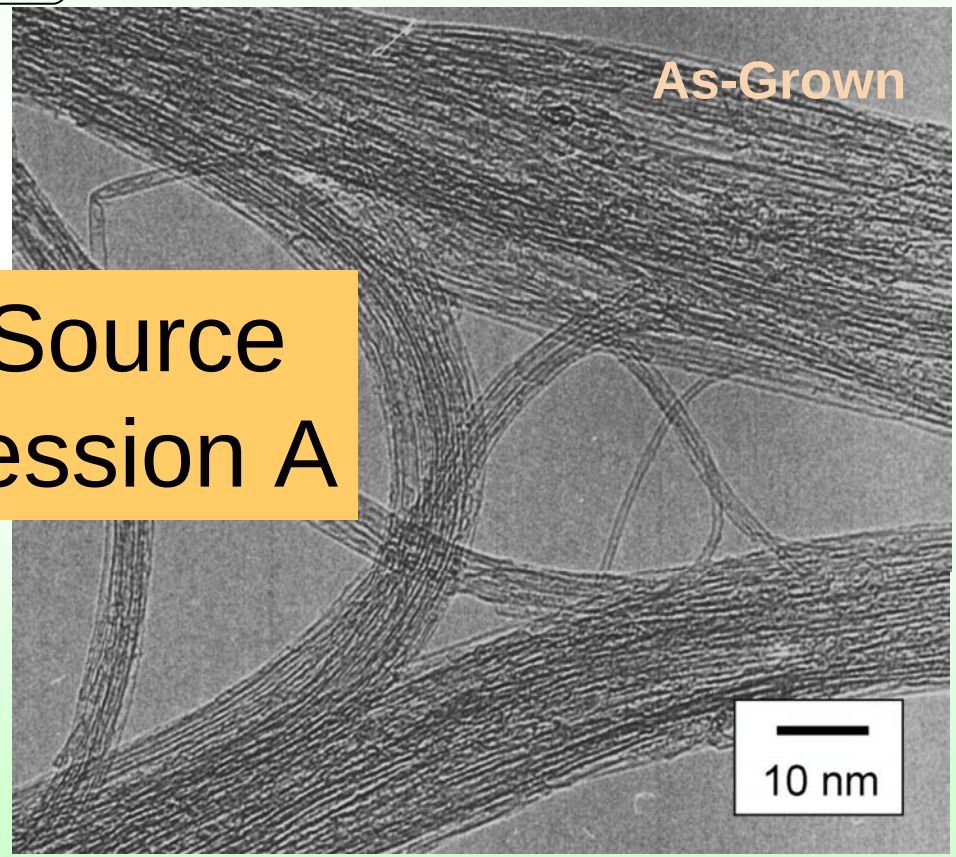
http://www.photon.t.u-tokyo.ac.jp

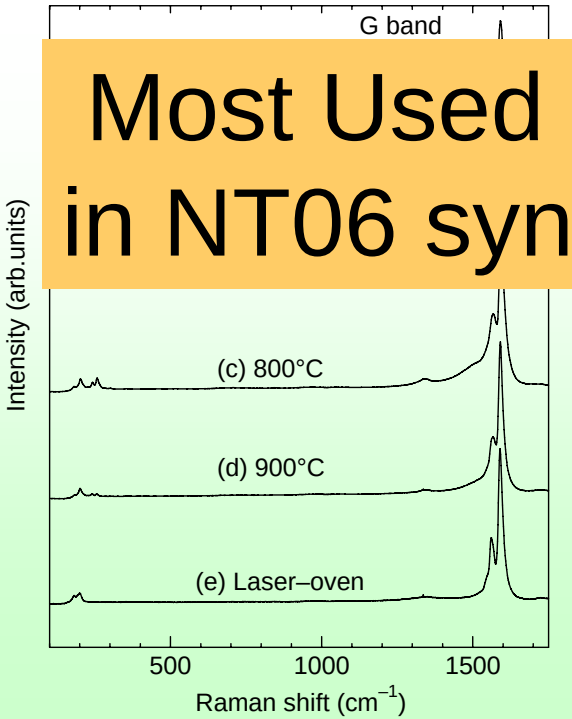
Department of Mechanical Engineering
The University of Tokyo

Alcohol CCVD on Catalysts Supported with Zeolite



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

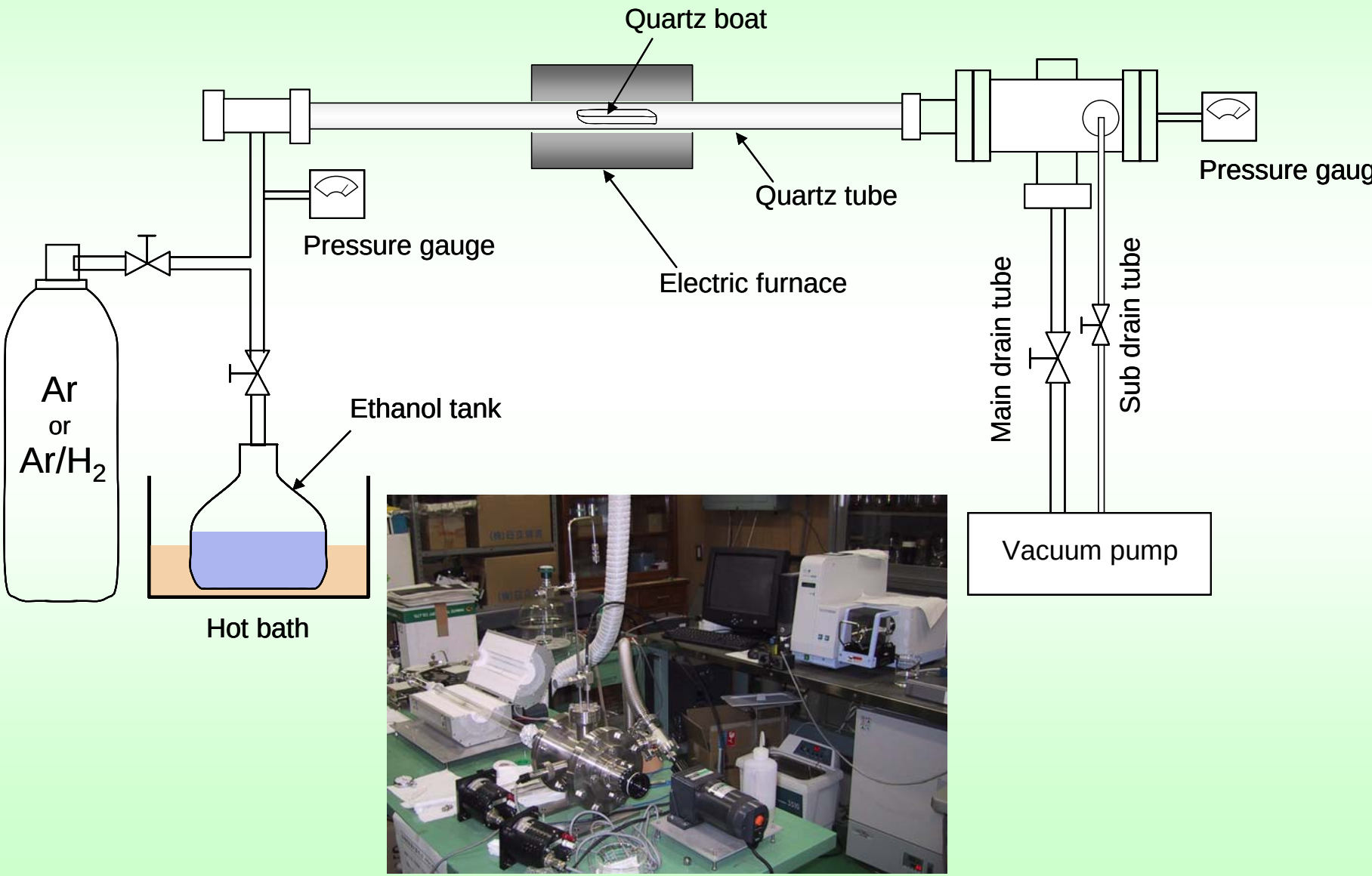




Most Used Carbon Source in NT06 synthesis session A

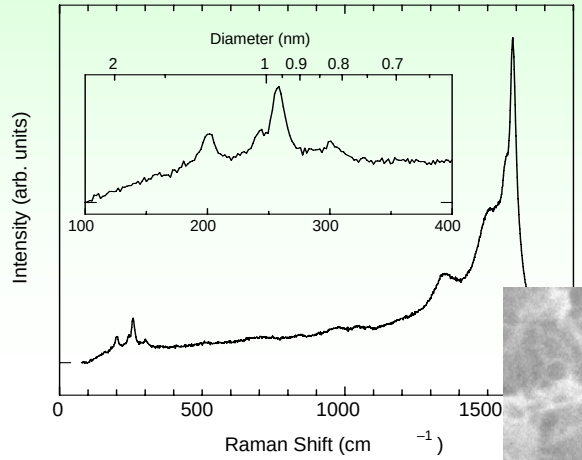
S. Maruyama et al., Chem. Phys. Lett. 360 (2002) 229.

ACCVD Experimental Apparatus



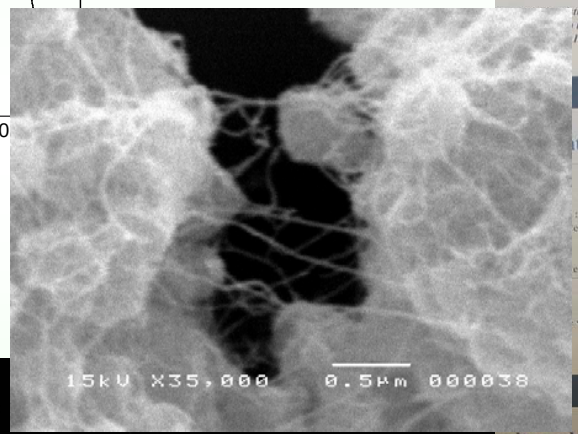
ACCVD is Simple!!

High School Students Presented
at Fullerene-Nanotubes General Symposium @ Univ. of Tokyo, July 28, 2004



Synthesis of Single-walled Carbon Nanotubes
from Alcohol by CCVD Method

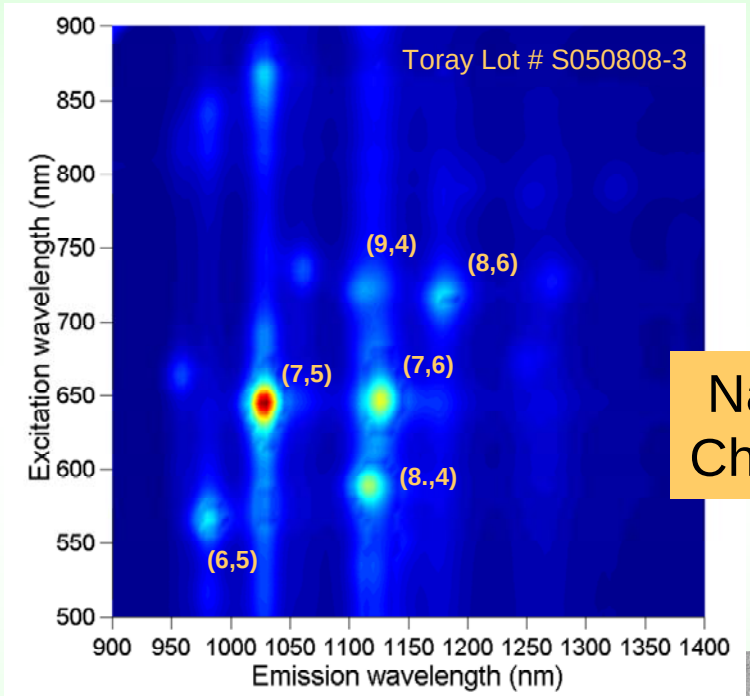
○Miki Kanao, Kieko Sawaguchi and Masaru Moriyasu
東京工業大学工学部附属工業高等学校



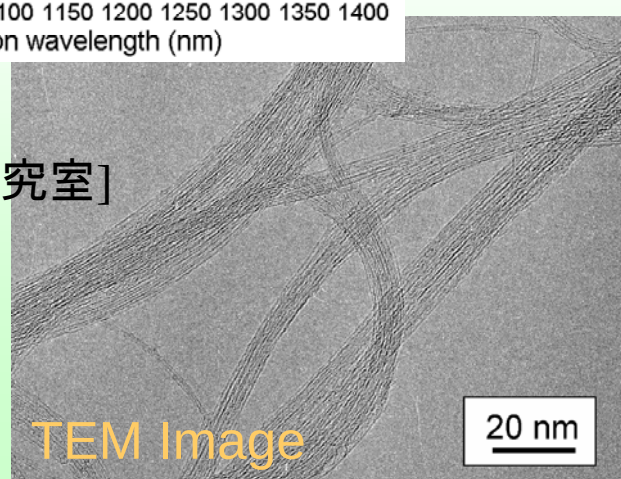
Large Scale ACCVD Production by Toray

High purity SWNTs from Ethanol on Zeolite

Purified 10 g sample



Narrow Chirality



Toray Industries, Inc. [東レ株式会社]
Chemicals Research Laboratories [化成品研究所ケミカル研究室]
9-1, Oe-cho, Minato-ku, Nagoya 455-8502 JAPAN
URL:http://www.toray.co.jp
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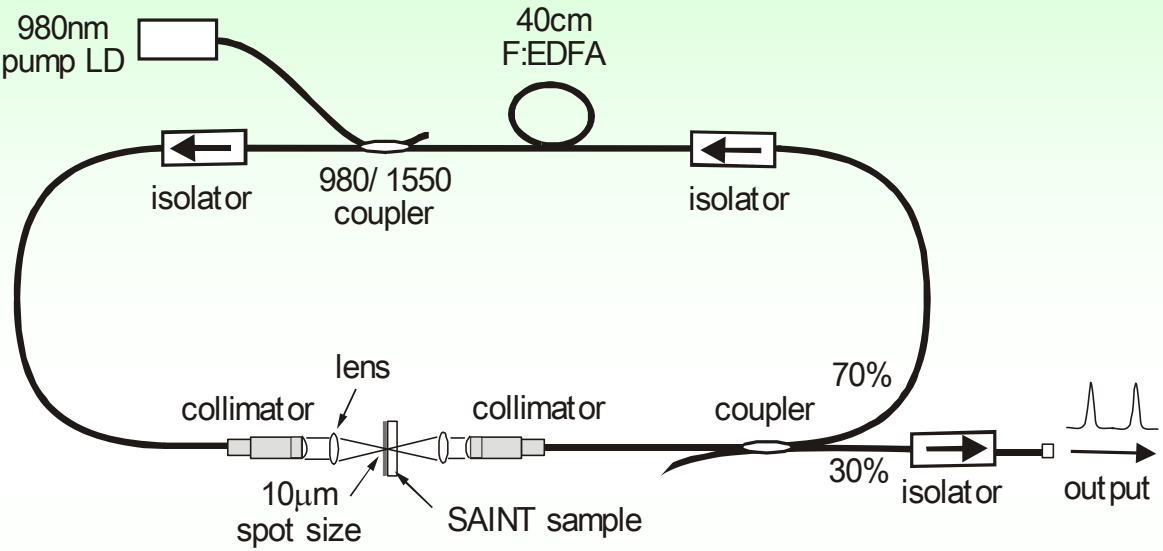
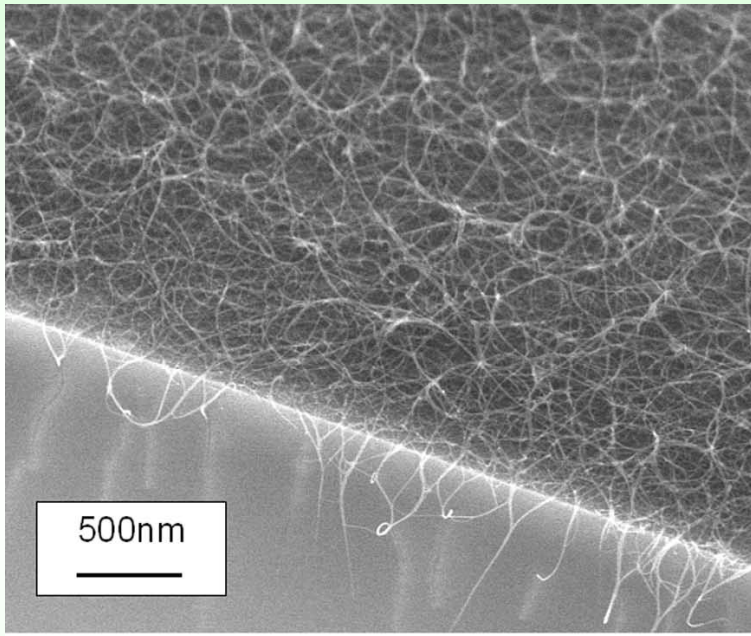
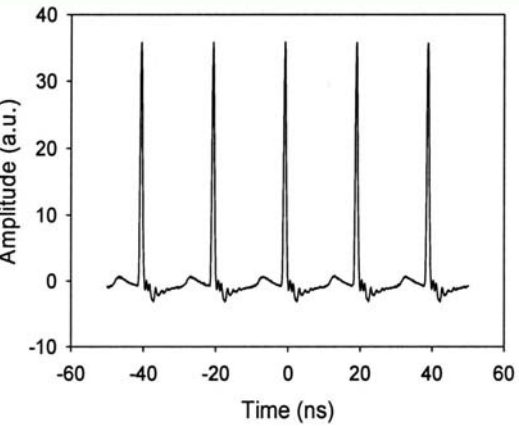
TEL +81 (52)-613-5276, FAX +81 (52)-613-5347
e-mail: yuji_ozeki@nts.toray.co.jp

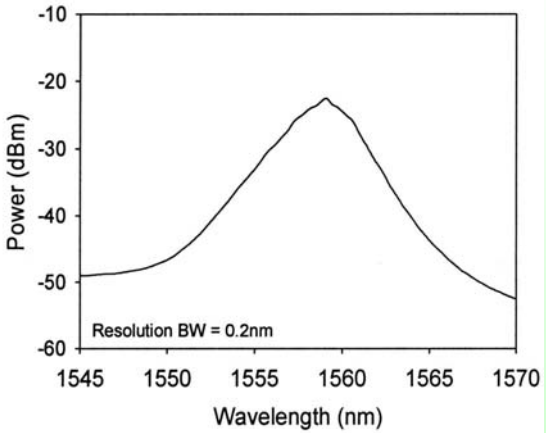
Saturable Absorbers: Application to Mode-Locked Fiber Lasers



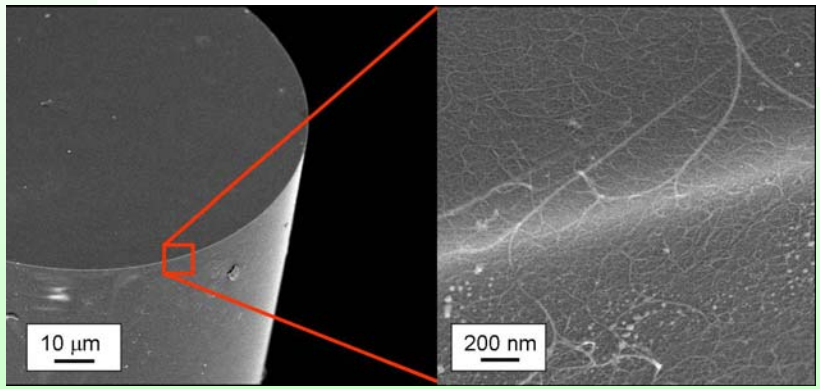




(a)

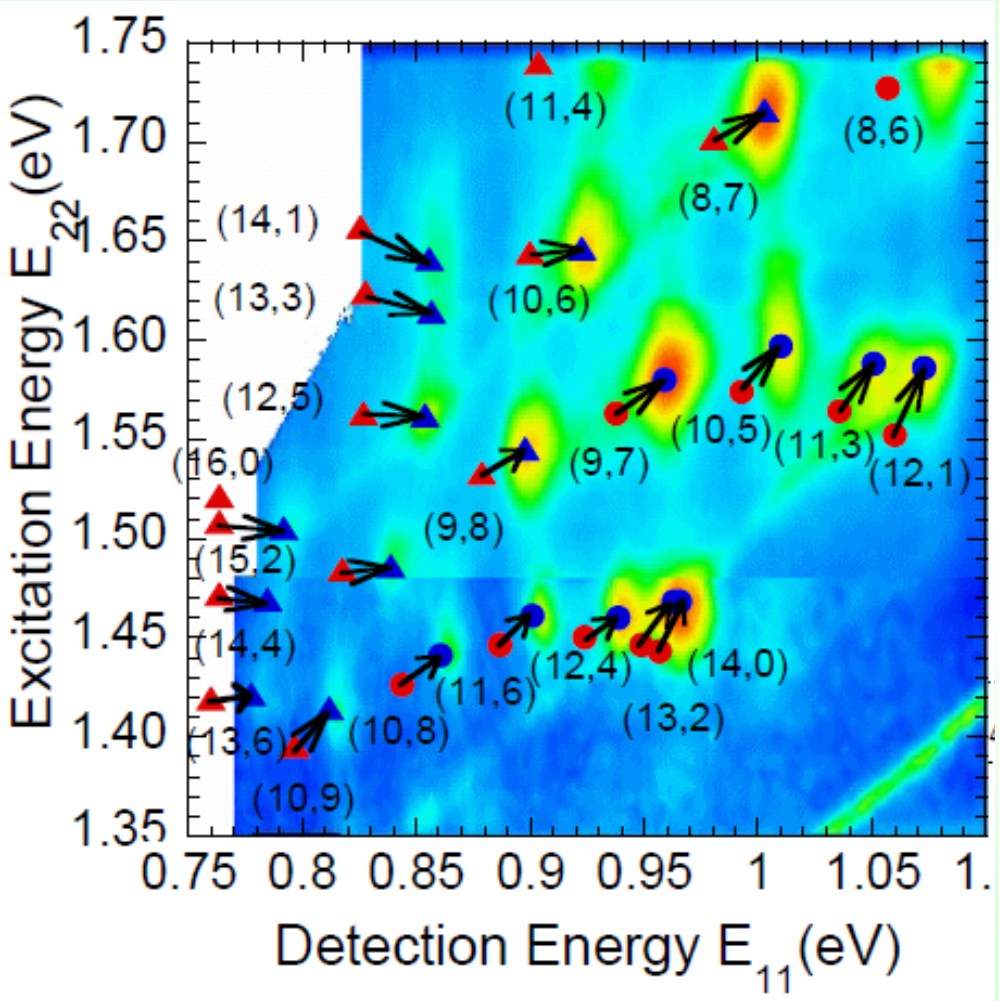


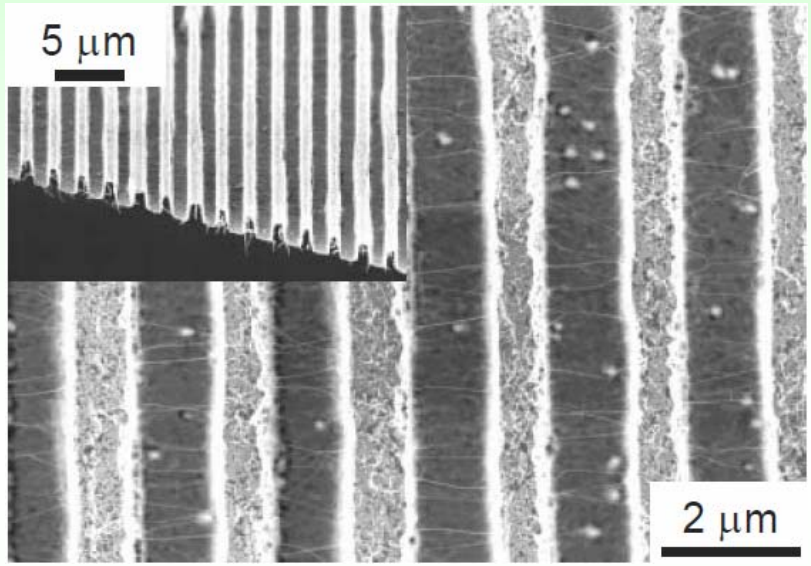
(b)



S. Yamashita, S. Maruyama, Y. Murakami, Y. Inoue, H. Yaguchi, M. Jablonski, S. Y. Set, Optics Letters, 29 (2004) 1581.

Photoluminescence of SWNTs suspended in air



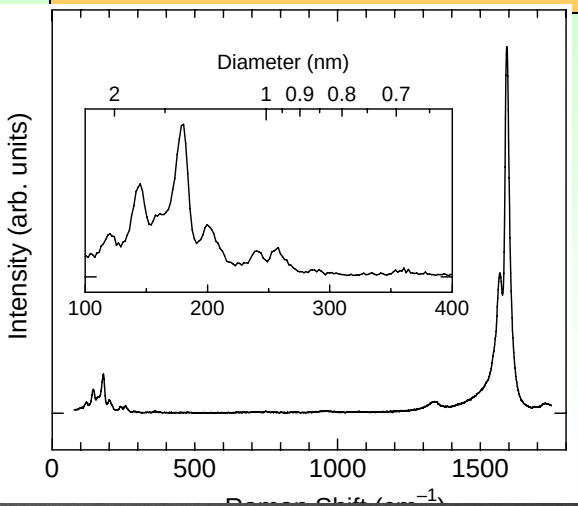


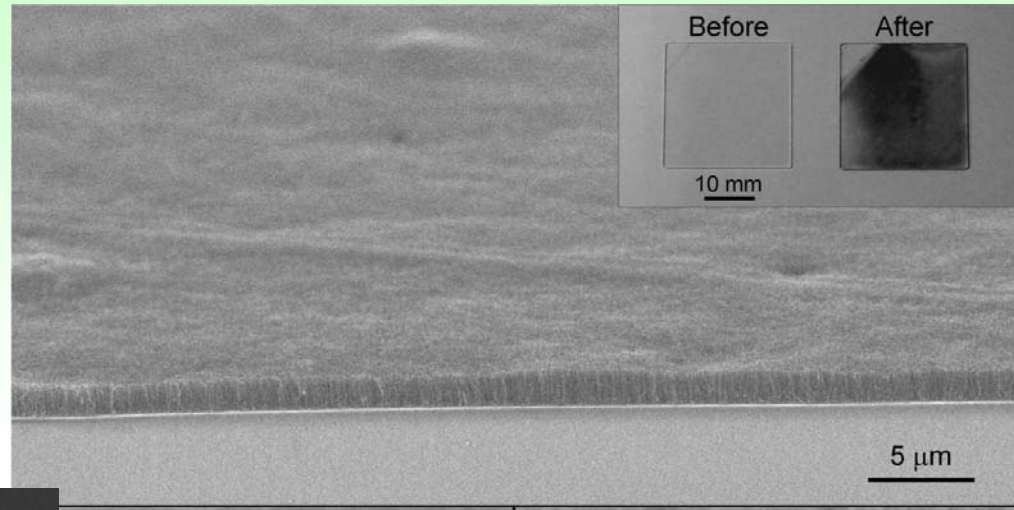
●:Suspended (Type-I)
▲:Suspended (Type-II)
Our experiment

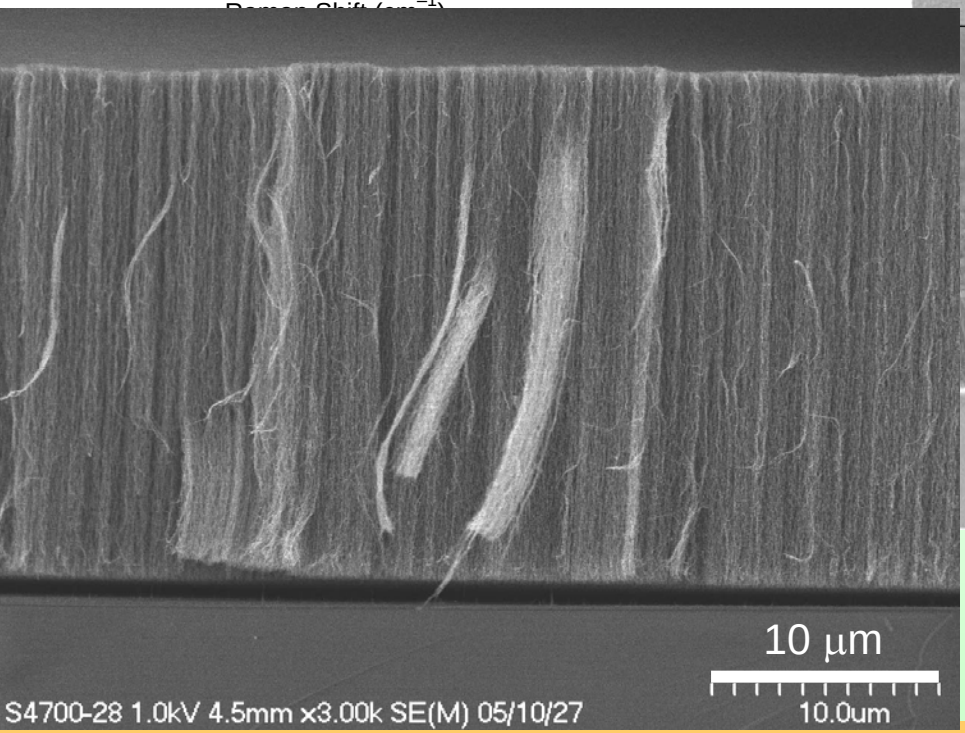
●:SDS-wrapped (Type-I)
▲:SDS-wrapped (Type-II)
(R.B. Weisman *et al. Nano Lett.* **3** (2003) 1235.)

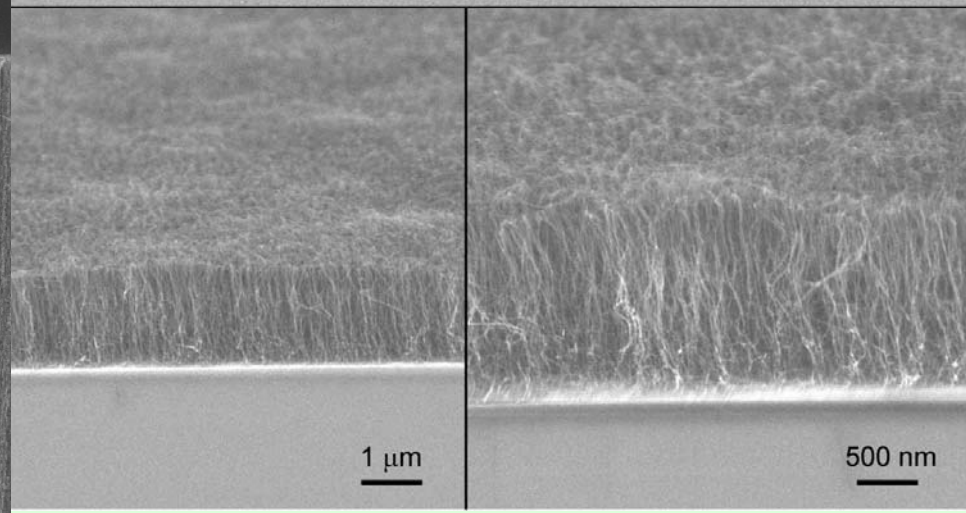
S. Iwasaki, Y. Ohno, Y. Murakami, S. Kishimoto, S. Maruyama, T. Mizutani (2005)

Vertically Aligned SWNTs on Quartz Substrate



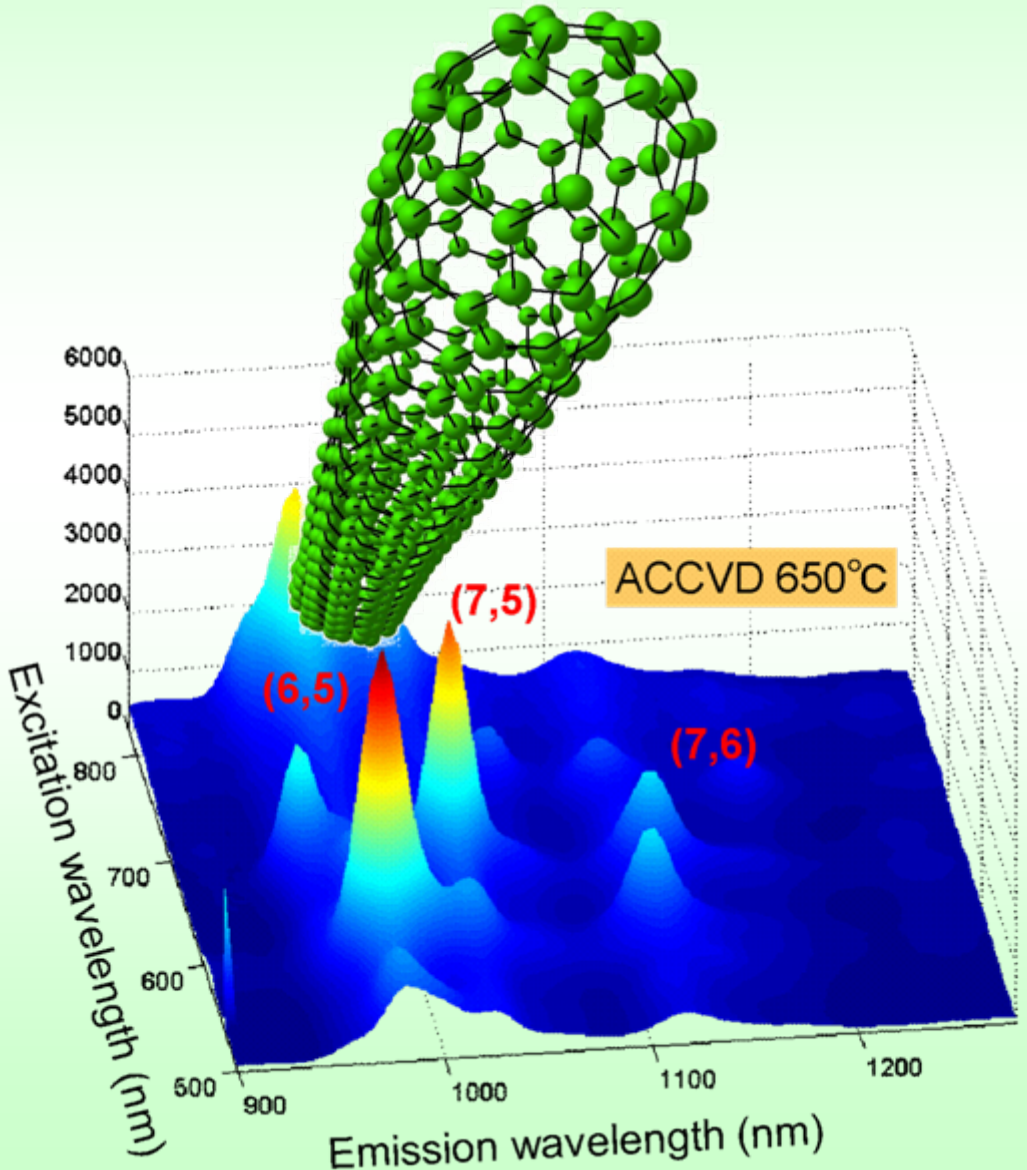




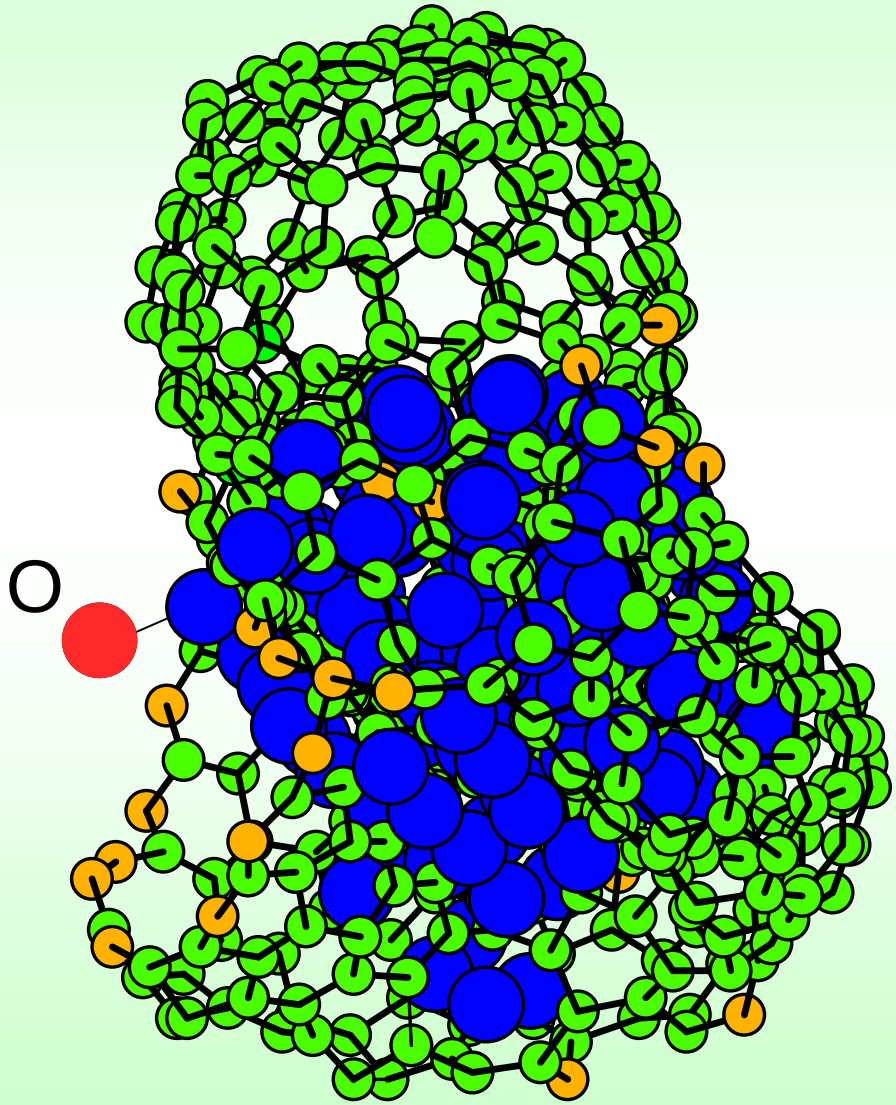


Y. Murakami, S. Chiashi, Y. Miyauchi, M. Hu, M. Ogura, T. Okubo, S. Maruyama, Chem. Phys. Lett. 385 (2004) 298

Narrow Chirality Growth

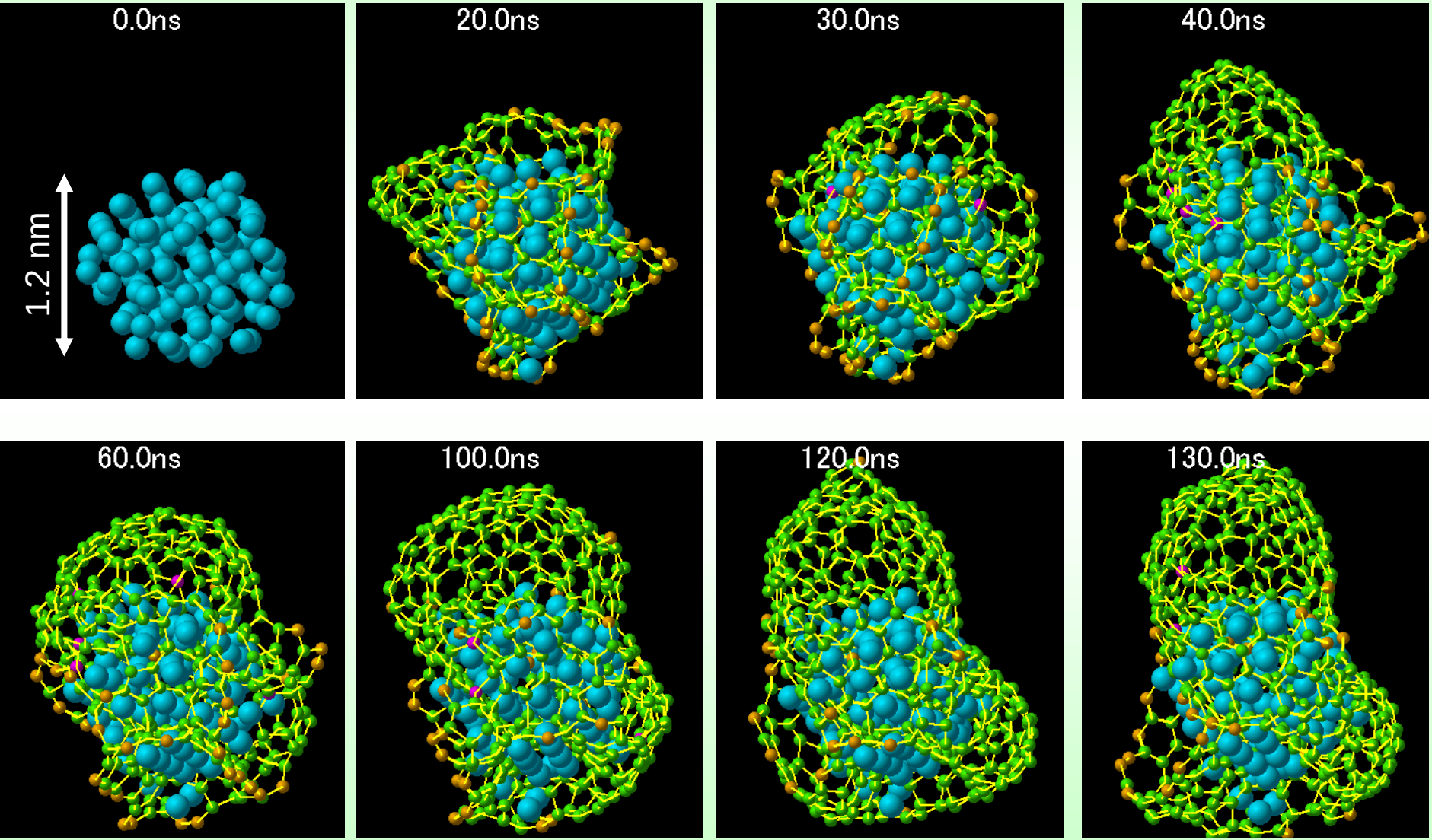


Catalysts and Alcohol Catalytic CVD Method



Molecular Dynamics Simulation for Mechanism

500 Carbon & Ni_{108} : 2500K



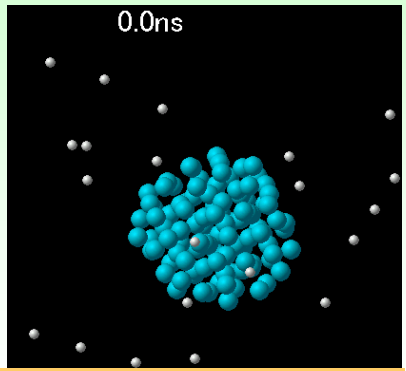
Y. Shibuta & S. Maruyama, Chem. Phys. Lett. 382 (2003) 381.

ACCVD Directly on Flat Surfaces (Dip-Coat)

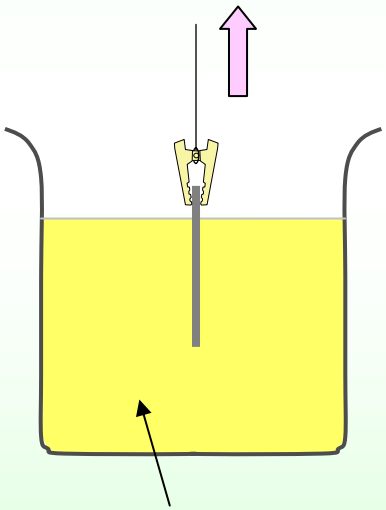
10 min soak
& 4 cm/min

400 °C in Air, 5 min

Heat up to 800 °C
in Ar/H_2 (3 % H_2)



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

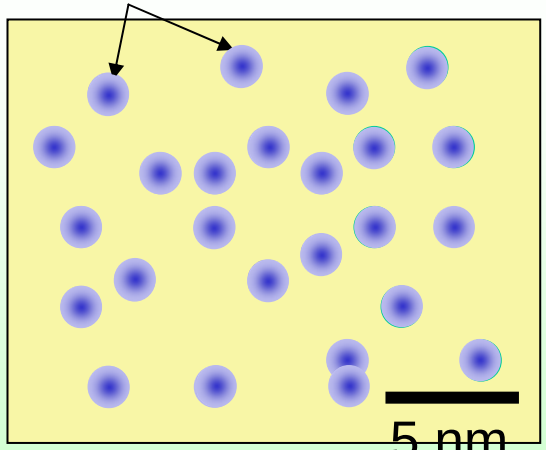


Mo/Co 0.01wt % (each)
Ethanol Solution

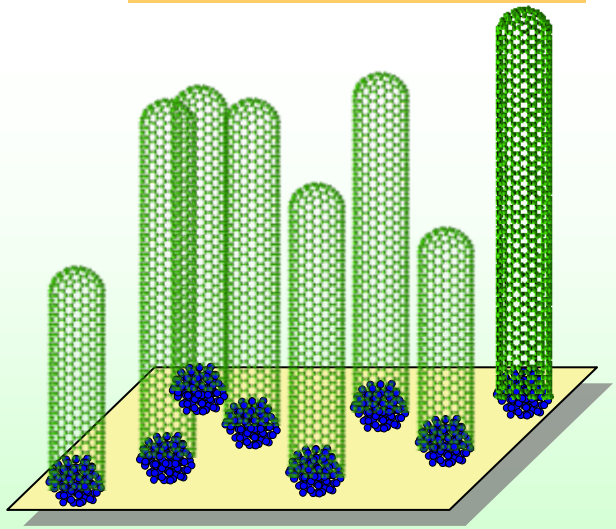
$(CH_3COO)_2Mo$

$(CH_3COO)_2Co\text{-}4H_2O$

1.5 nm Metal
Particles

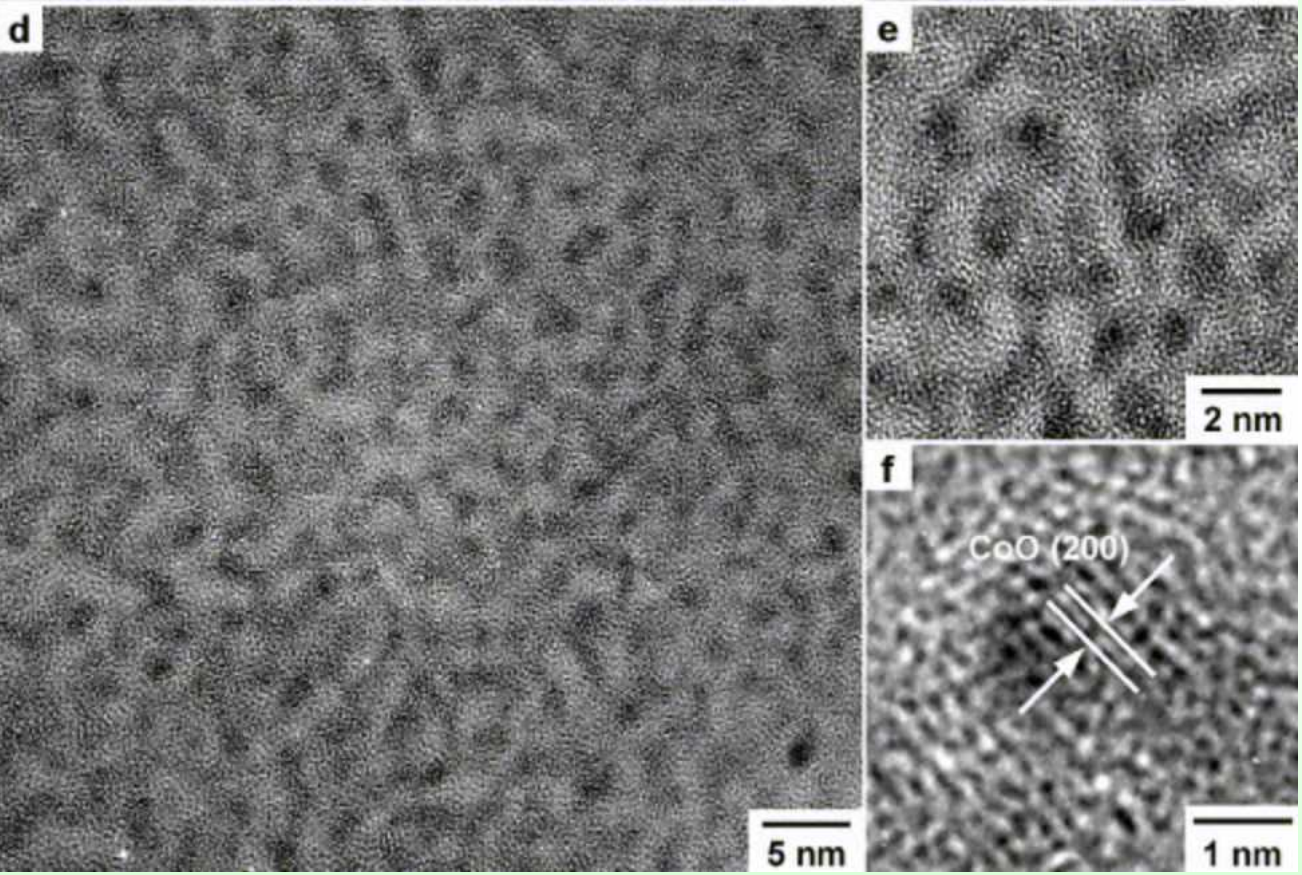


Si or Quartz Substrate



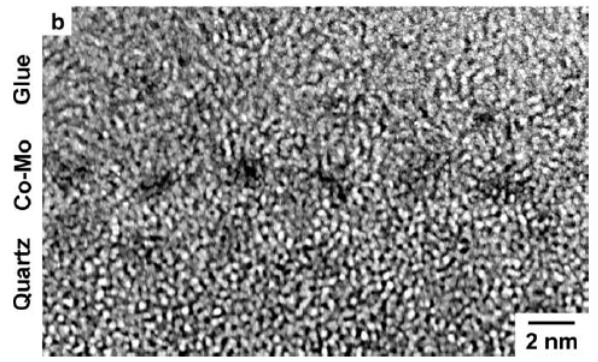
bundle.pv

TEM images of Co-Mo catalysts on SiO_2/Si after reduction

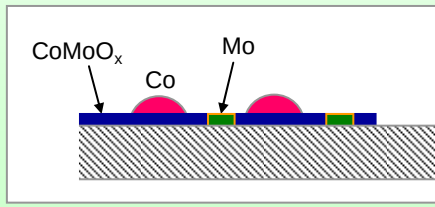


Plan TEM [Quartz/catalyst/SiO2(10 nm)]

Slicing & Punching
Mech. Grinding
Ar Ion Milling



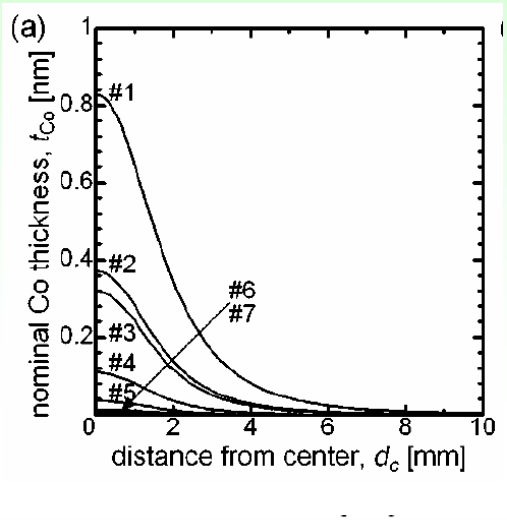
XTEM
[Quartz/catalyst/glue
/catalyst/Quartz]

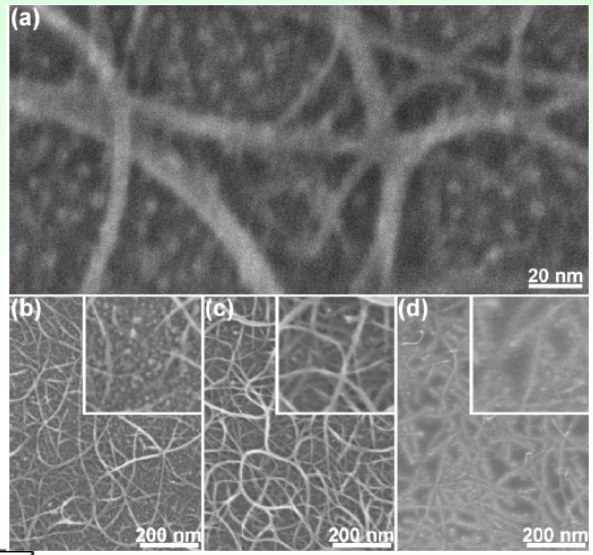


M. Hu, Y. Murakami, M. Ogura, S. Maruyama, T. Okubo, J. Catalysis, 225 (2004) 230.

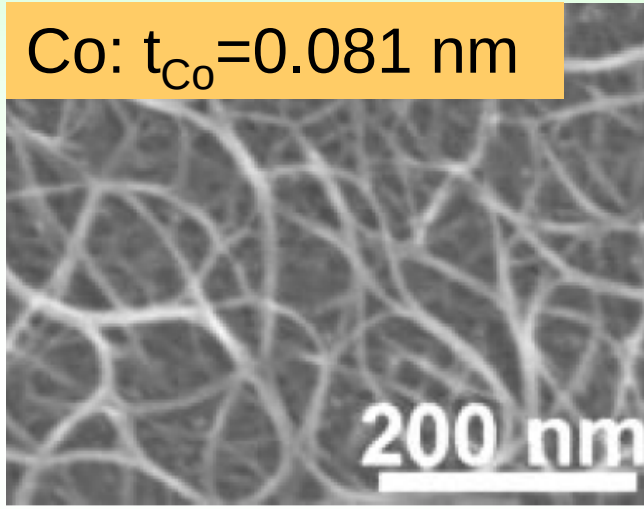
Combinatorial Method to Prepare Catalysts
Ni Grows SWNTs

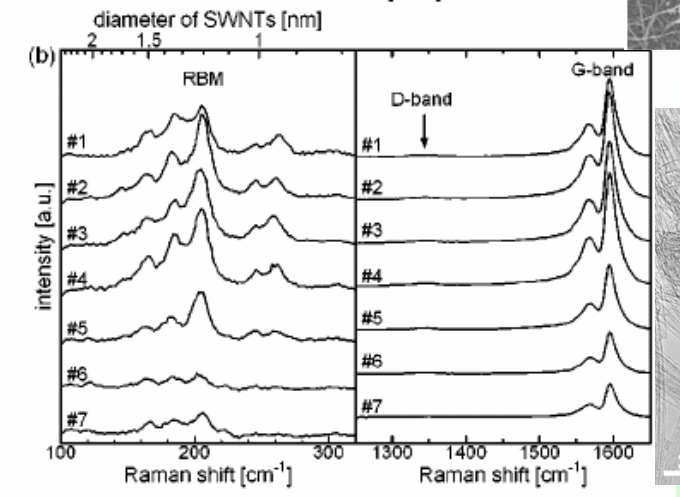
Best Condition

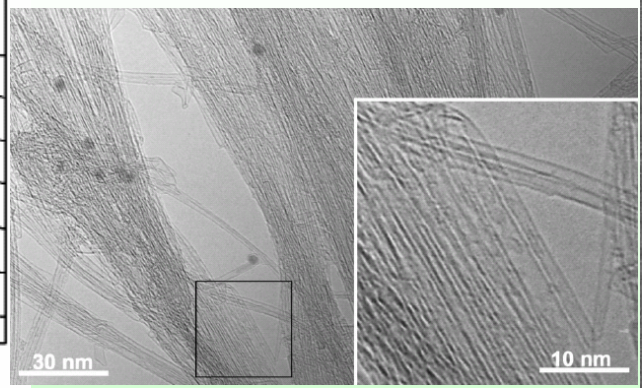


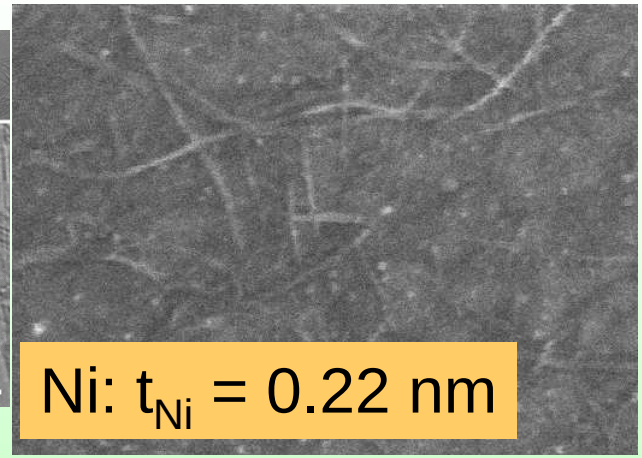


Co: t_{Co}=0.081 nm







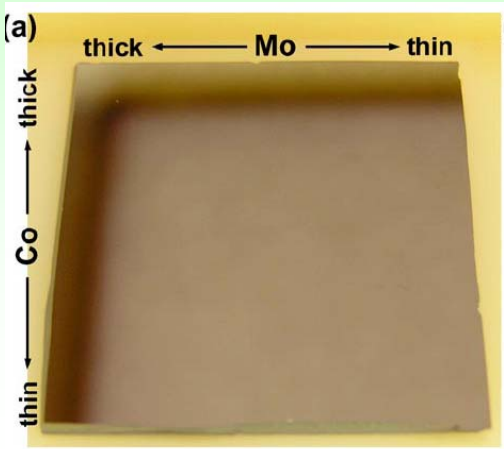


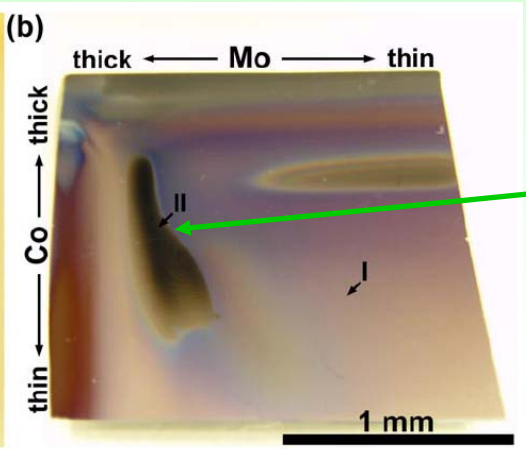
Ni: t_{Ni} = 0.22 nm

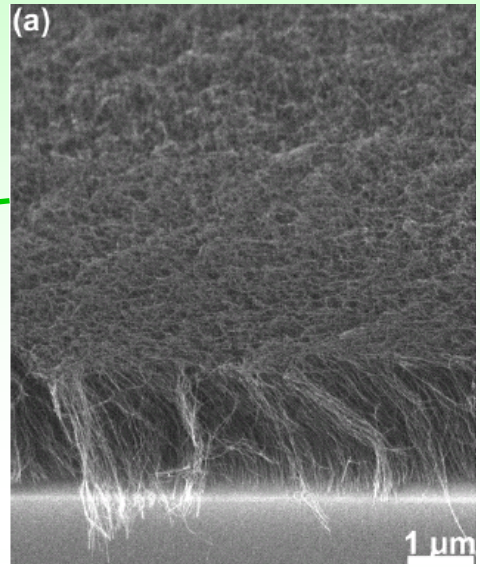
S. Noda, Y. Tsuji, Y. Murakami, S. Maruyama, Appl. Phys. Lett., 86 (2005) 173106.

K. Kakehi, S. Noda, S. Chiashi, S. Maruyama (2006)

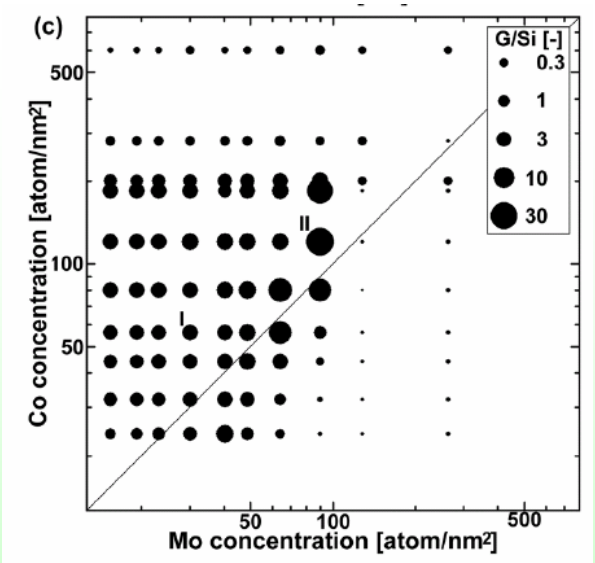
Combinatorial Method for (Co-Mo) Catalysts

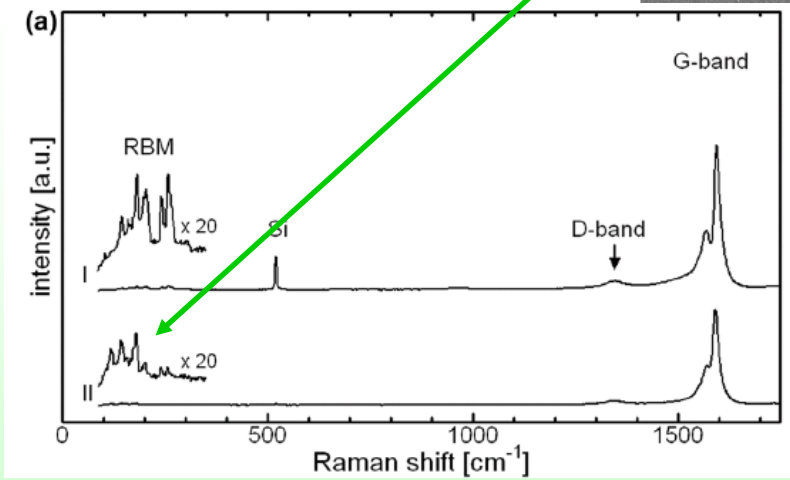






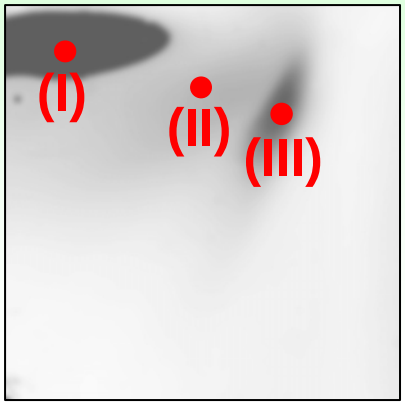
Vertically Aligned





S. Noda, H. Sugime, T. Osawa, Y. Tsuji, S. Chiashi, Y. Murakami, and S. Maruyama, Carbon 44 (2006) 1414.

Combinatorial Method for (Co-Mo) Catalysts (2)

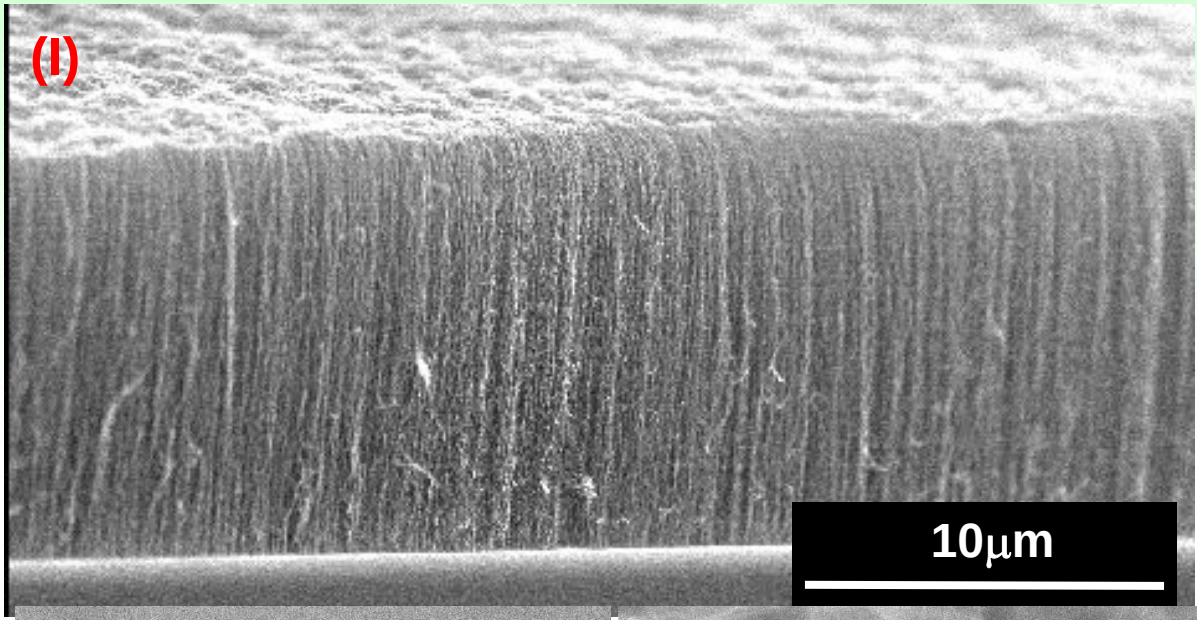


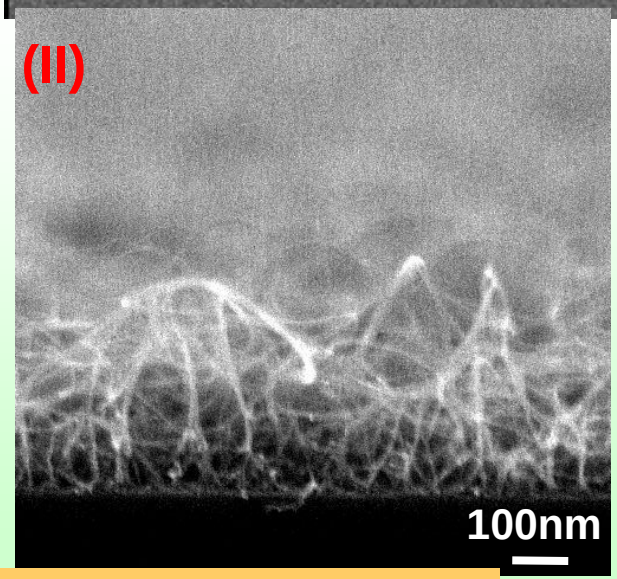
thick
↑
Co
↓
thin

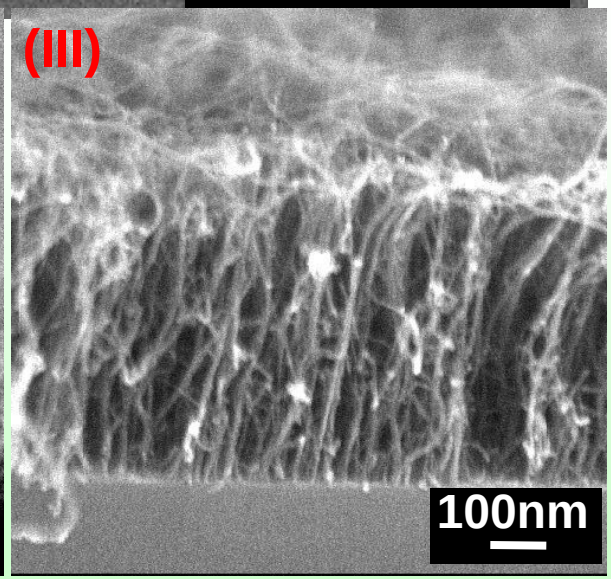
thin ← Mo → thick

Co/Mo [nm]
(I) 0.33/0.049
(II) 0.19/0.13
(III) 0.13/0.34

Reduction temperature : 800℃
Reaction temperature : 800℃
Pressure of ethanol : 30Torr
Reaction time : 10min

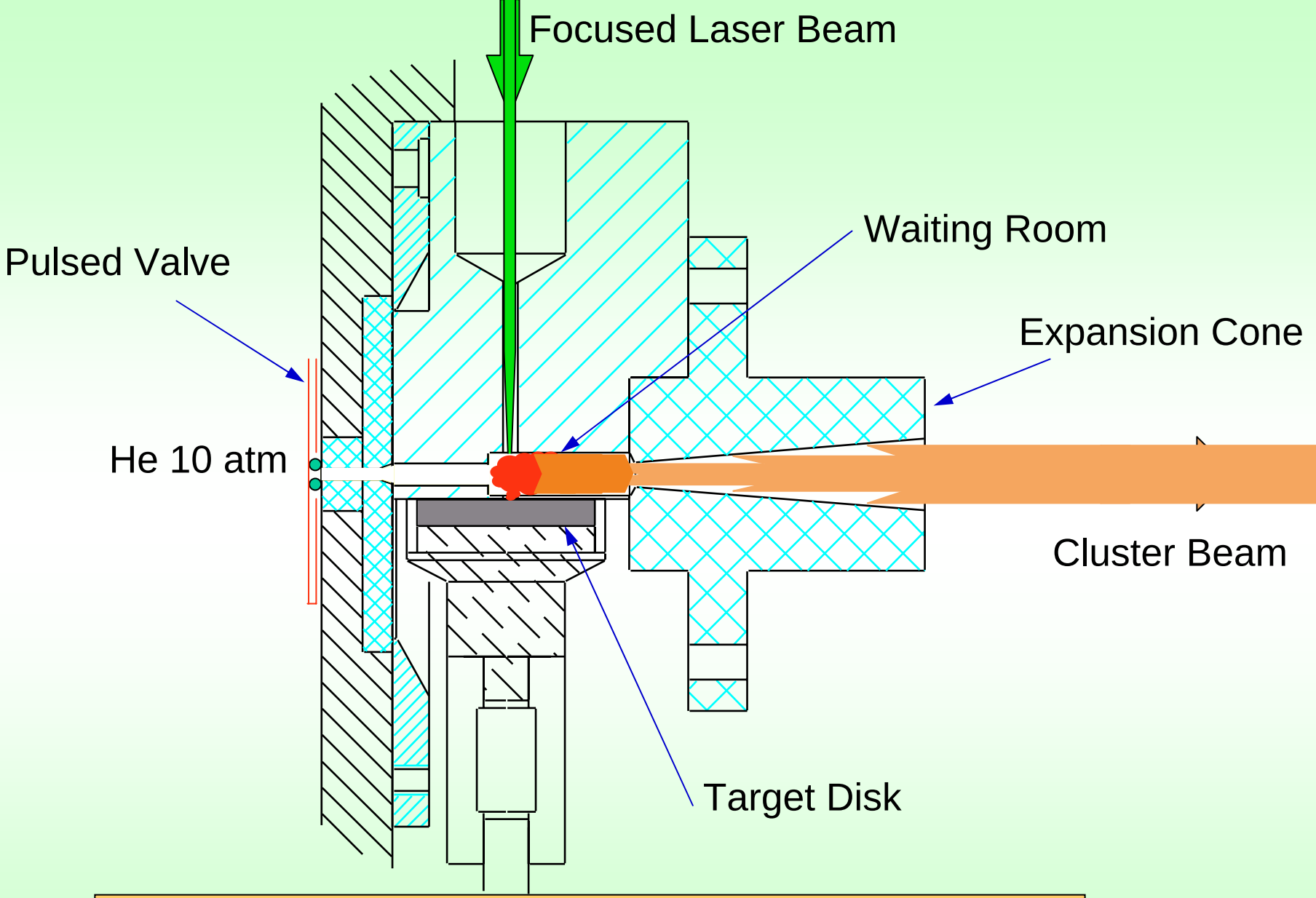




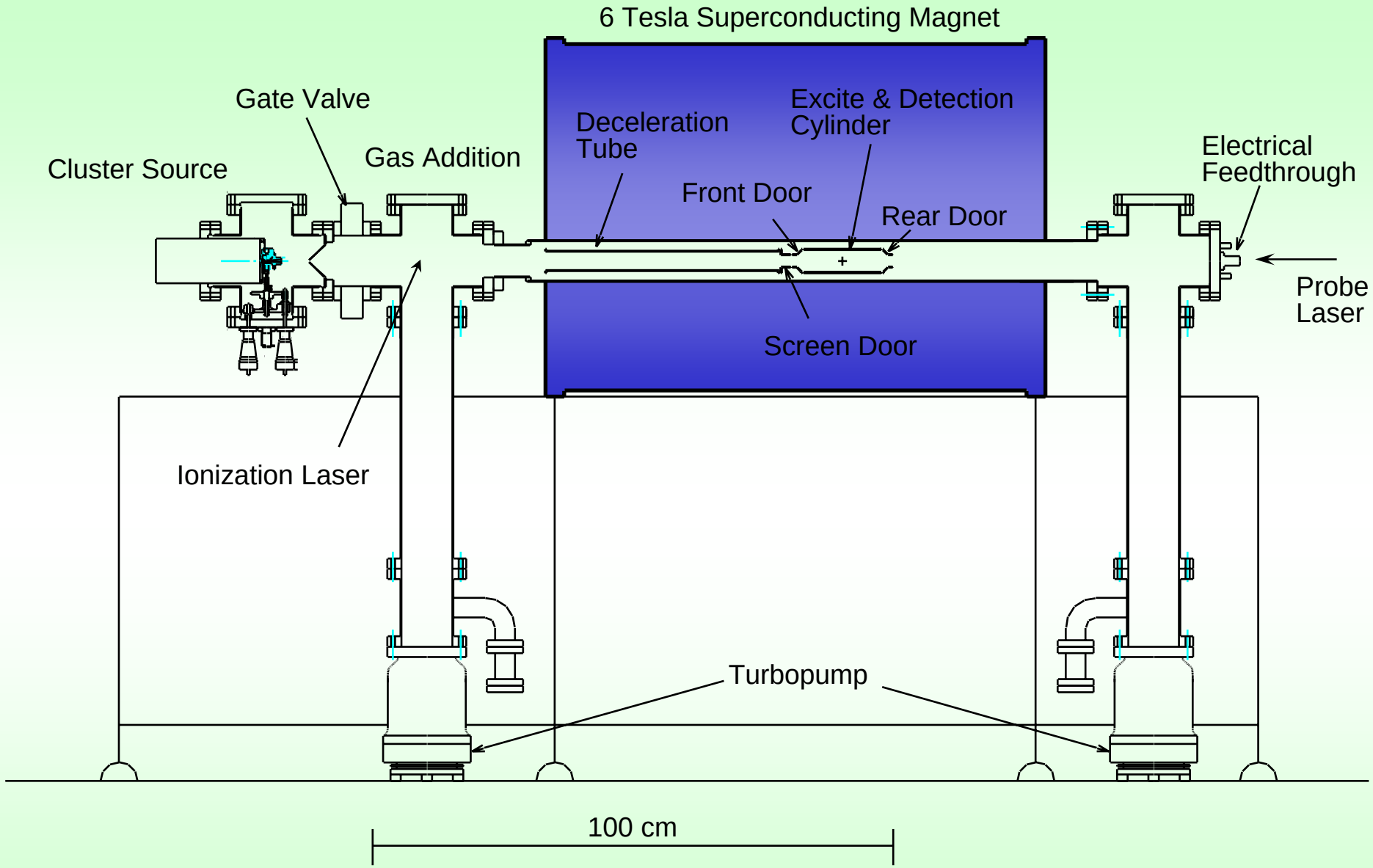


H. Sugime, S. Noda, S. Maruyama, Y. Yamaguchi (2006).

Initial Reaction on Catalyst

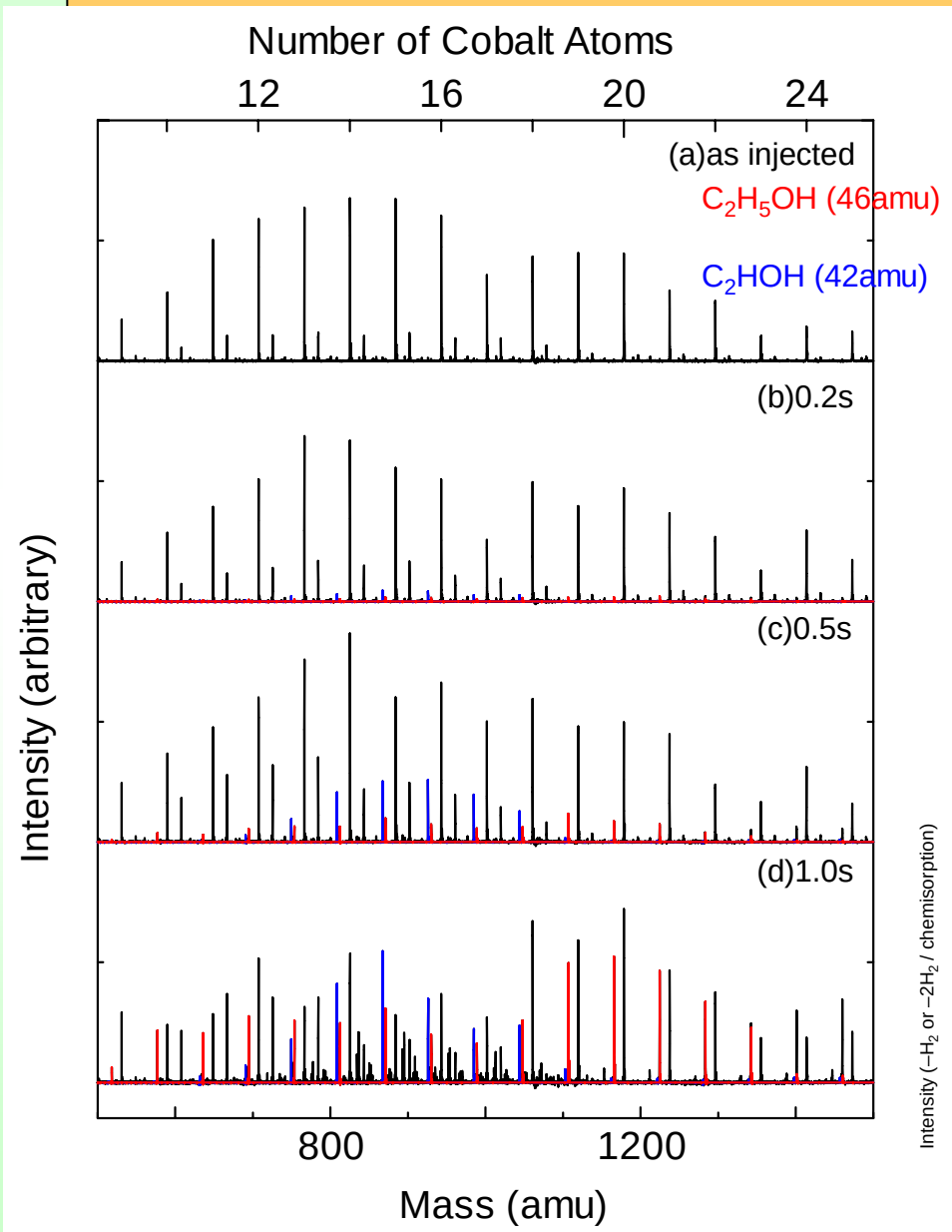


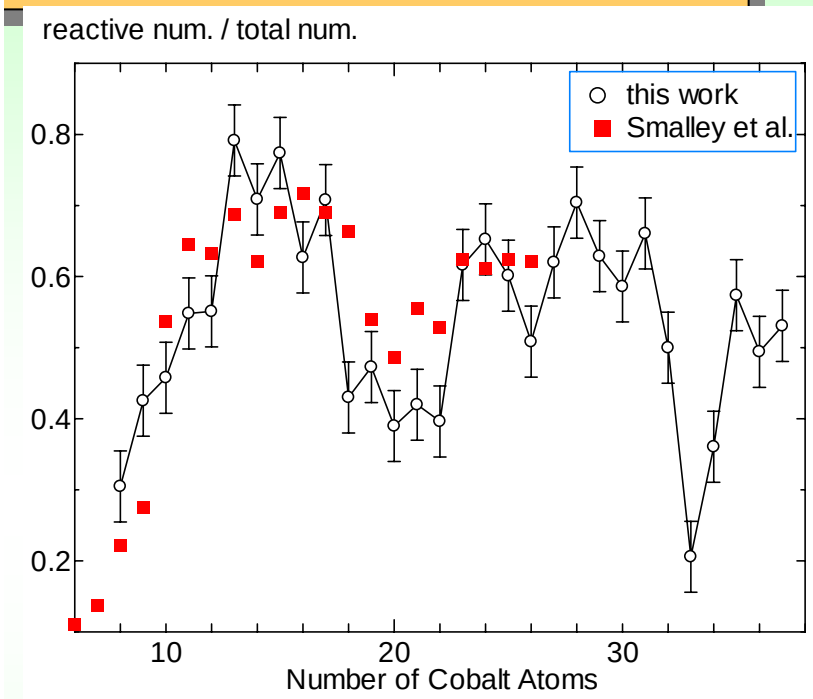
Cluster Source Nozzle for FT-ICR

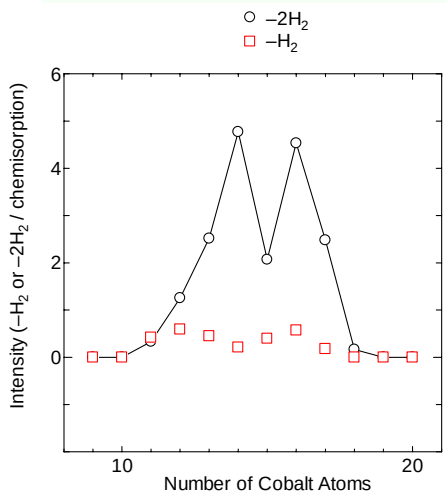


FT-ICR (Fourier Transform Ion Cyclotron Resonance) Mass Spectrometer

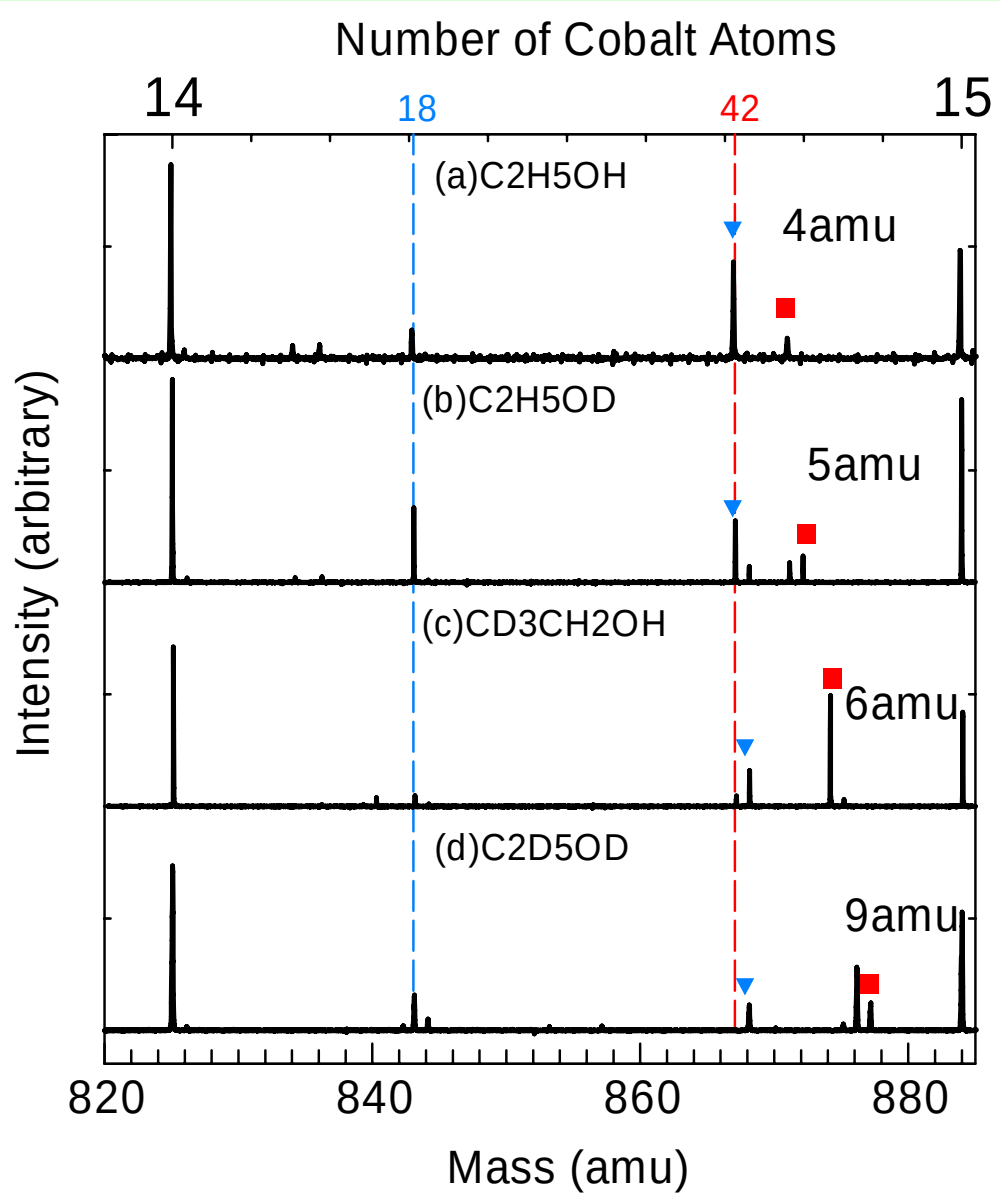
FT-ICR Study of Initial Reaction

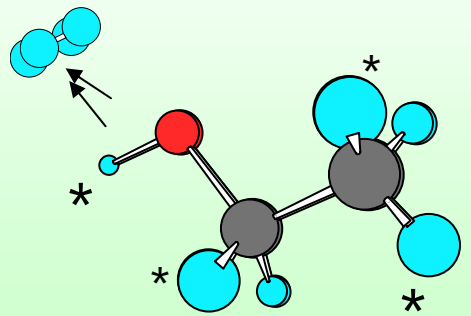




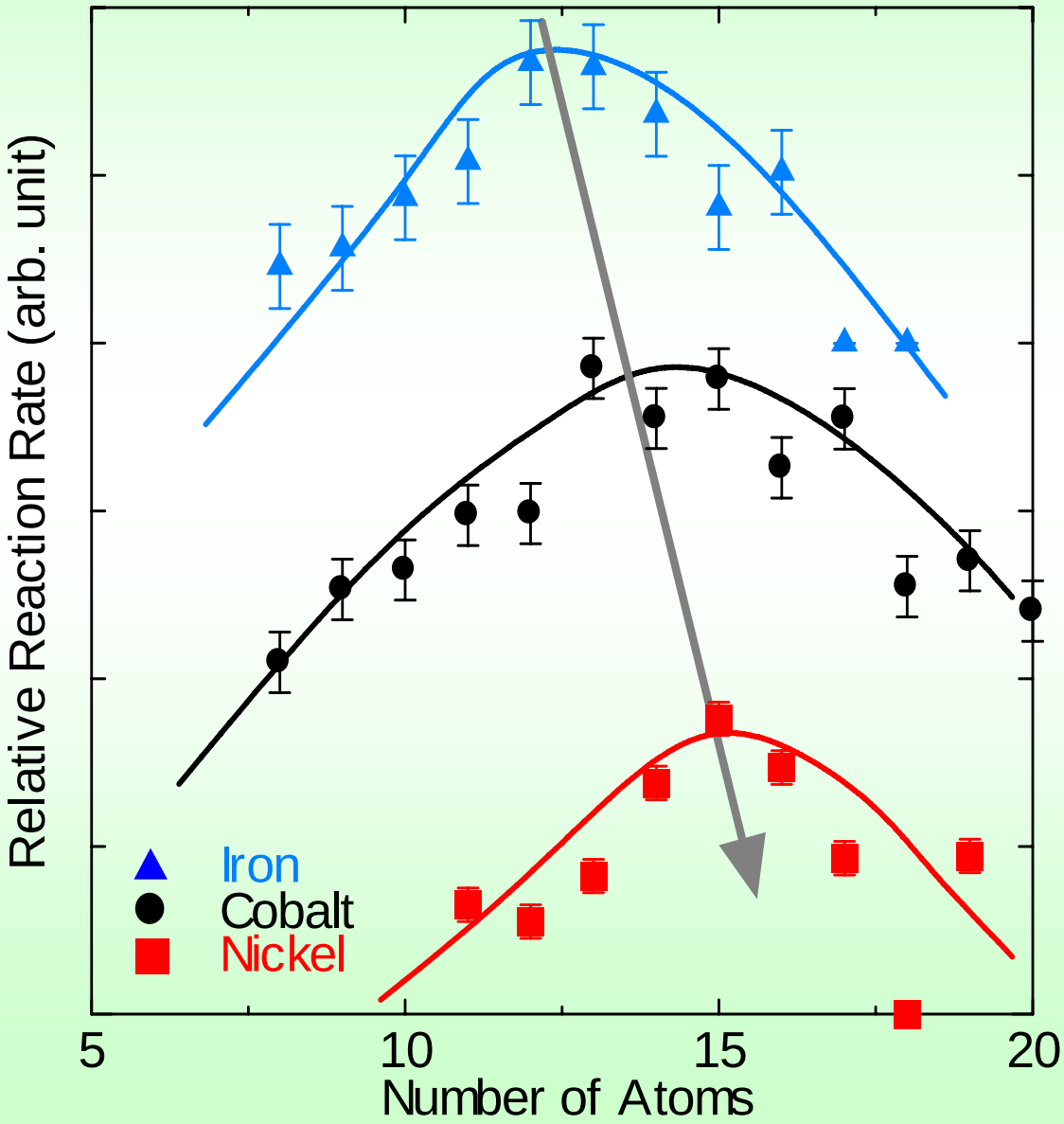


FT-ICR Chemical reaction of cobalt clusters (cation) with ethanol



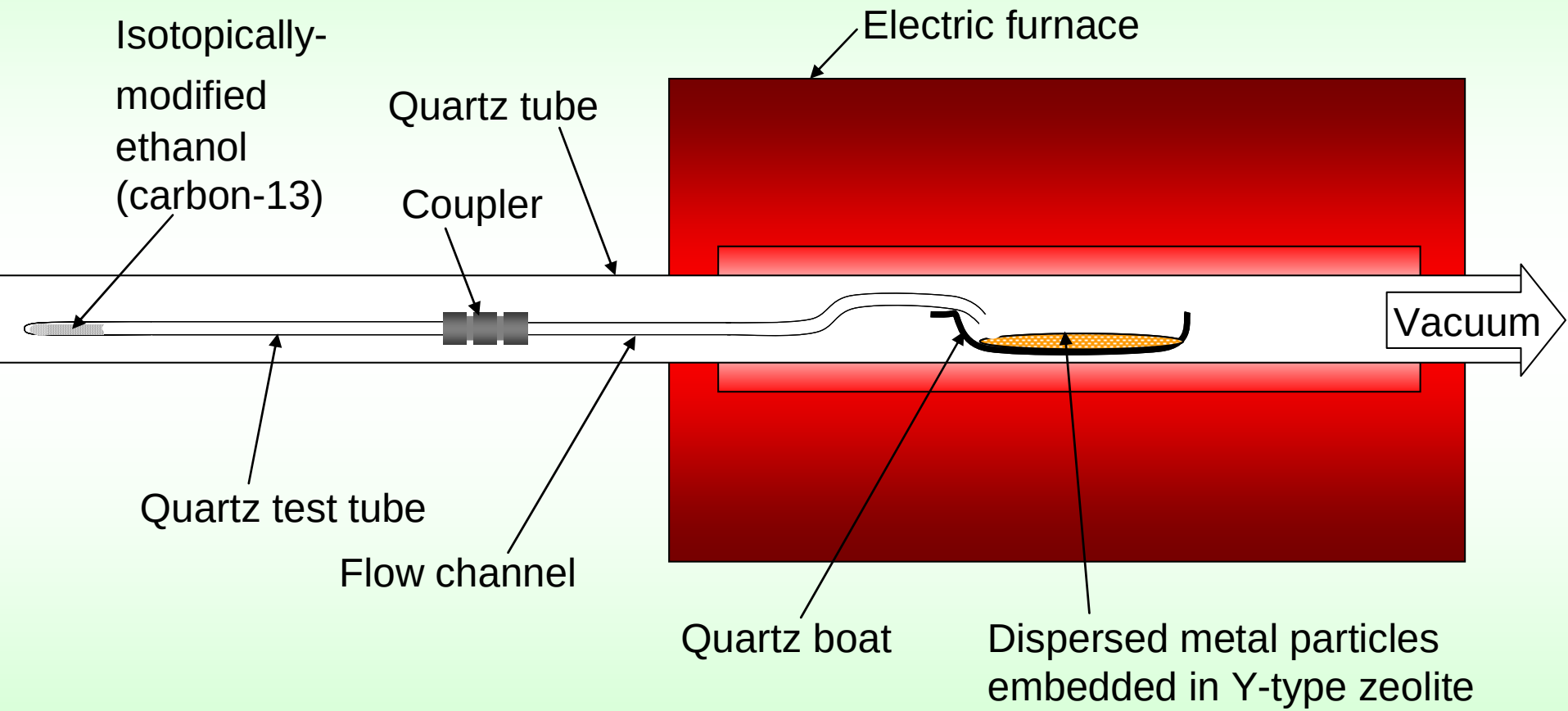


FT-ICR Study of Initial Reaction



- Iron
  - ✧Simple chemisorption
- Cobalt
  - ✧Simple chemisorption
  - ✧Dehydrogenation
- Nickel
  - ✧Dehydrogenation

Single-Walled Carbon-13 Nanotubes (SW^{13}CNTs)



ACCVD technique optimized for the efficient production of SWNTs from very small amount of ethanol

Comparison of Raman Spectra

(d) ② ①

(c) $^{13}CH_3$- $^{13}CH_2$- OH

(b) $^{12}CH_3$- $^{13}CH_2$- OH

(a) $^{13}CH_3$- $^{12}CH_2$- OH

$^{12}CH_3$- $^{12}CH_2$- OH ← Normal ethanol

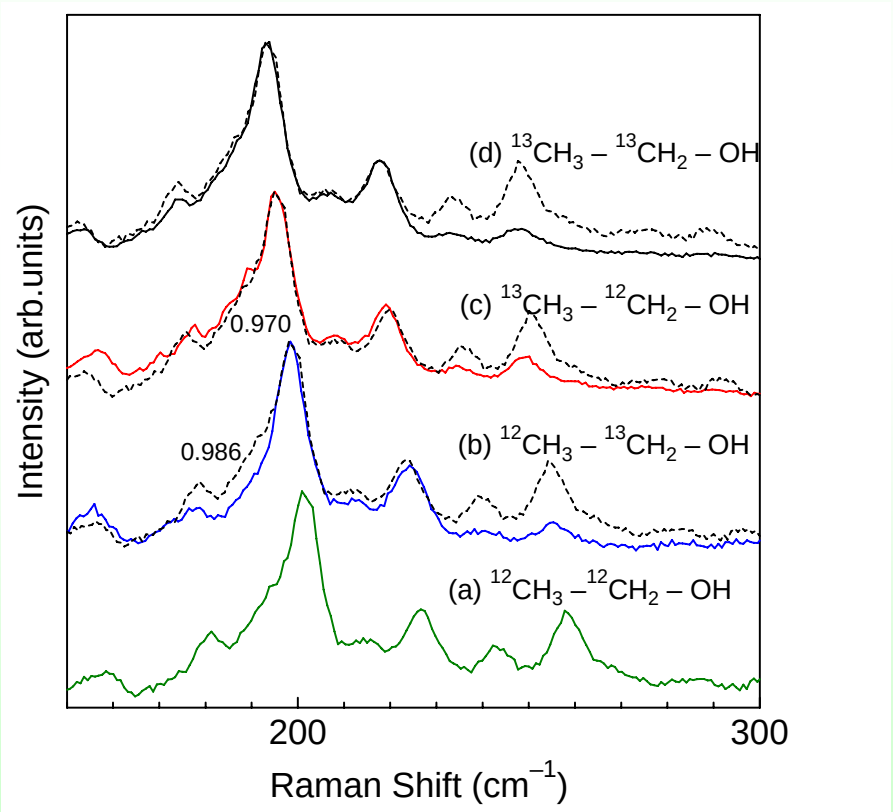
SWNTs with various amount of ^{13}C abundance were synthesized from 3 types of isotope-modified ethanol

Assuming…

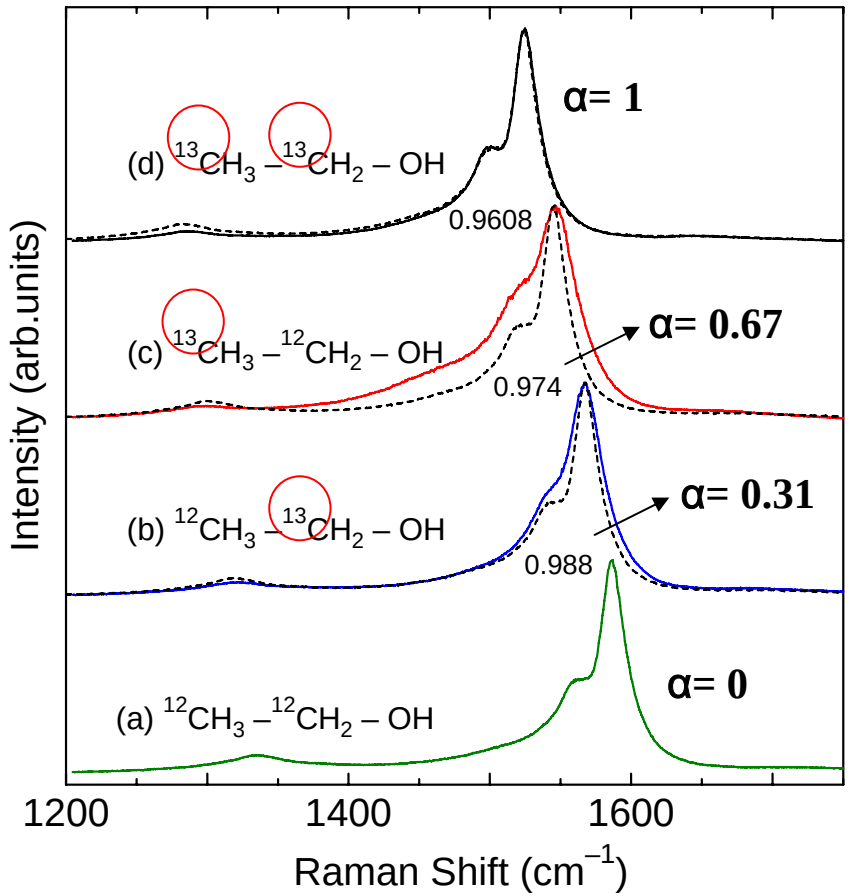
$$\nu_{vib} \propto \sqrt{\frac{1}{12}(1-\alpha)+\frac{1}{13}\alpha}$$

α : Ratio of ^{13}C in a SWNT

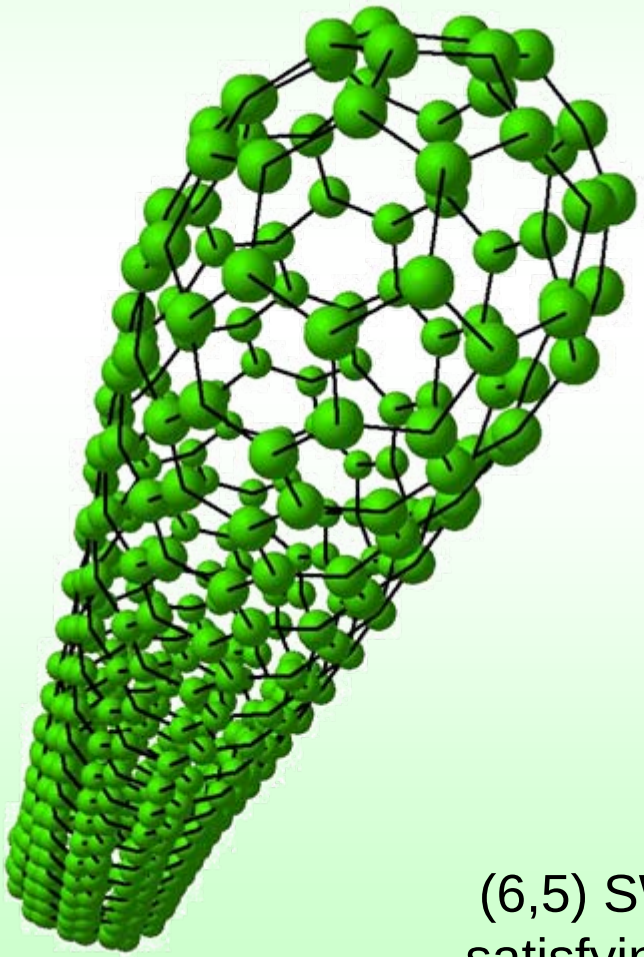
$$\nu_{\alpha} = \nu_{12C} \times \sqrt{(1-\alpha)+\frac{12}{13}\alpha}$$ ⇦ Scaling factor



Two carbon atoms in an ethanol molecule are not equally used for the SWNT formation in ACCVD process



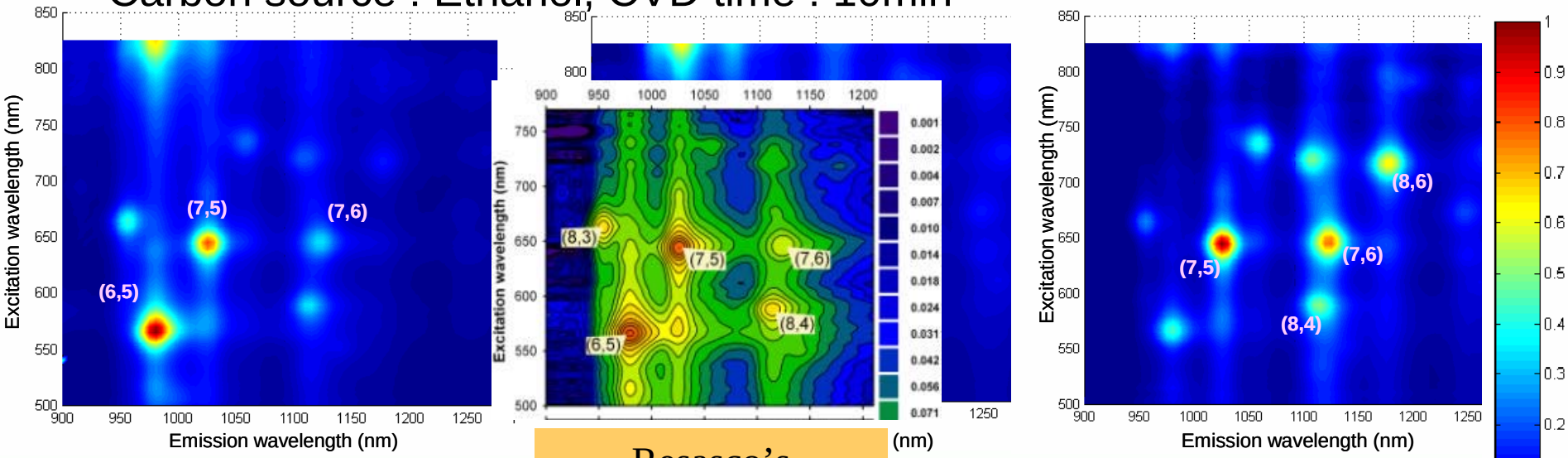
Determination of Chirality



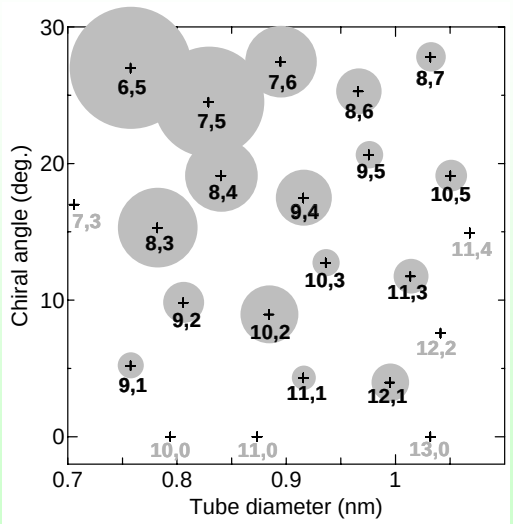
(6,5) SWNT with unique cap structure satisfying Isolated Pentagon Rule (IPR)

CVD Temperature Dependence

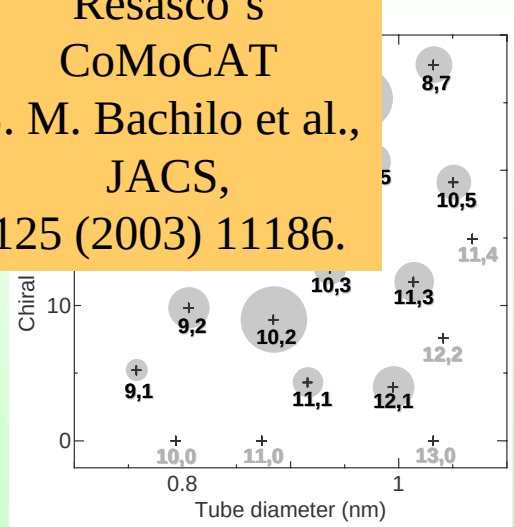
Carbon source : Ethanol, CVD time : 10min



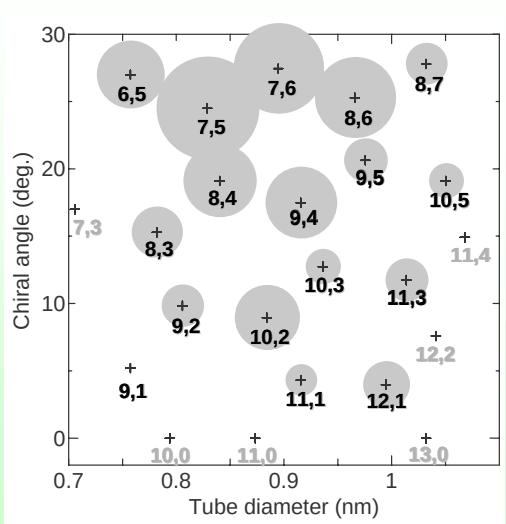
Resasco's CoMoCAT
S. M. Bachilo et al., JACS,
125 (2003) 11186.



650℃

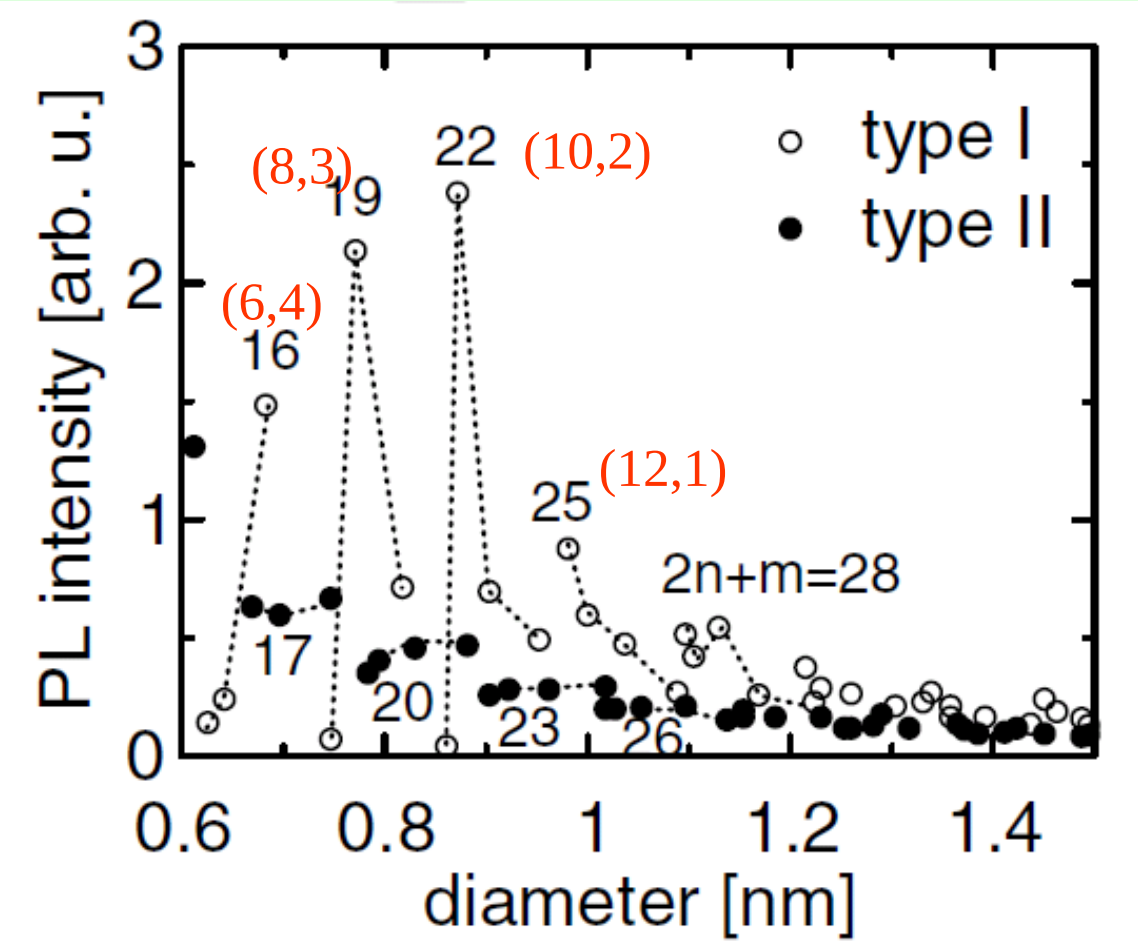


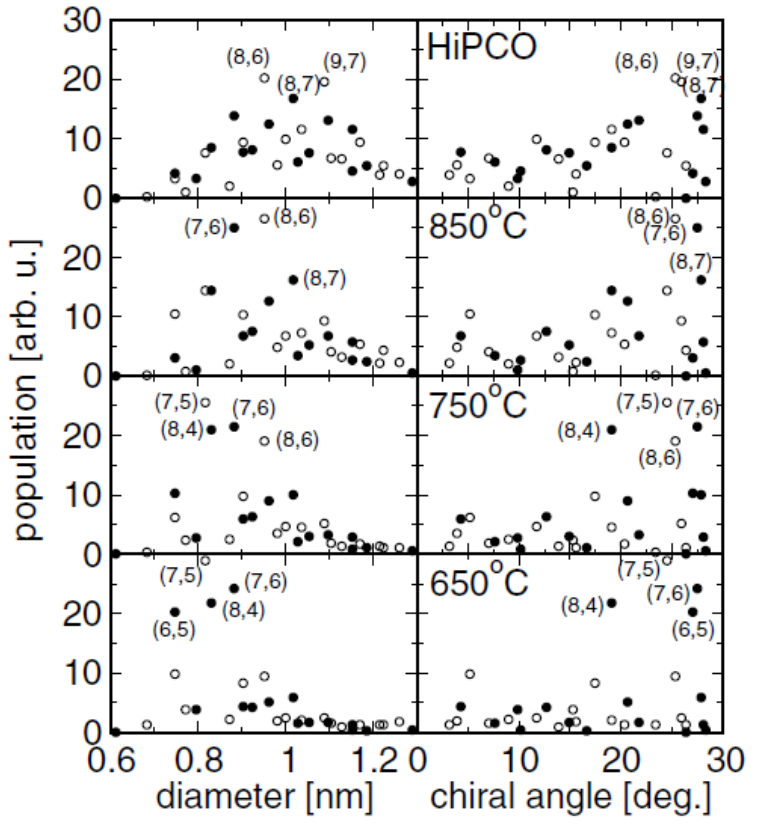
750℃



850℃

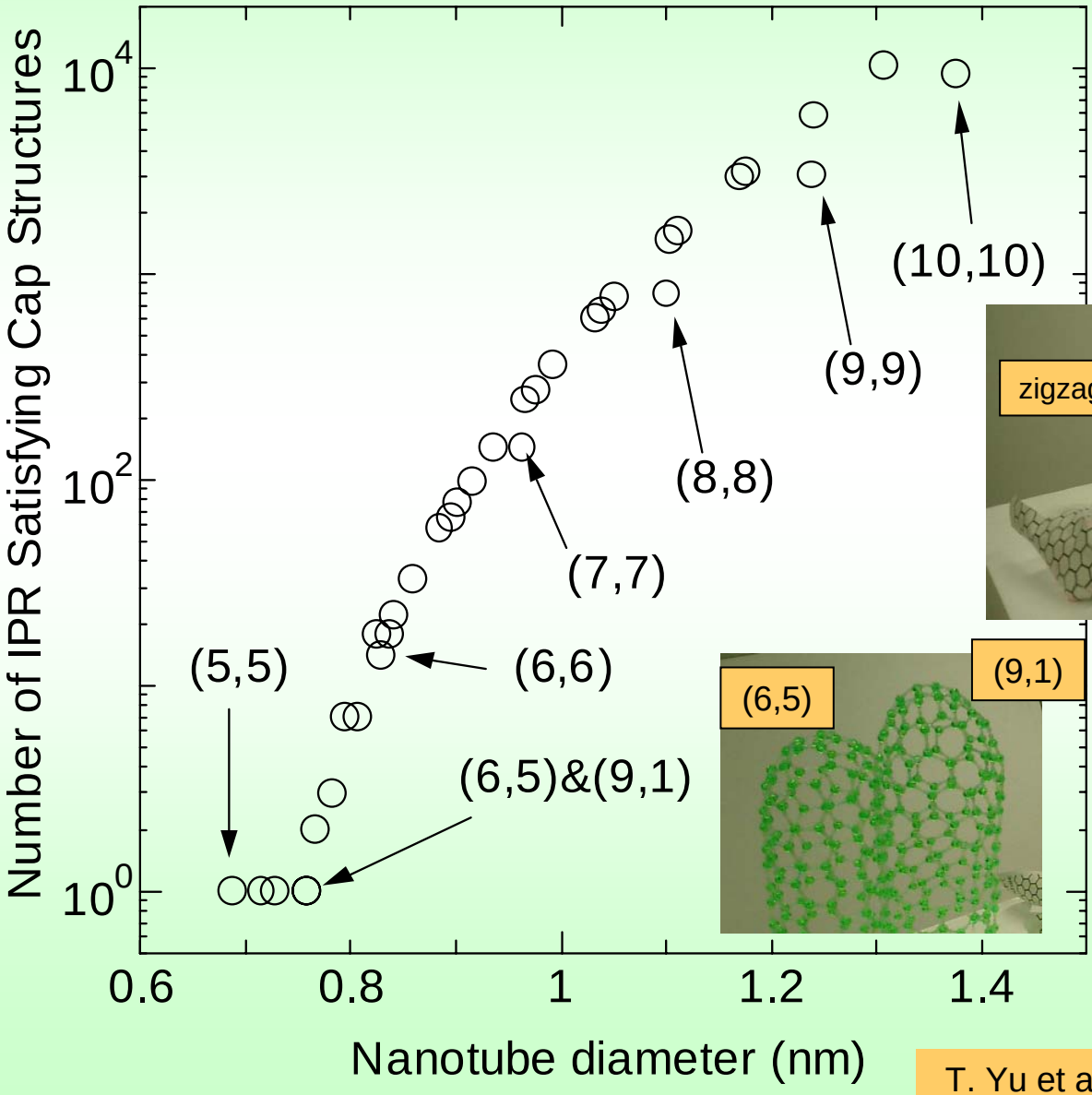
Chirality dependent quantum yield

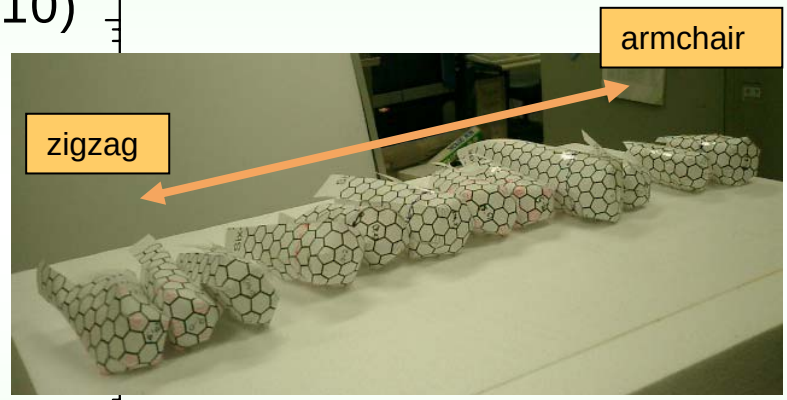




Y. Oyama, R. Saito, K. Sato, J. Jiang, Ge.G. Samsonidze, A. Gruneis, Y. Miyauchi, S. Maruyama, A. Jorio, G. Dresselhaus, M.S. Dresselhaus, Carbon in press.

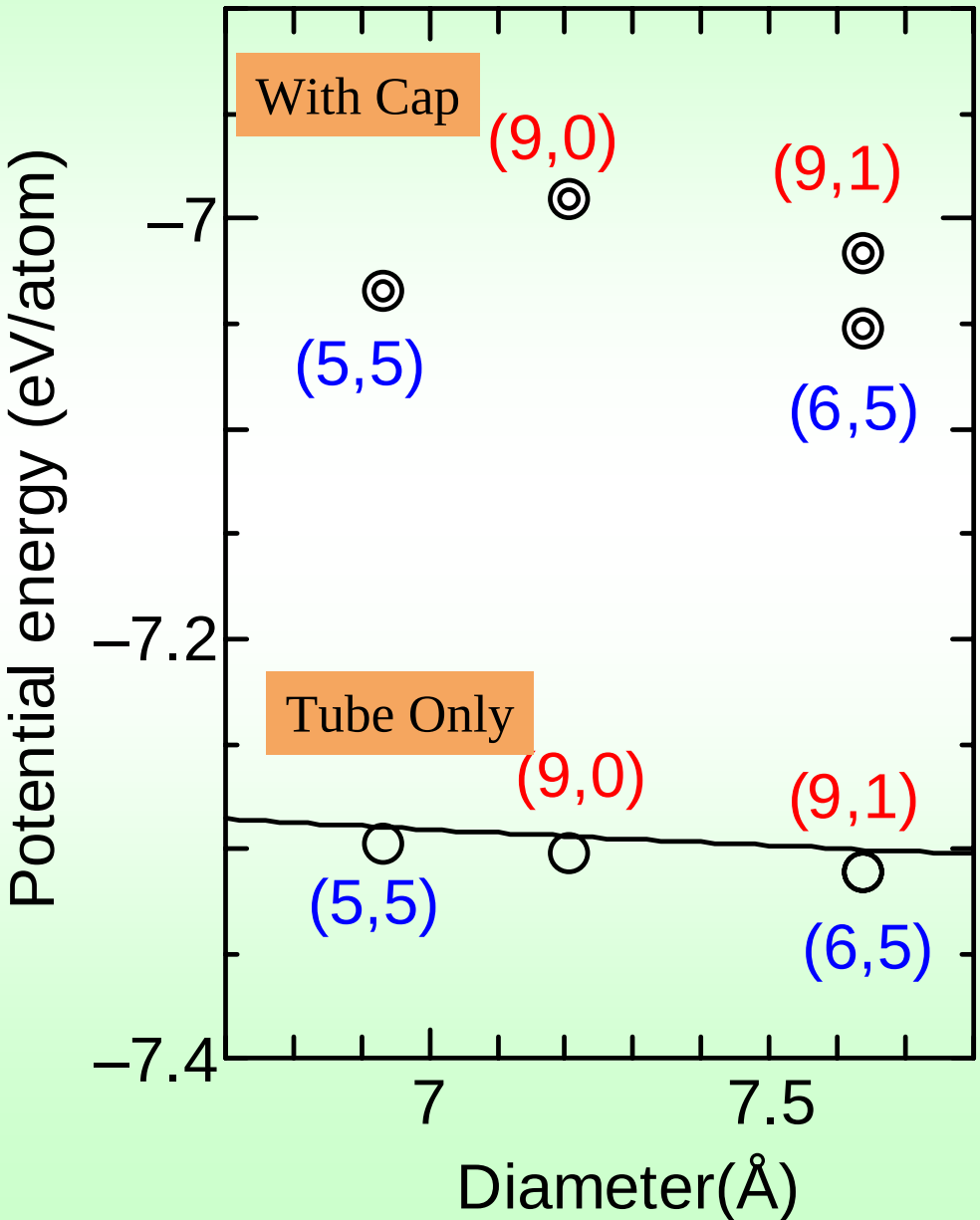
IPR (Isolated Pentagon Rule)-Satisfying Cap Structure

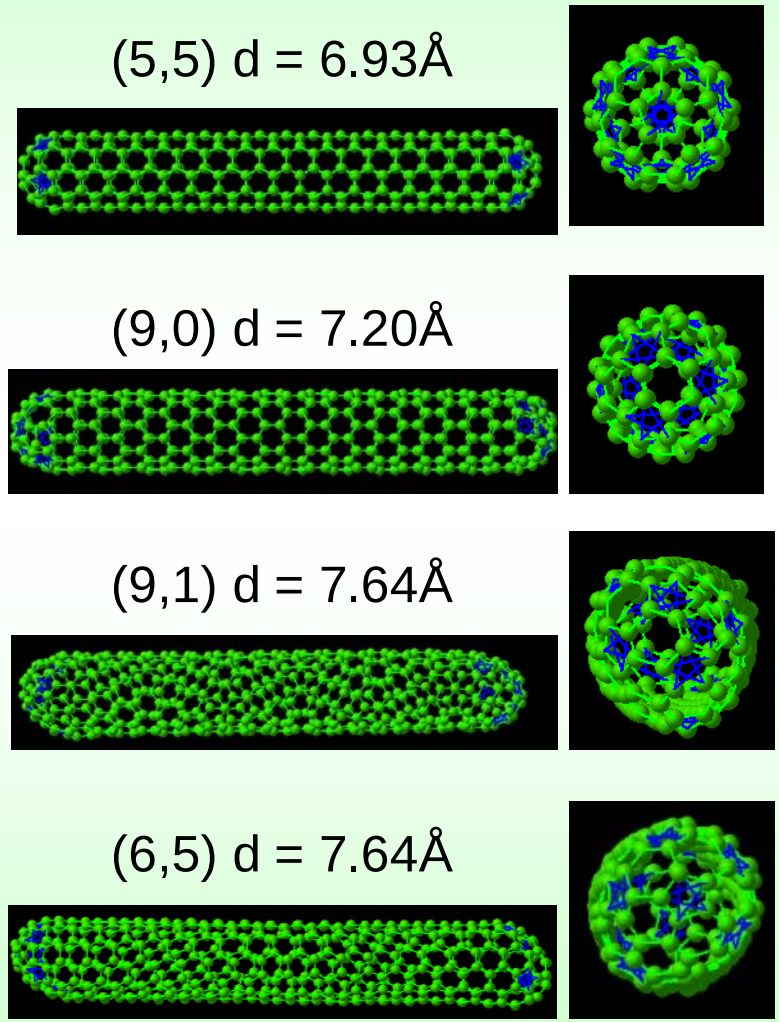




T. Yu et al., Fullerene Sci. Tech., 7, 769 (1999).

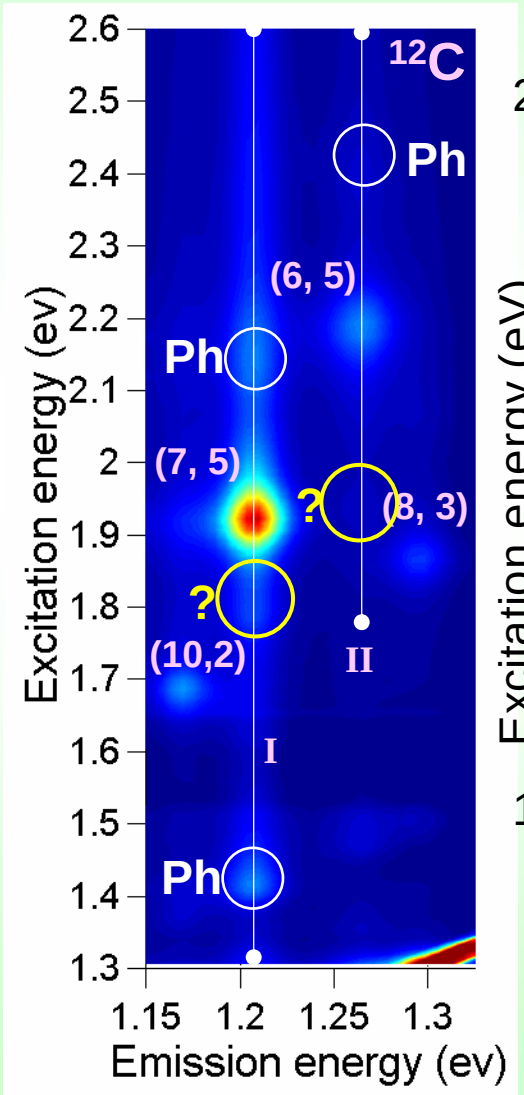
Energy of Nanotube Cap Structure

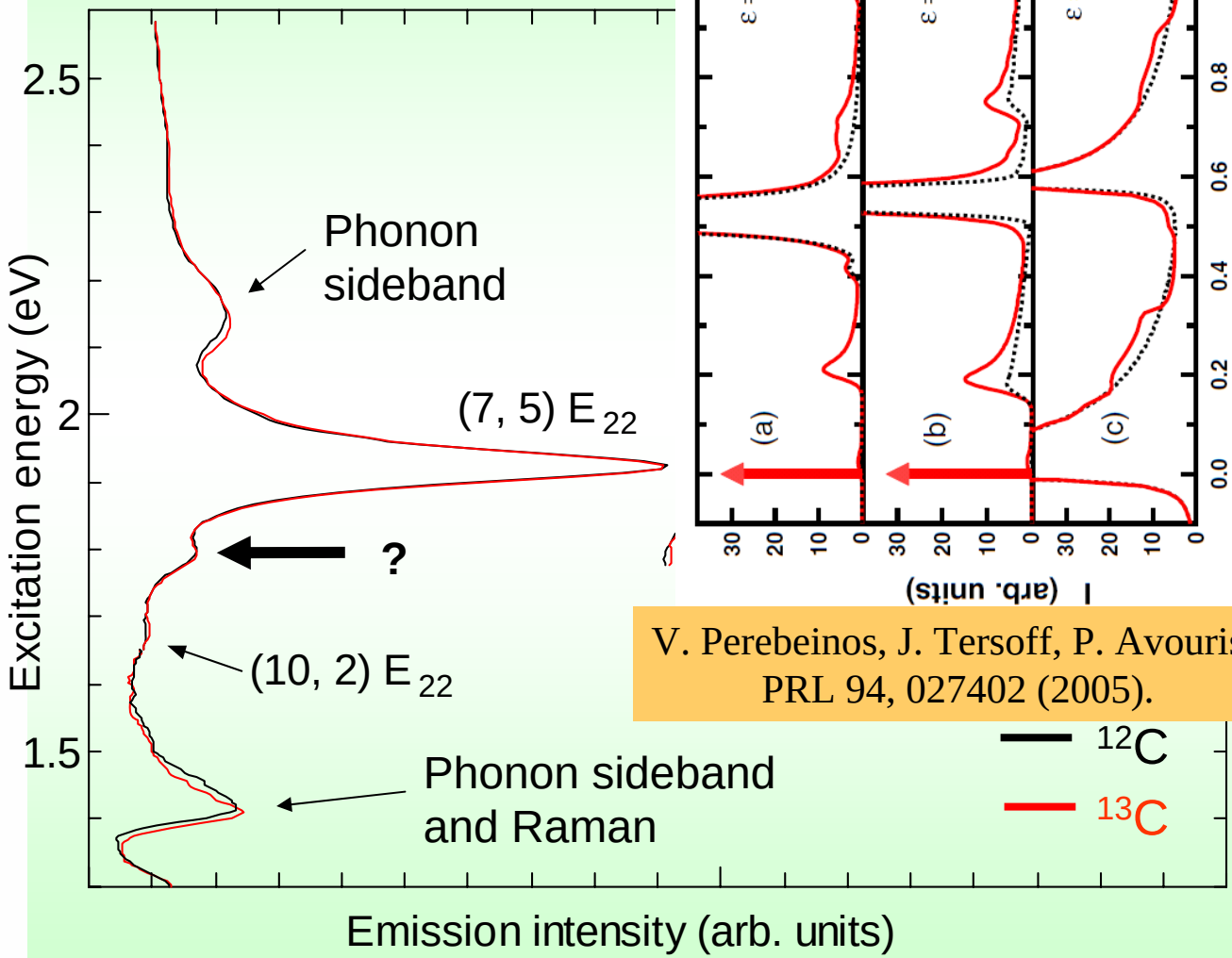




Brenner potential

PL peaks other than Eii ~ Phonon Sideband



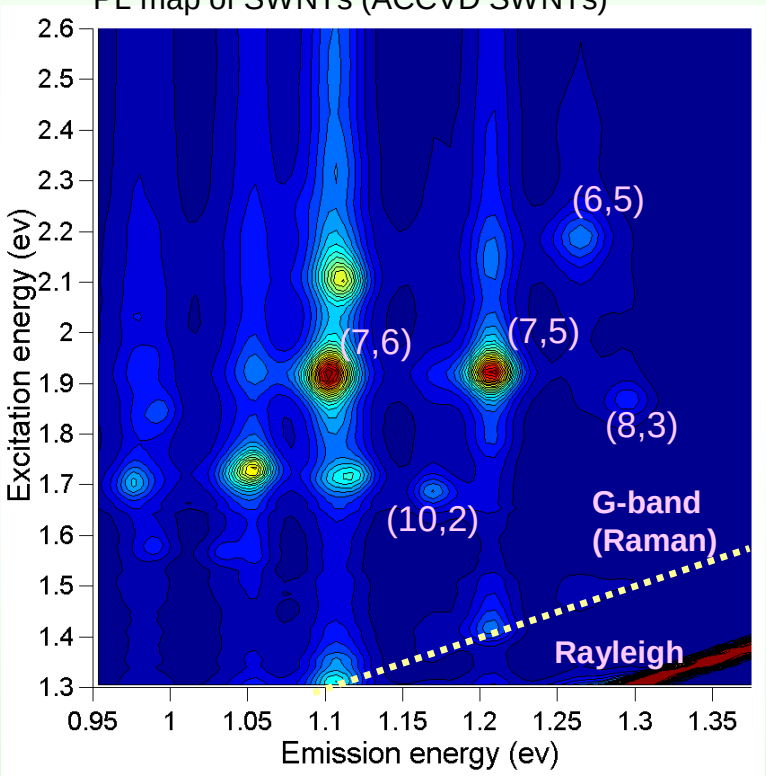


V. Perebeinos, J. Tersoff, P. Avouris, PRL 94, 027402 (2005).

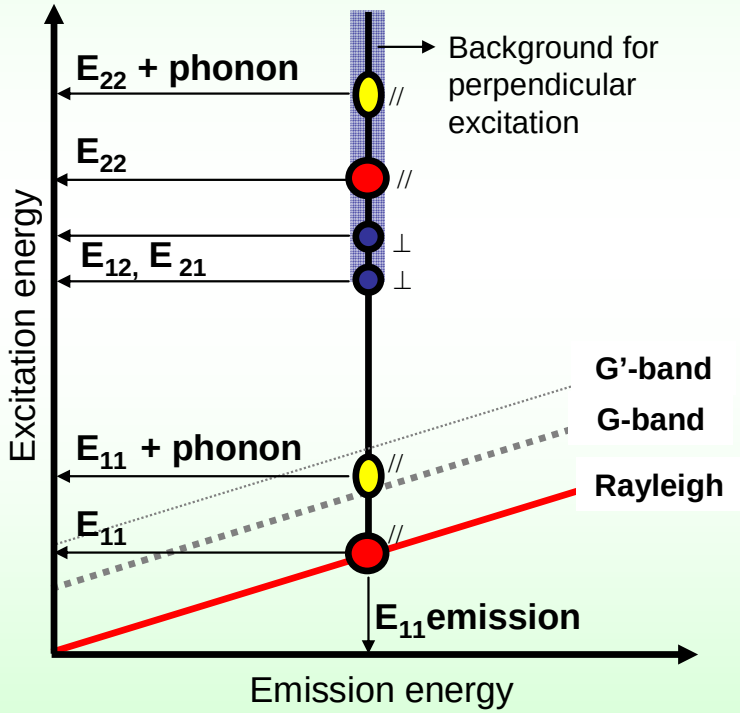
Y. Miyauchi and S. Maruyama, Phys.Rev. B, in press.

PL peaks other than Eii

PL map of SWNTs (ACCVD SWNTs)

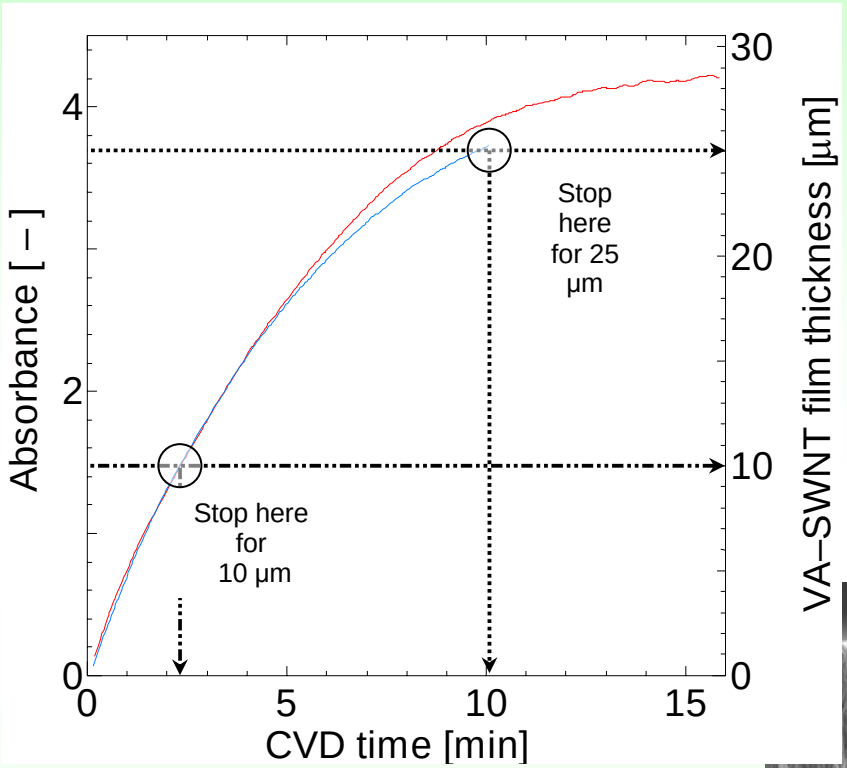


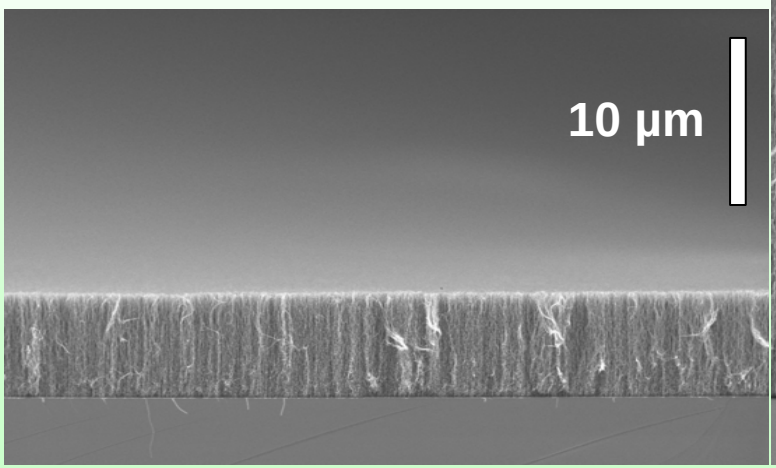
Schematic of PL peak positions in a PL map

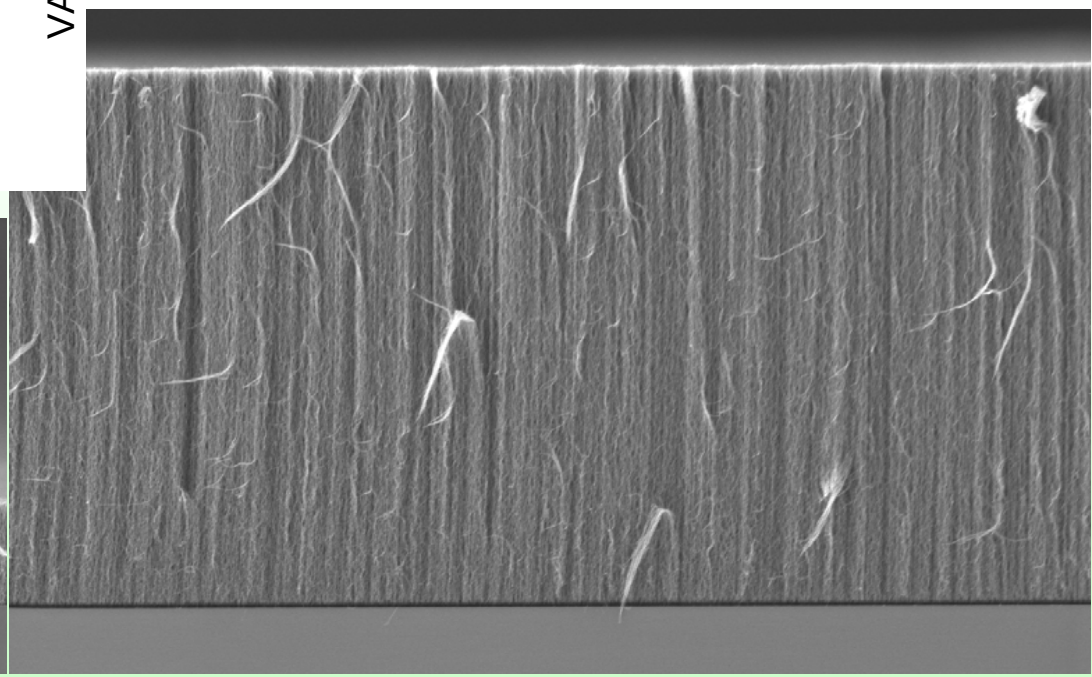


Y. Miyauchi, PhD thesis (2006)

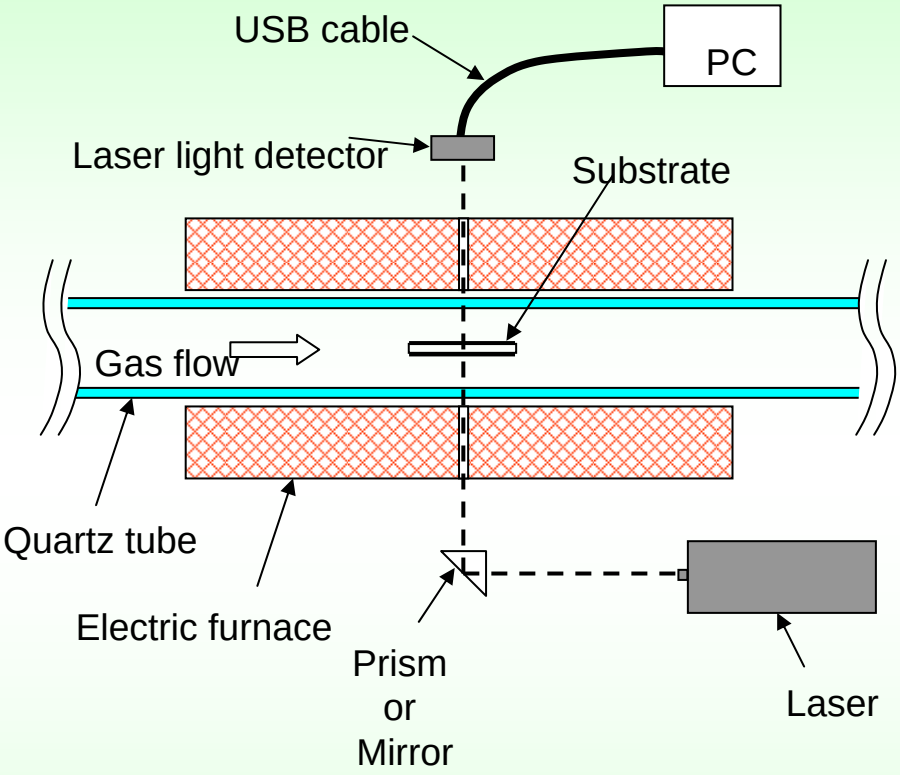
Vertically Aligned SWNTs and Growth Process

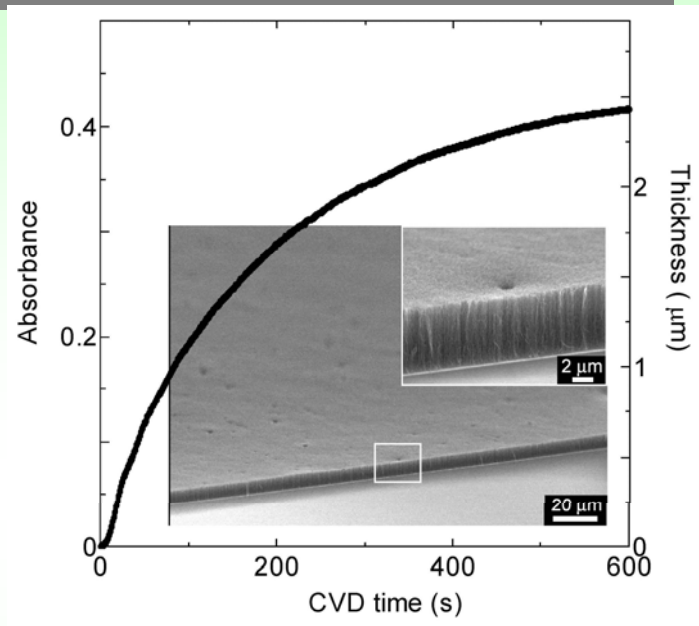


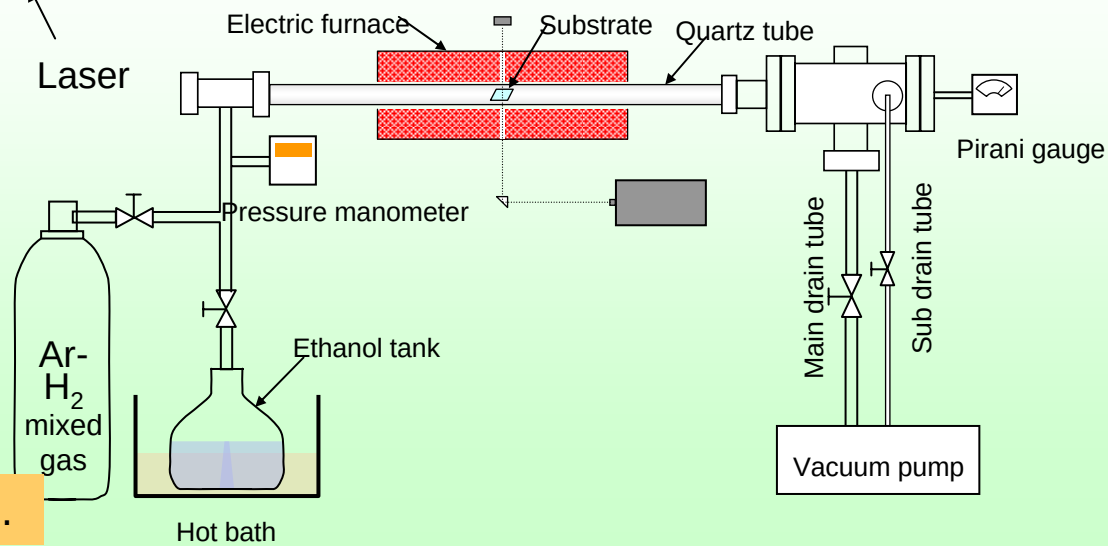




In-situ Measurement of Film Thickness

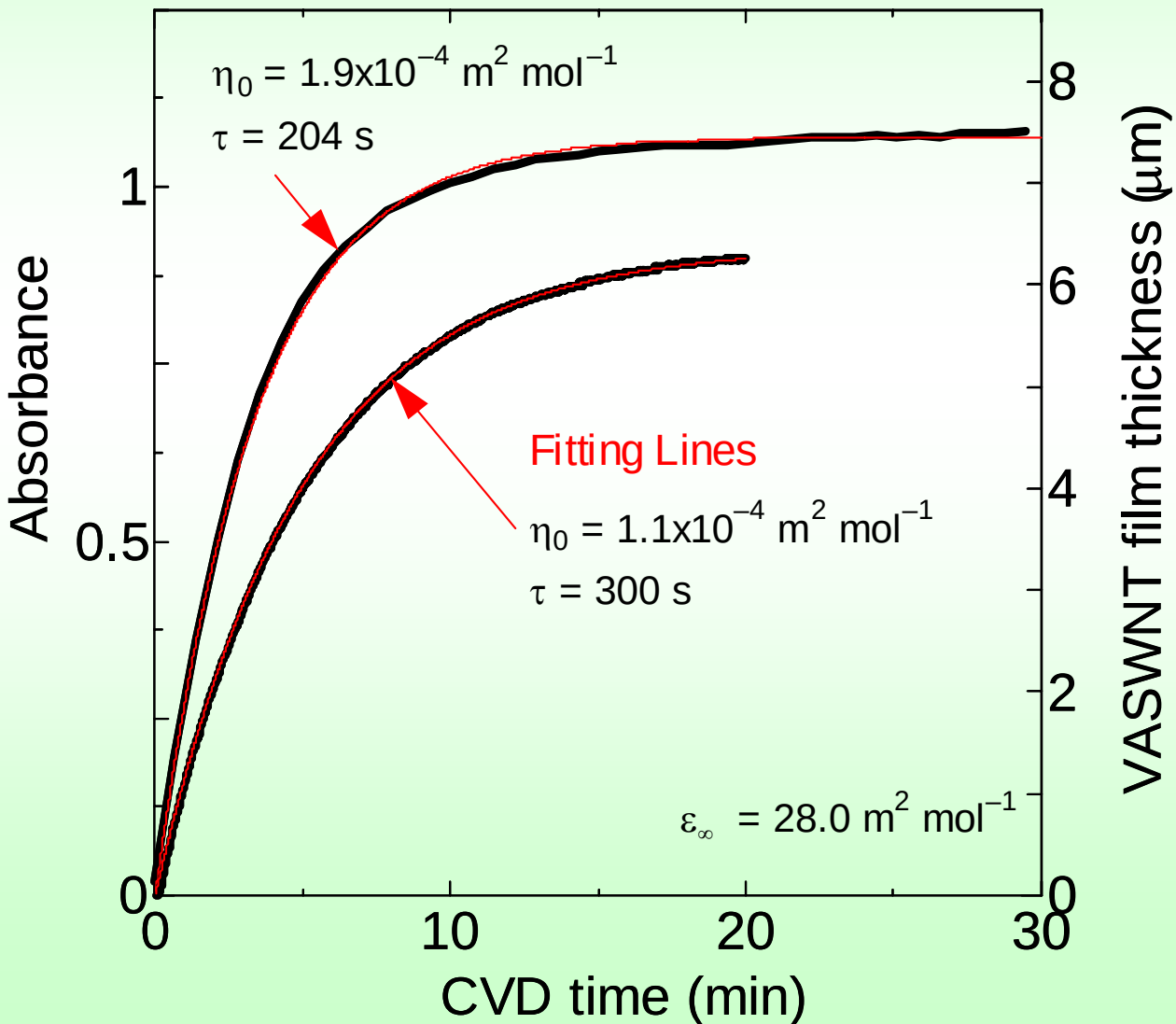






S. Maruyama et al., CPL 403 (2005) 320.

Catalyst-Consumption Growth Model



Growth Model

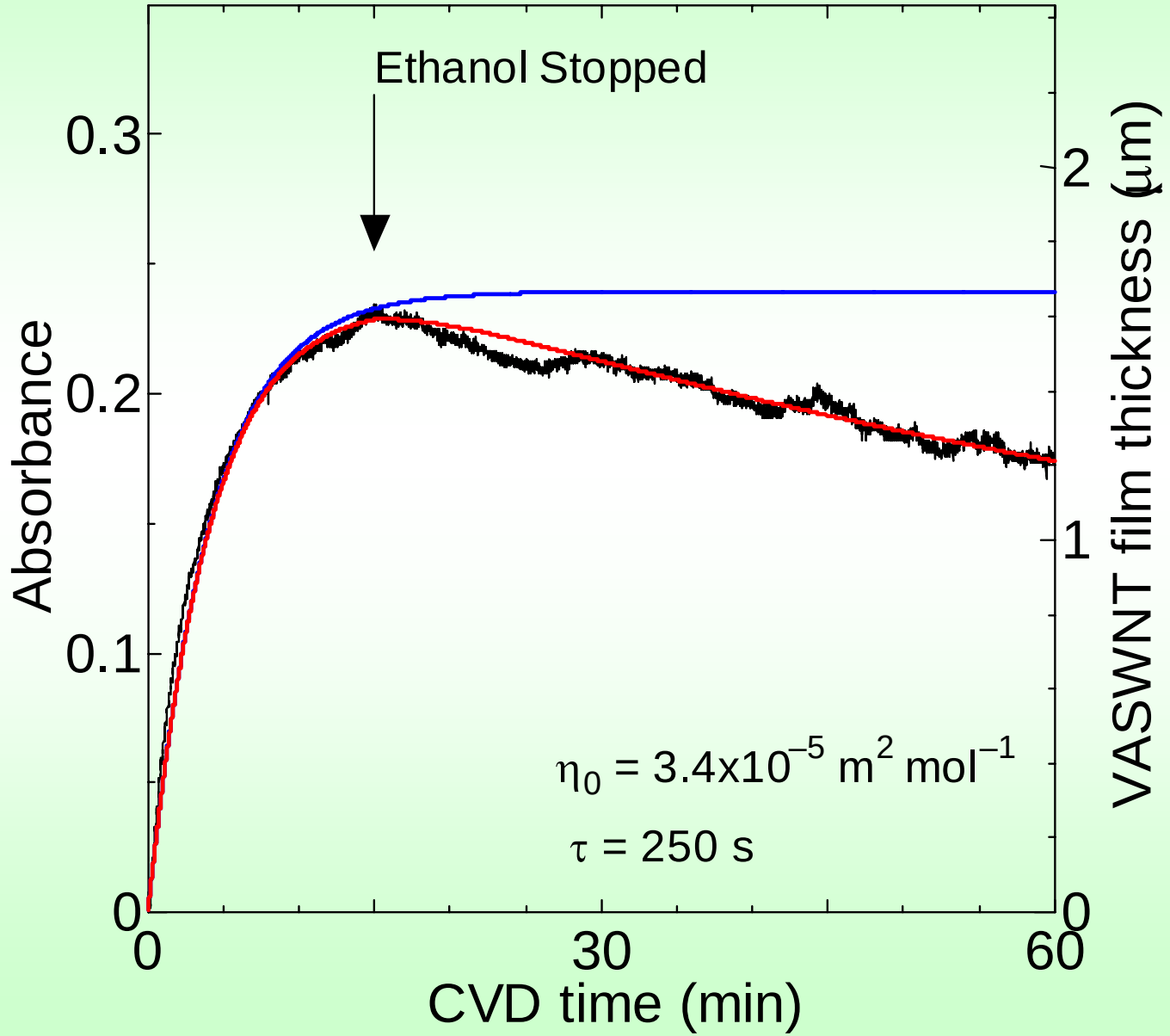
Catalyst Activity η

$$\frac{d\eta}{dt} = -\tau\eta$$

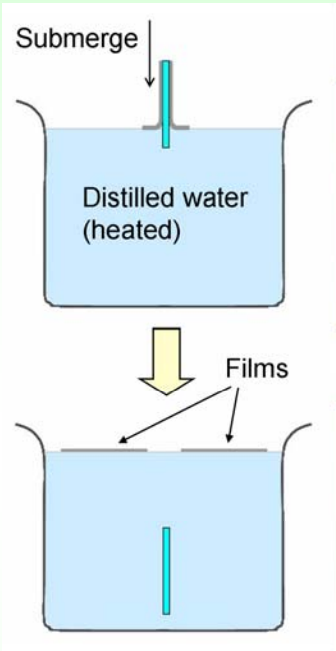
Carbon Mass C(t)

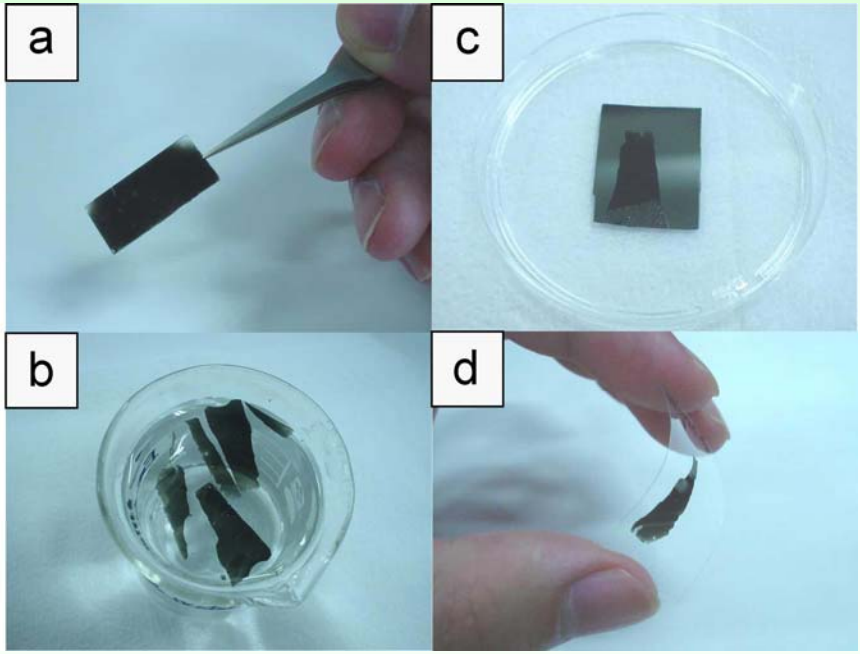
$$C(t) = \eta_0\tau\left(1 - e^{-t/\tau}\right)$$

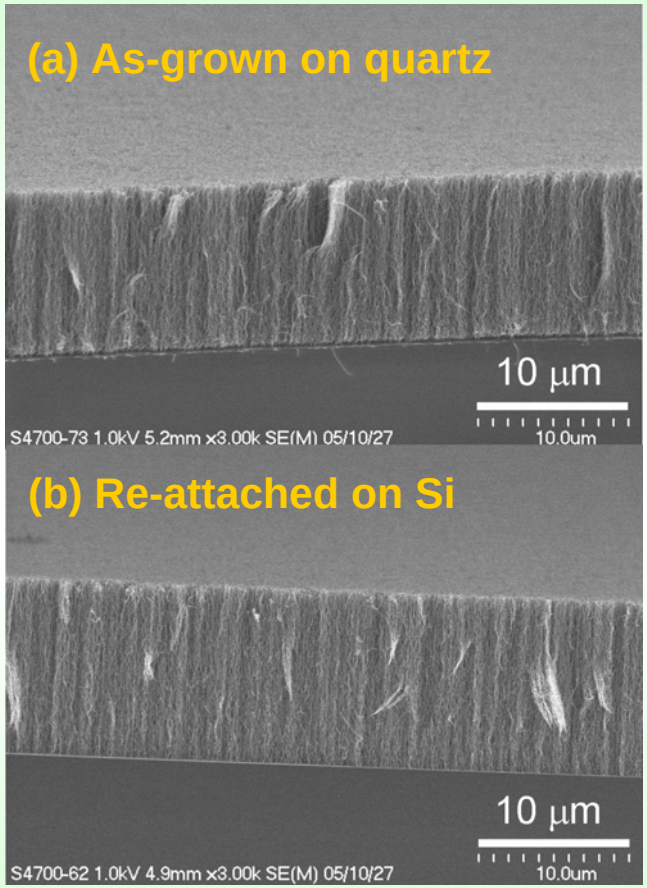
Additional Burning of SWNTs

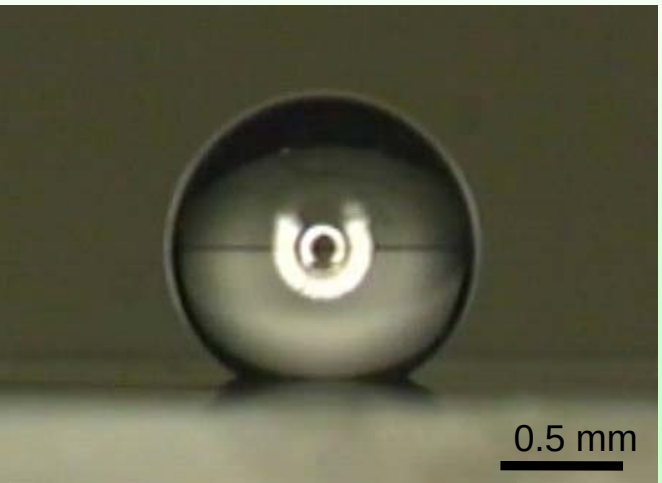


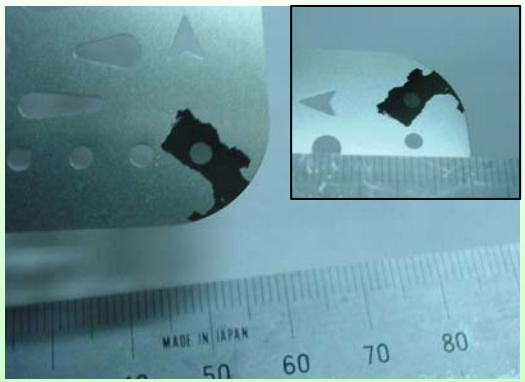
Detachment of VA-SWNT films with hot water





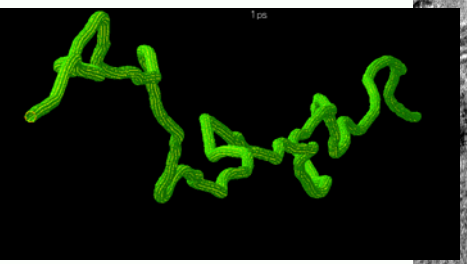


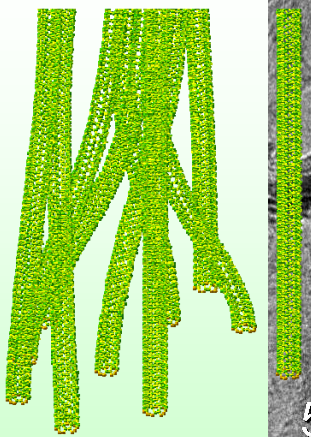


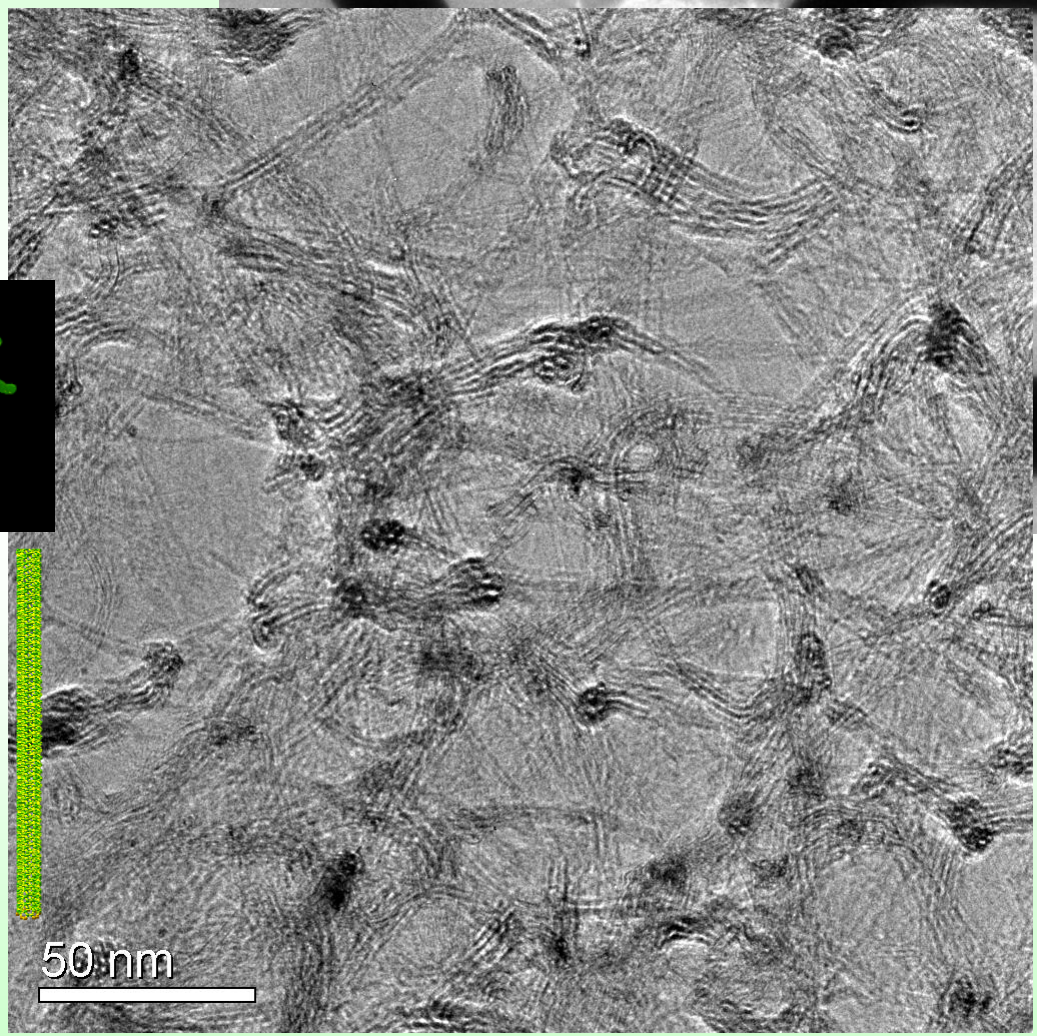


Y. Murakami and S. Maruyama, Chem. Phys. Lett. 422(2006) 575.

TEM Image from Top of Carpet

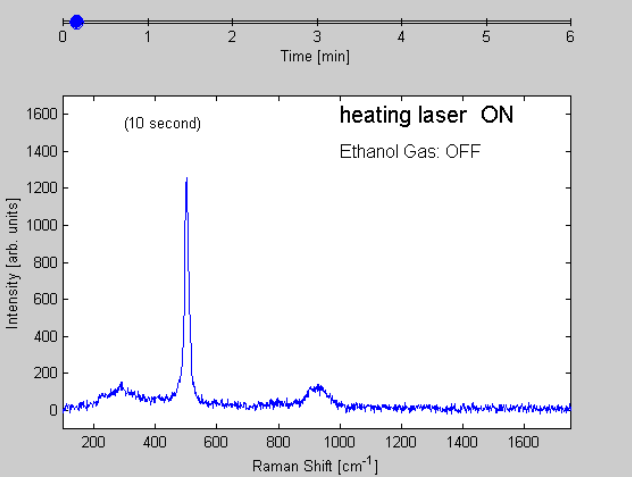






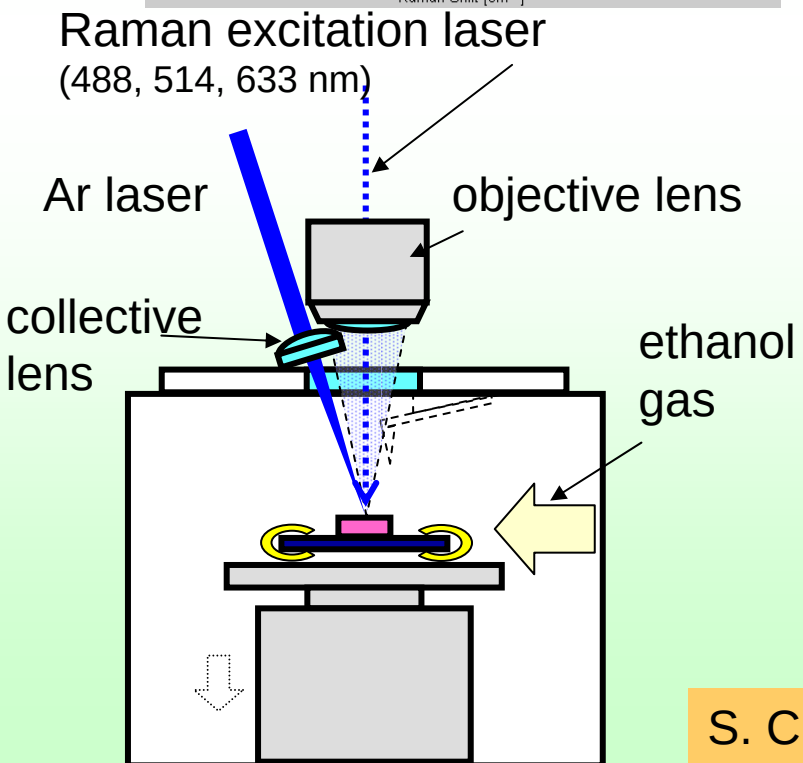
Hidetsugu Shiozawa & Thomas Pichler (IFW-Dresden e.V.),
Erik Einarsson, Shigeo Maruyama

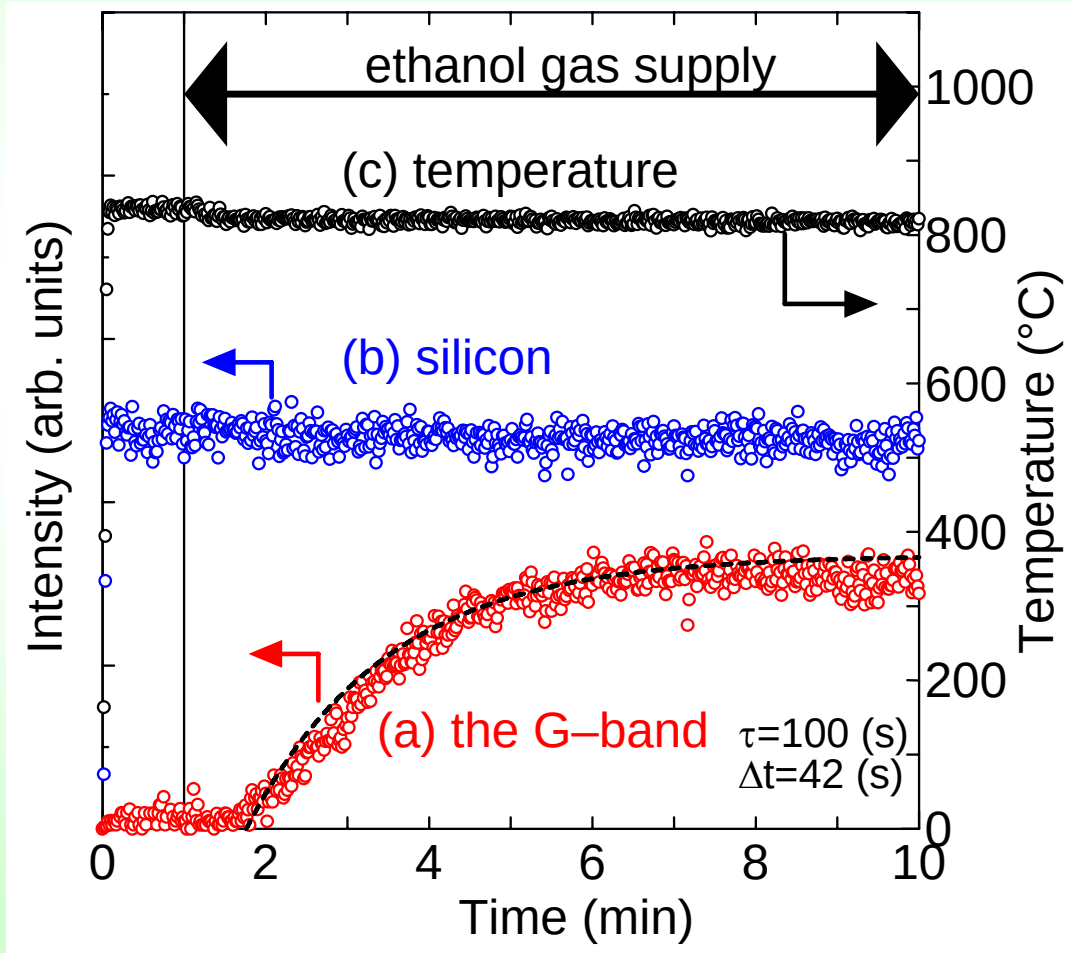
Laser ACCVD and in situ Raman Measurements



$$y = A\left[1 - \exp\left(\frac{t - \Delta t}{\tau}\right)\right]$$

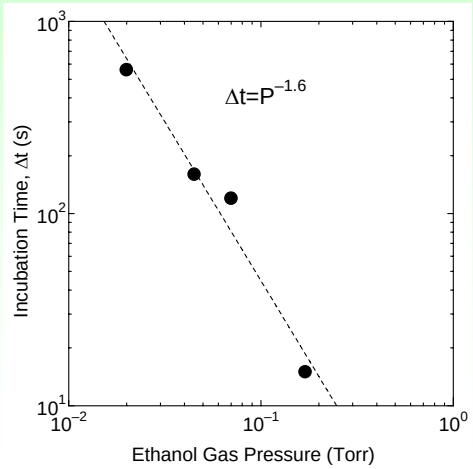
τ =100 ~ 200 (s)
Δt=30~40 (s)





S. Chiashi, M. Kohno, Y. Takata, S. Maruyama, (2005)

Laser ACCVD and in situ Raman Measurements



$$y = A\left[1 - \exp\left(\frac{t - \Delta t}{\tau}\right)\right]$$

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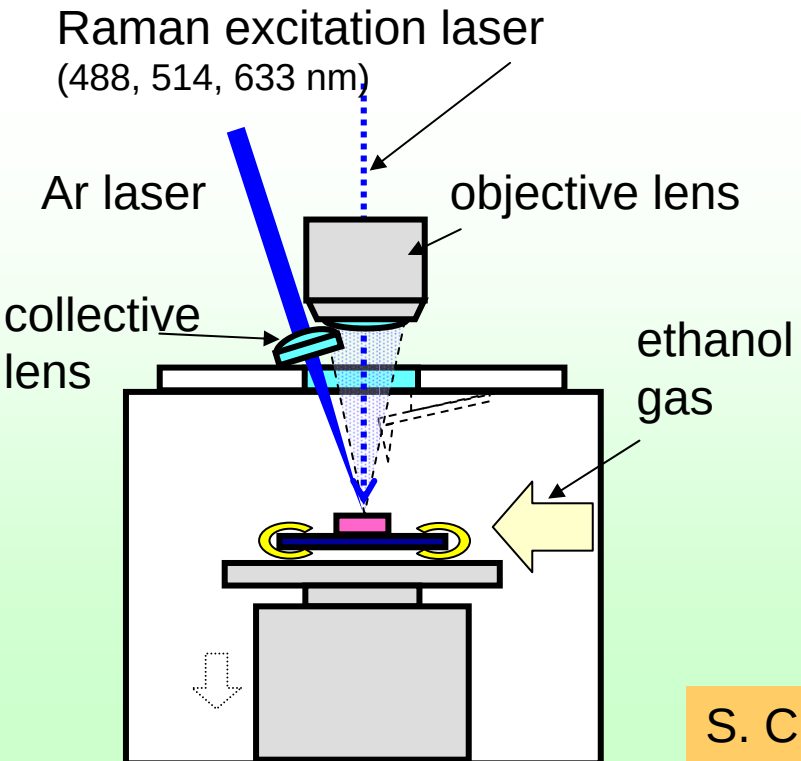

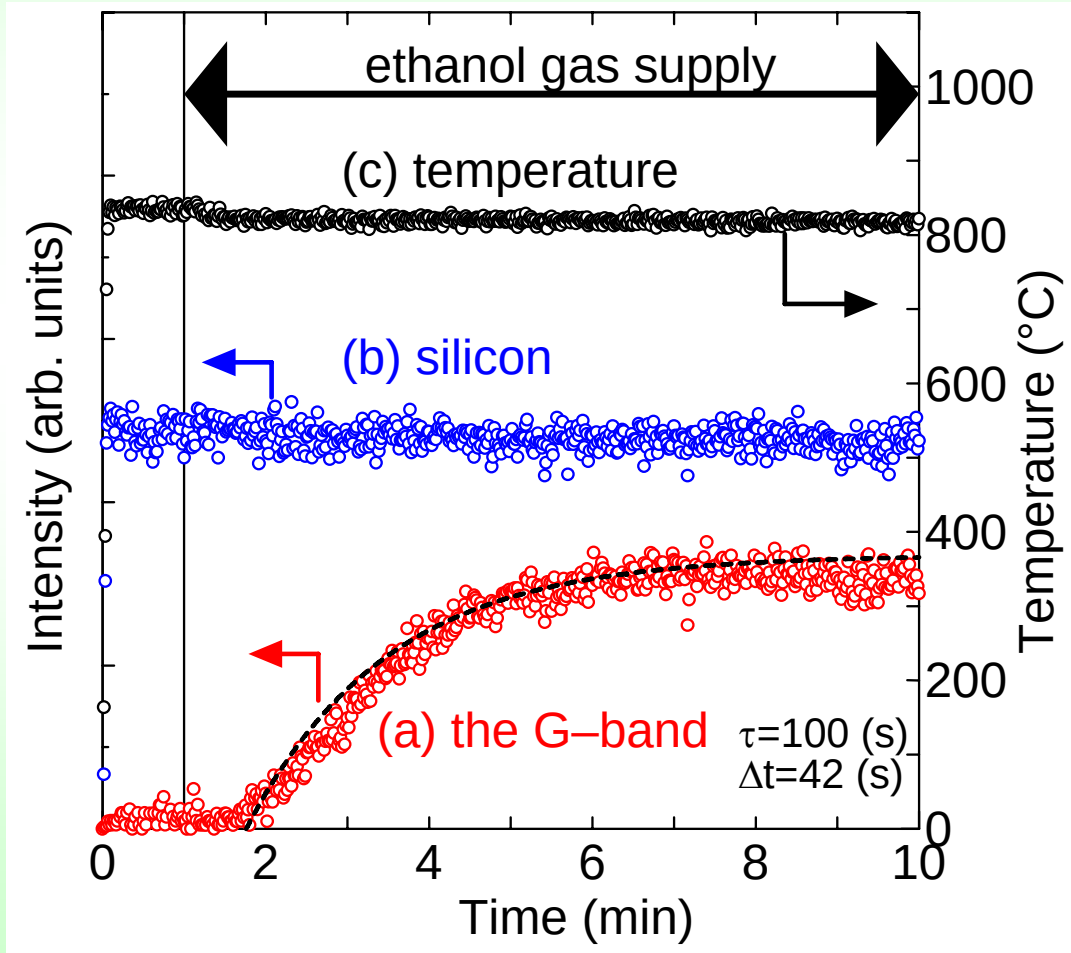

S. Chiashi, M. Kohno, Y. Takata, S. Maruyama, (2005)

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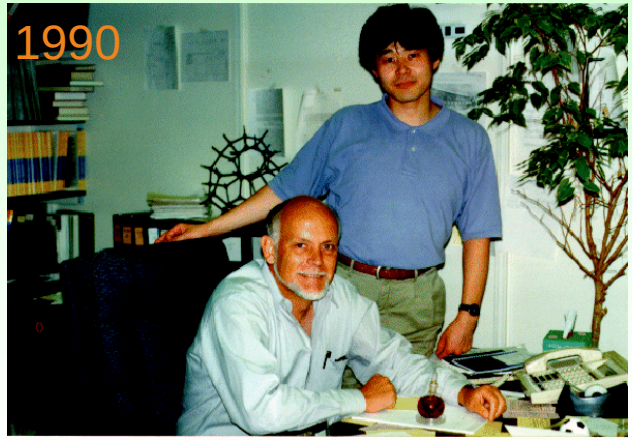
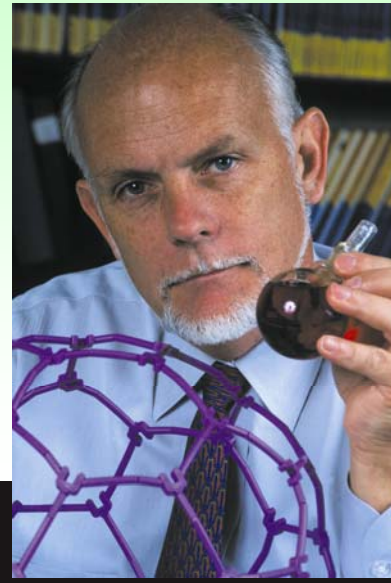
Mr. M. Sunose @ Seki-Tech.
Mr. N. Masuyama@ J-Power Co. Ltd., Mr. Y. Kondo@ Konica-Minolta,
Mr. S. Watanabe, Ms. M. Nakagawa, Mr. R. Tamochi @ Hitachi Science Systems

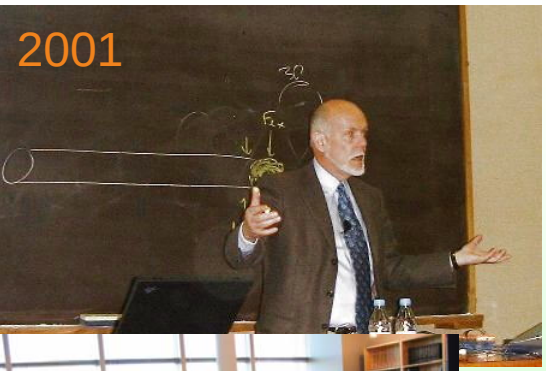
JSPS, MEXT, Toray, XNRI, J-Power, DENSO,
Konica-Minolta, Tokyo-Gas, SEL, Toso

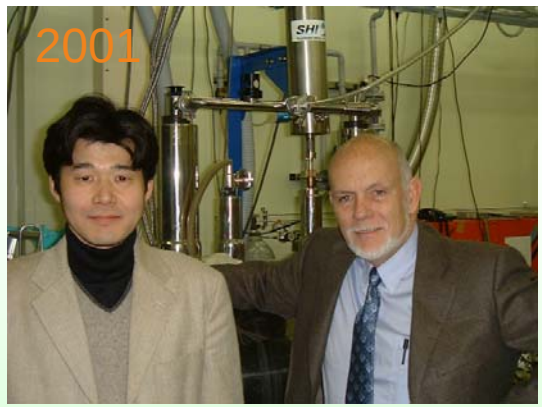
Professor Richard E. Smalley at Rice University (1943-2005)

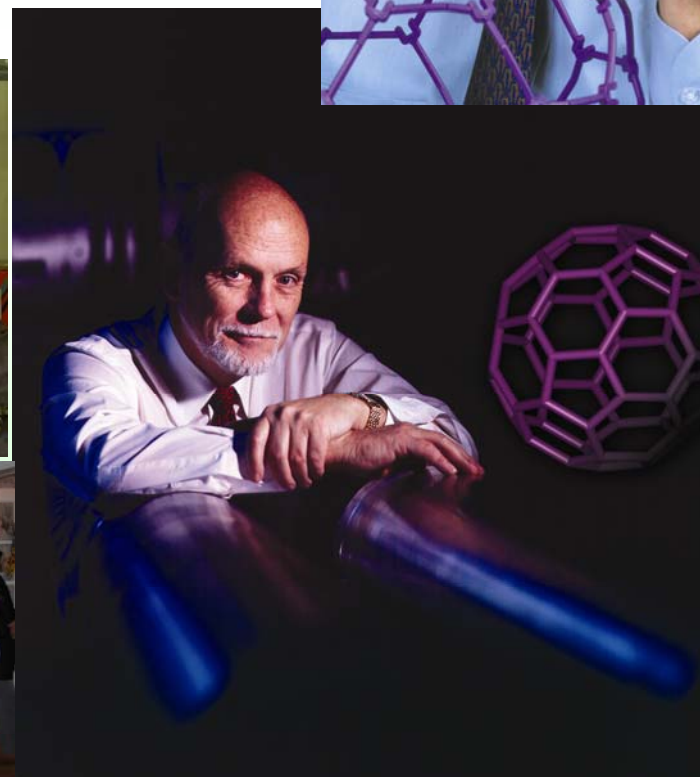
1943: Born in Akron, Ohio on June 6
1976: PhD from Princeton,
Assistant Professor at Rice
Laser Vaporization Cluster Beam
1984: Discovery of C60
1996: Nobel Prize in Chemistry with Kroto and Curl
1996: Bulk Production of SWNTs
Then HiPco Process
2000: Testified for National Nanotechnology Initiative
2000: Found Carbon Nanotechnology Inc.
Application of Nanotechnology to Energy Problem
2005: Died at 62 on October 28, 2005



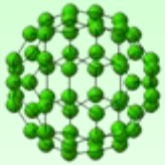








Catalytic CVD Synthesis of SWNTs from Fullerene



Dispersed metal particles
(Fe/Co 2.5wt%) embedded
in Y-type zeolite

Catalysts

$(CH_3CO_2)_2Fe$
$(CH_3CO_2)_2Co\text{-}4H_2O$ etc.

Supports

Zeolite USY
HSZ-390HUA

Quartz tube

Fullerene
C_{60} or C_{70}

Furnace A

Furnace B

vacuum

Inorganic adhesive

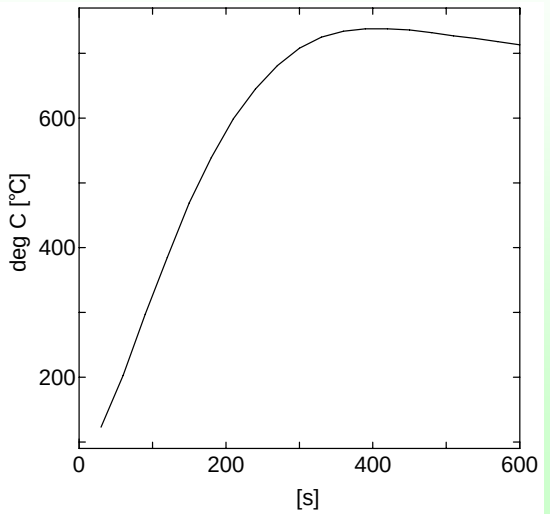
Thermocouple

Quartz wool

Quartz test tube

Quartz plate

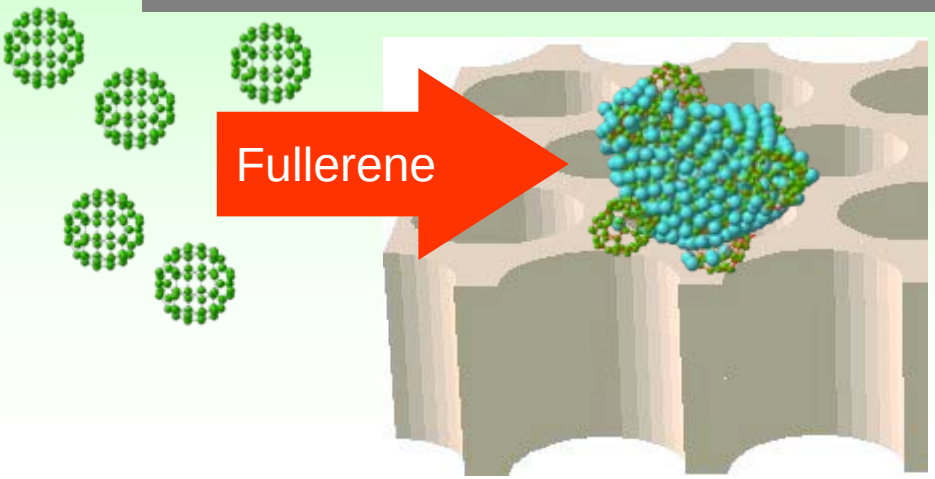
Temperature up curve of TC

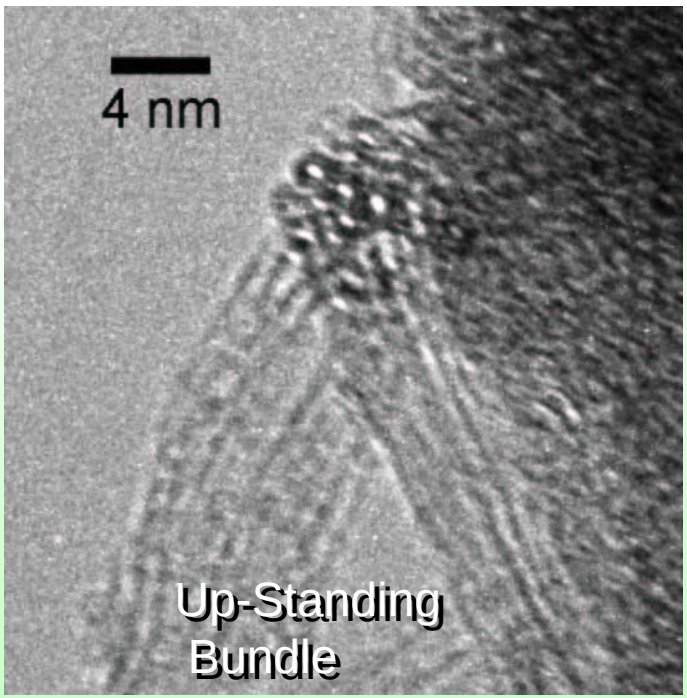


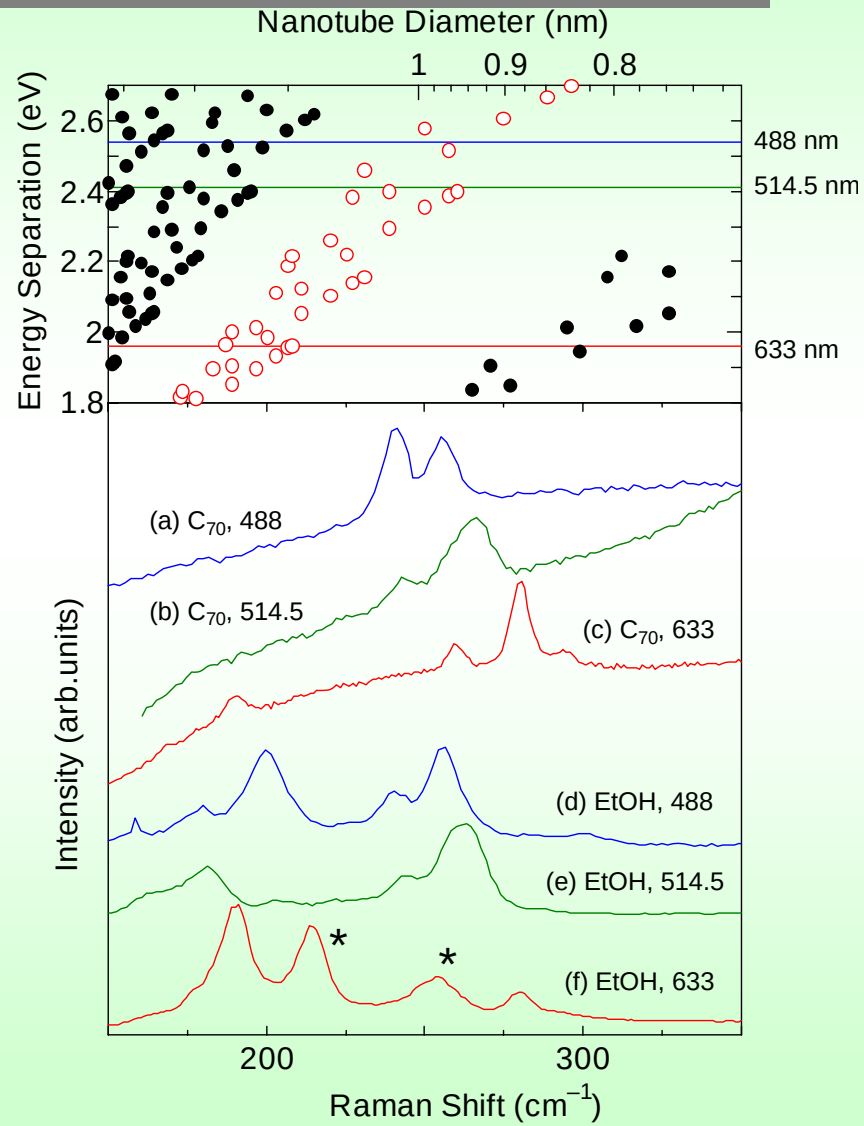
Temperature: Furnace B 825℃

Time: 10min

CCVD Generation of SWNTs from Fullerene

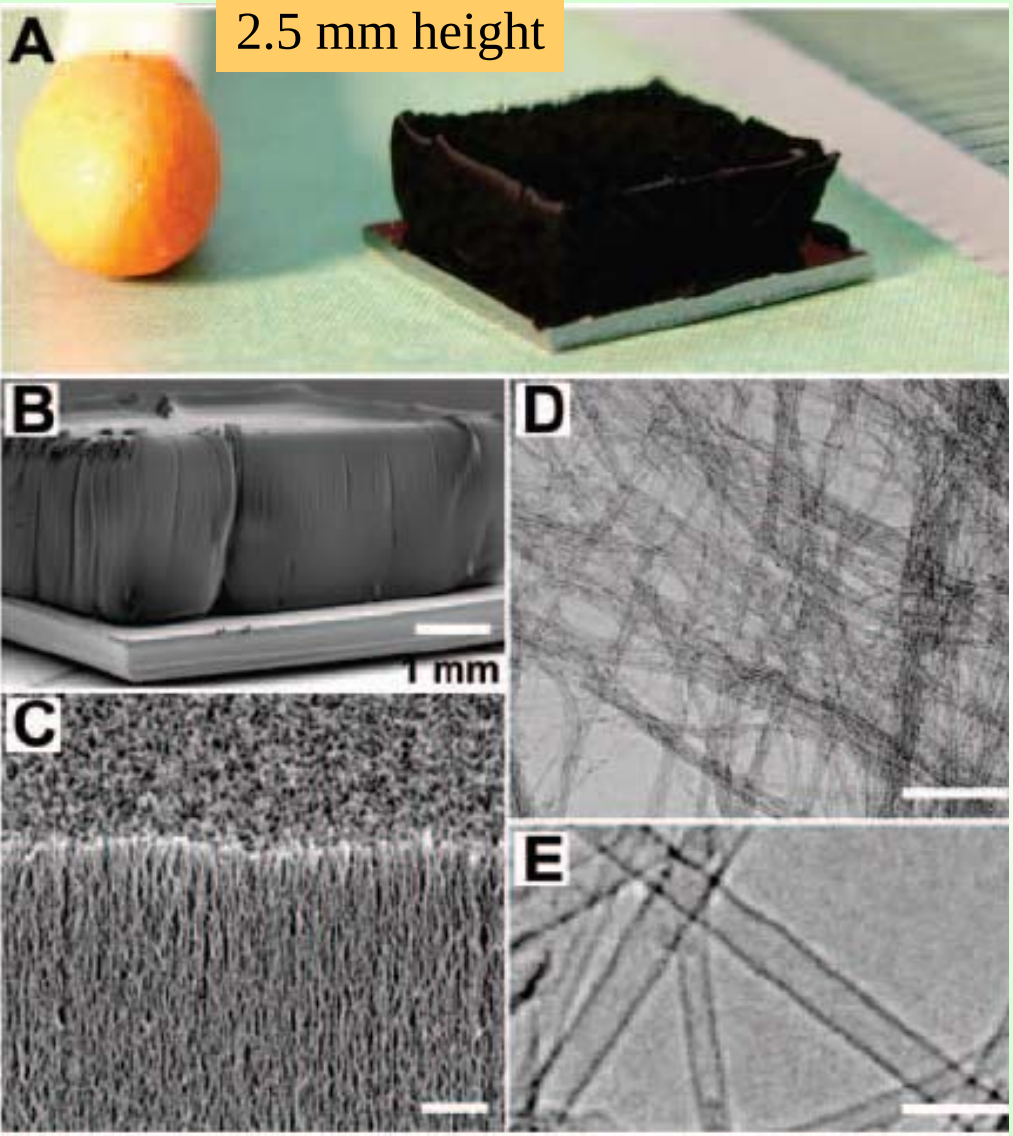




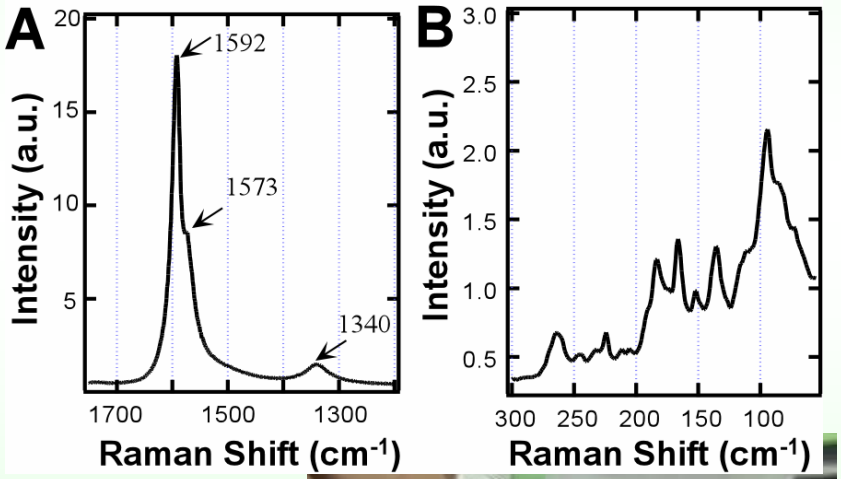


S. Maruyama et al, Chem. Phys. Lett., 375 (2003) 553.

Water Assisted Super-Growth

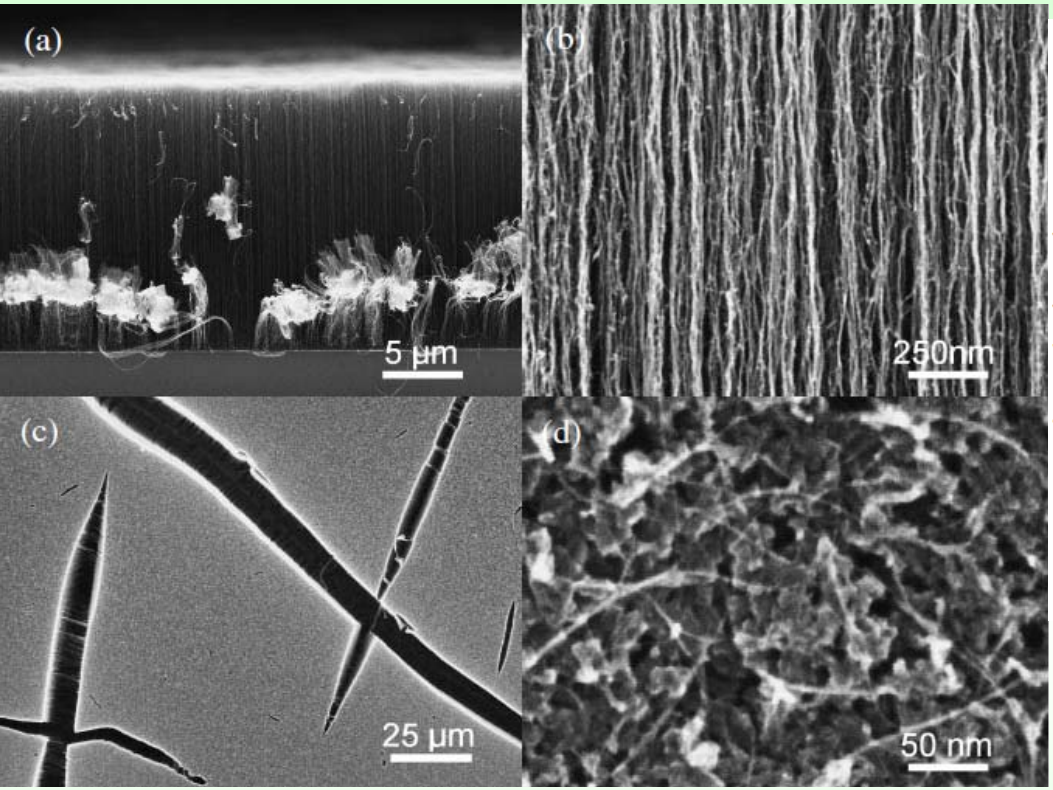


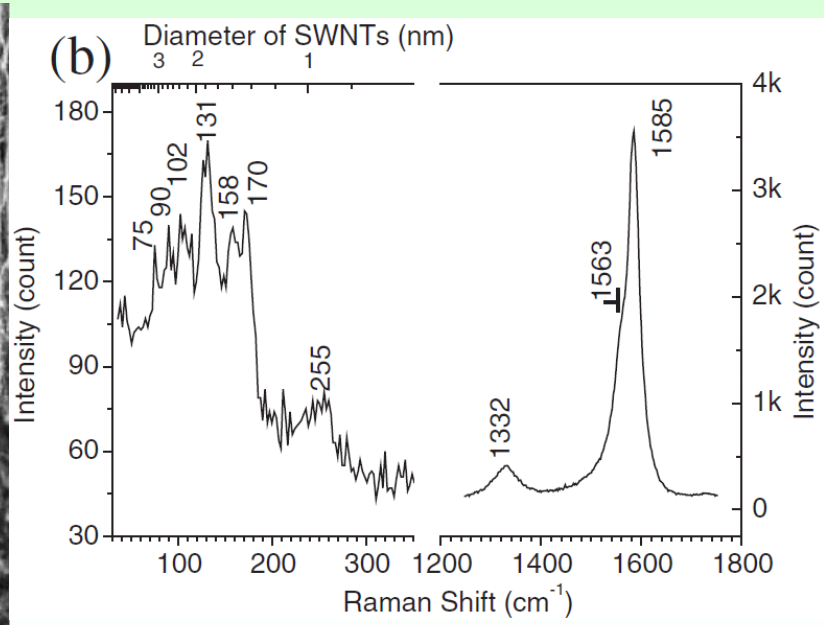
Catalysts: Al2O3 (10 nm)/Fe(1 nm)
Buffer: Ar (99.9999%) or He (99.9999%)
with 40% H2 (99.99999%)
Water:175 ppm
Source: 100 sccm ethylene (99.999%)
CVD Temp.: 750°C x 10 min



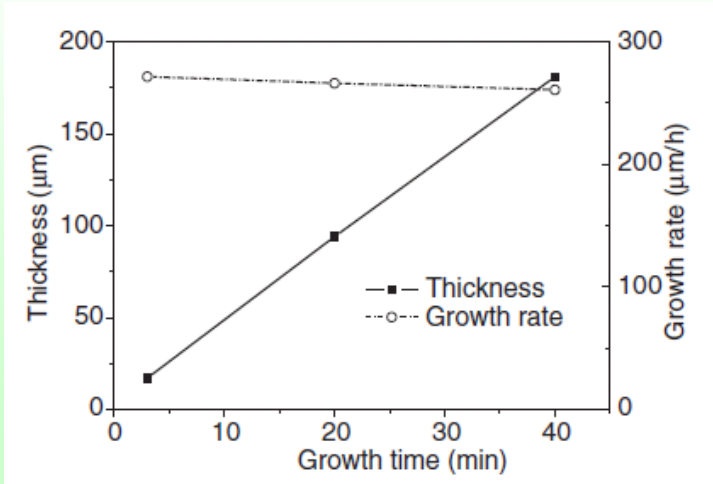
Iijima Group (K. Hata et al., Science, 2004)

Super Growth by Kawarada Group





270 micron/h

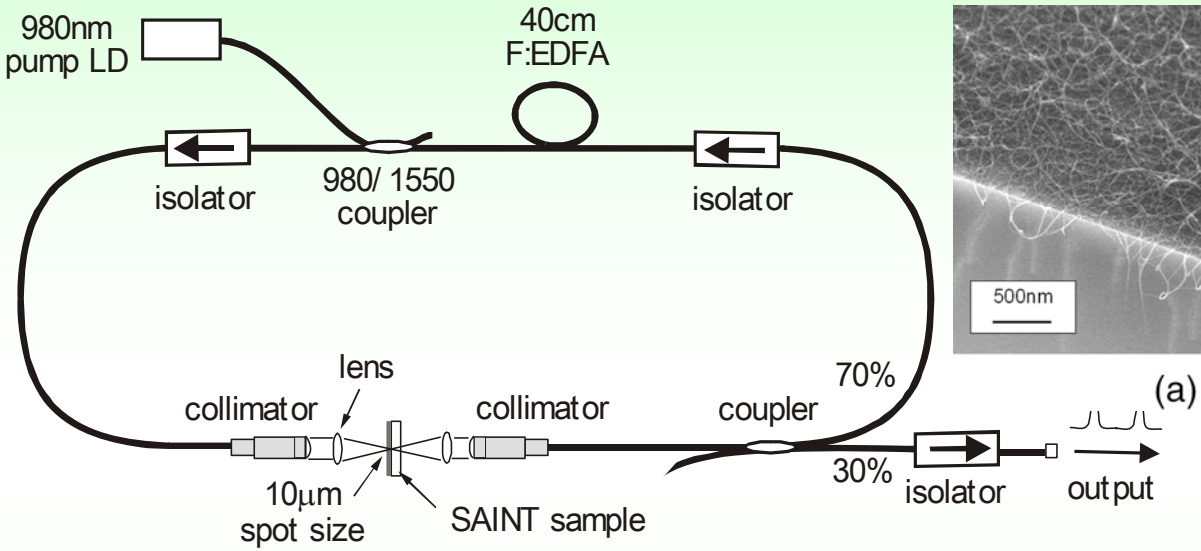


Point arc Microwave Plasma CVD
0.7nmAl2O3/0.5nmFe/5-70nmAl2O3 Catalysts

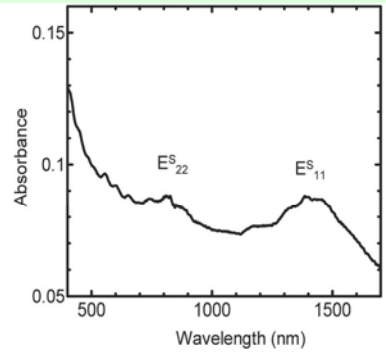
66kg/m3

G. Zhong, JJAP 44 (2005) 1558.

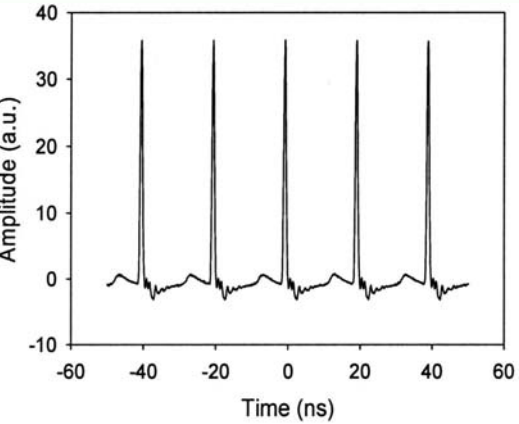
Saturable Absorbers: Application to Mode-Locked Fiber Lasers



(a)



(b)



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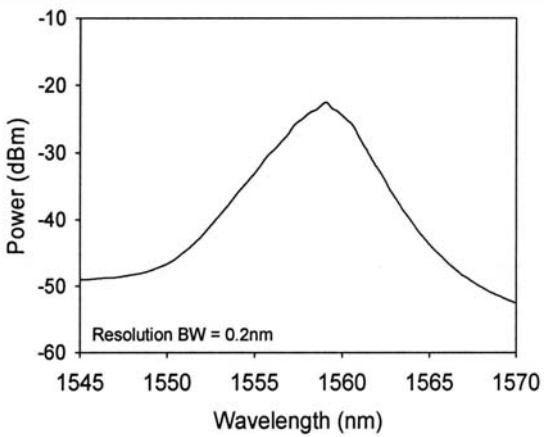

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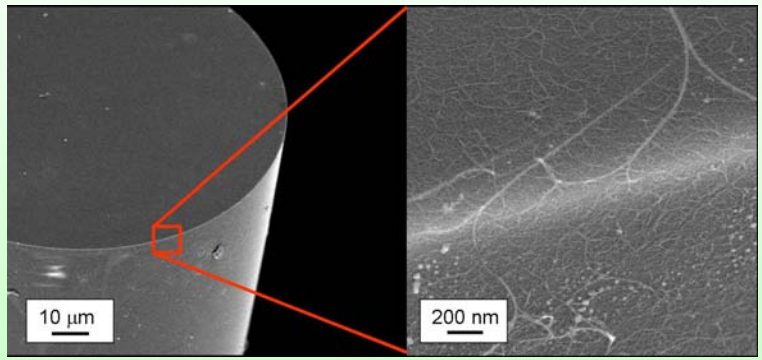
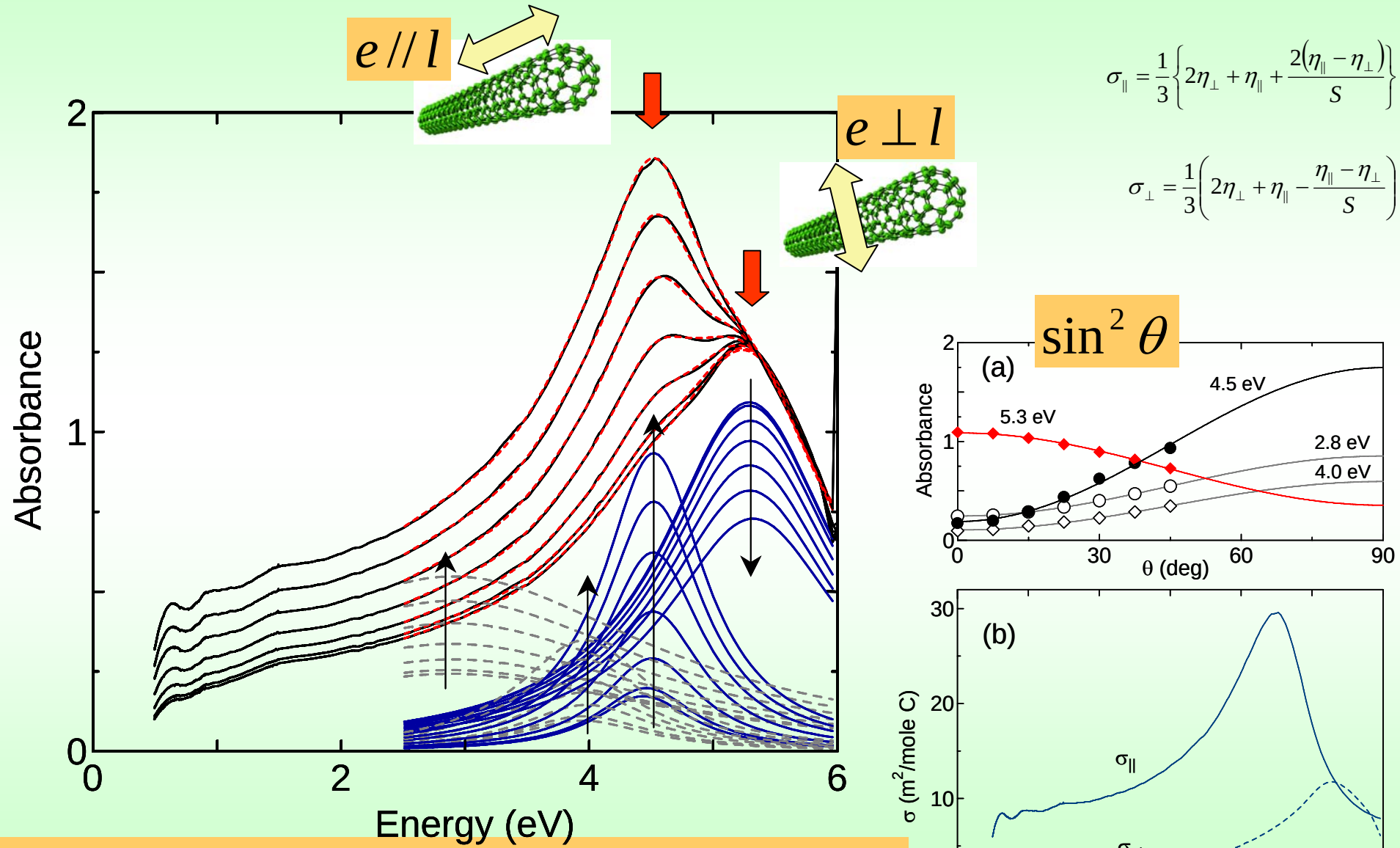


S. Yamashita, S. Maruyama, Y. Murakami, Y. Inoue, H. Yaguchi, M. Jablonski, S. Y. Set, Optics Letters, 29 (2004) 1581.

Polarized Optical Absorption of VA-SWNTs (2)

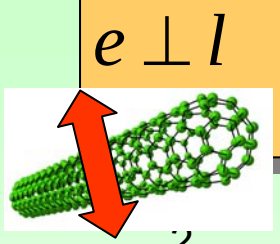


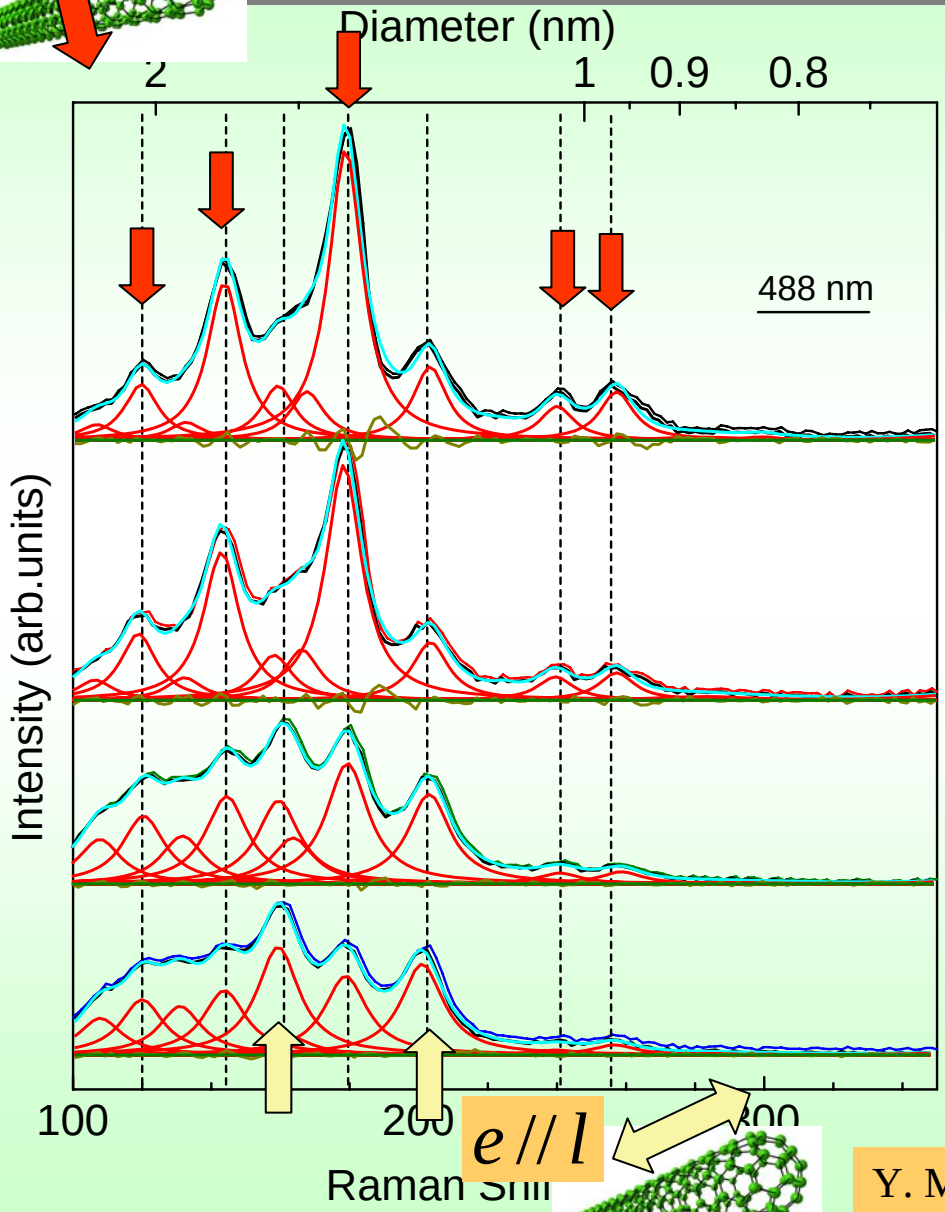
$$\sigma_{\parallel} = \frac{1}{3}\left\{2\eta_{\perp} + \eta_{\parallel} + \frac{2(\eta_{\parallel} - \eta_{\perp})}{S}\right\}$$

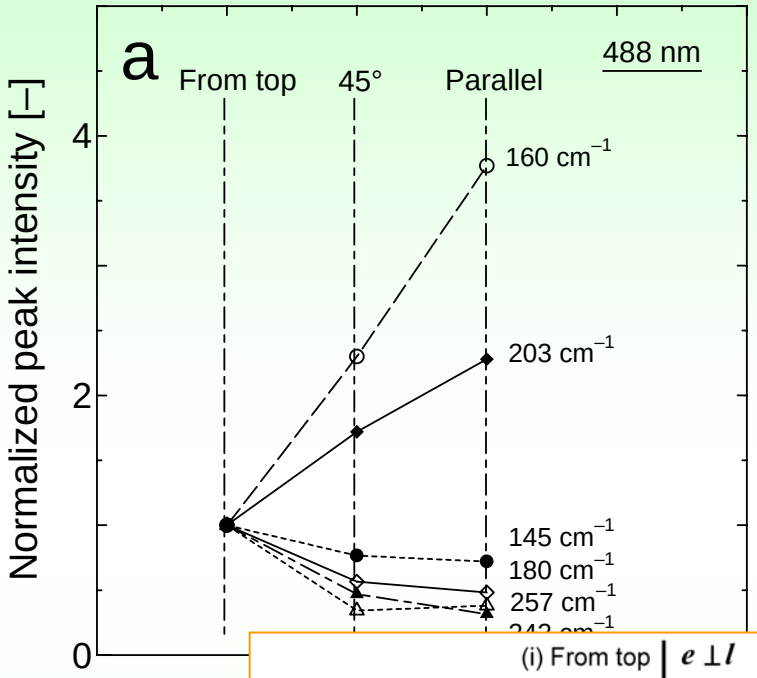
$$\sigma_{\perp} = \frac{1}{3}\left(2\eta_{\perp} + \eta_{\parallel} - \frac{\eta_{\parallel} - \eta_{\perp}}{S}\right)$$

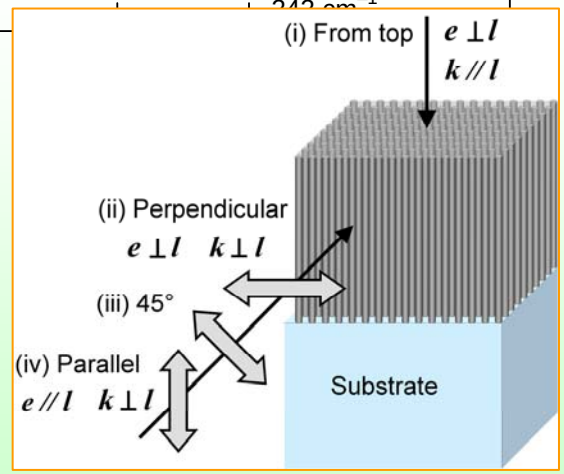
Y. Murakami, E. Einarsson, T. Edamura, S. Maruyama: Phys. Rev. Lett., 94, 087402(2005)

Anomalous Raman Scattering



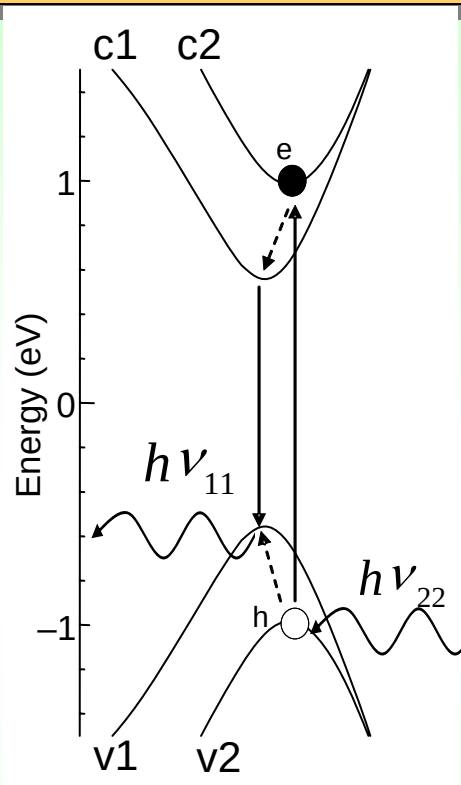


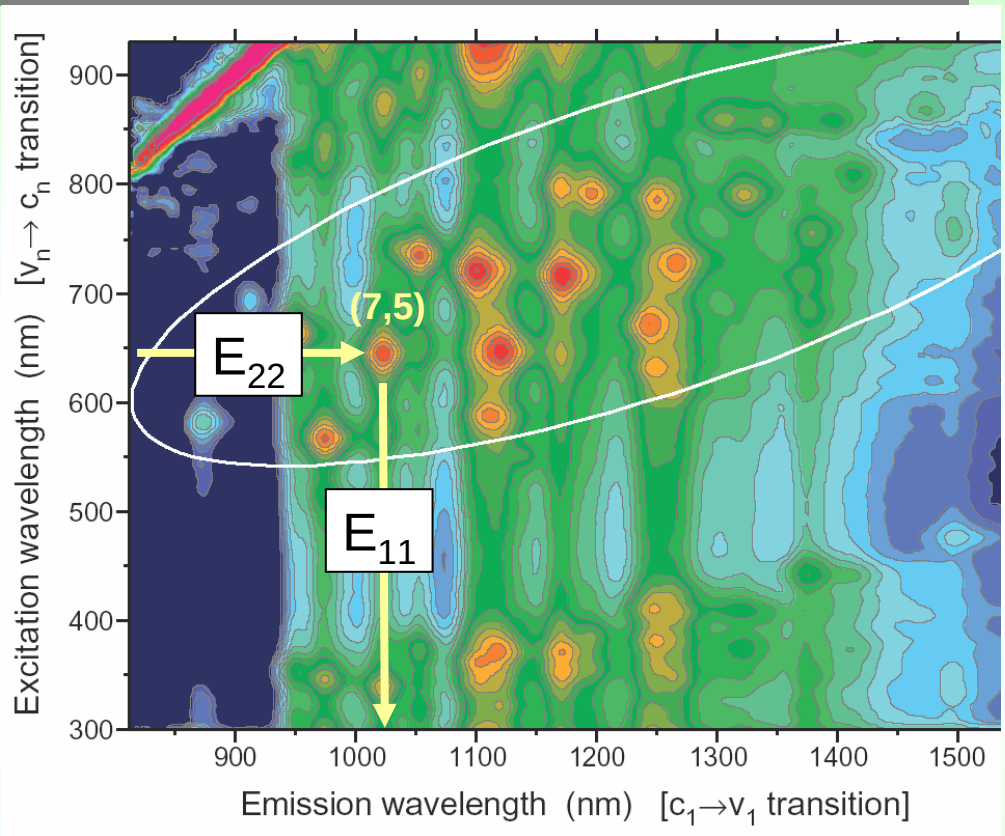


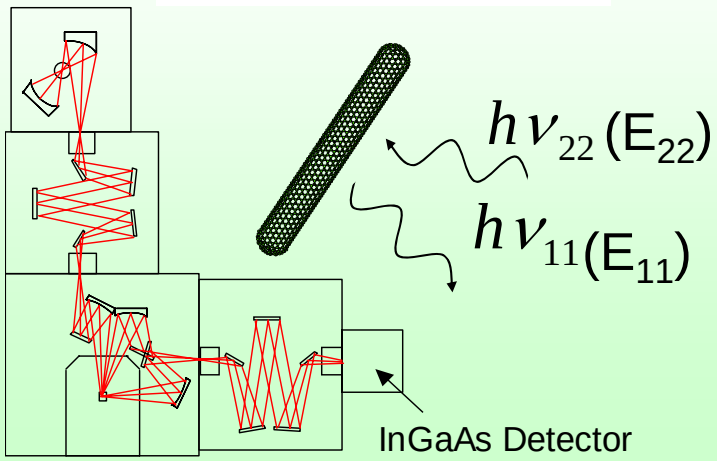


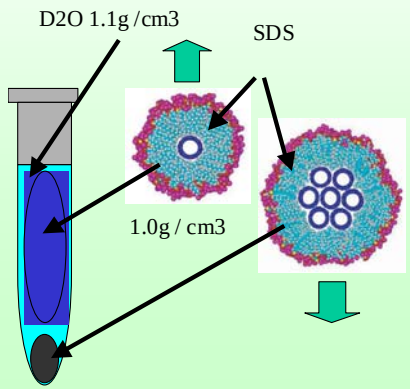
Y. Murakami, S. Chiashi, E. Einarsson, S. Maruyama: Phys. Rev. B, 7, 085403(2005)

Photoluminescence Spectroscopy of SWNTs









M. J. O'Connell *et al.*, Science 297 (2002) 593

S. M. Bachilo *et al.*, Science 298 (2002) 2361

Strong sonication

Super centrifuge 380,000g x 1h