カーボンナノチューブ化学

- 熱構造変化
- 開孔
- 内包
- エッジの化学
- その他

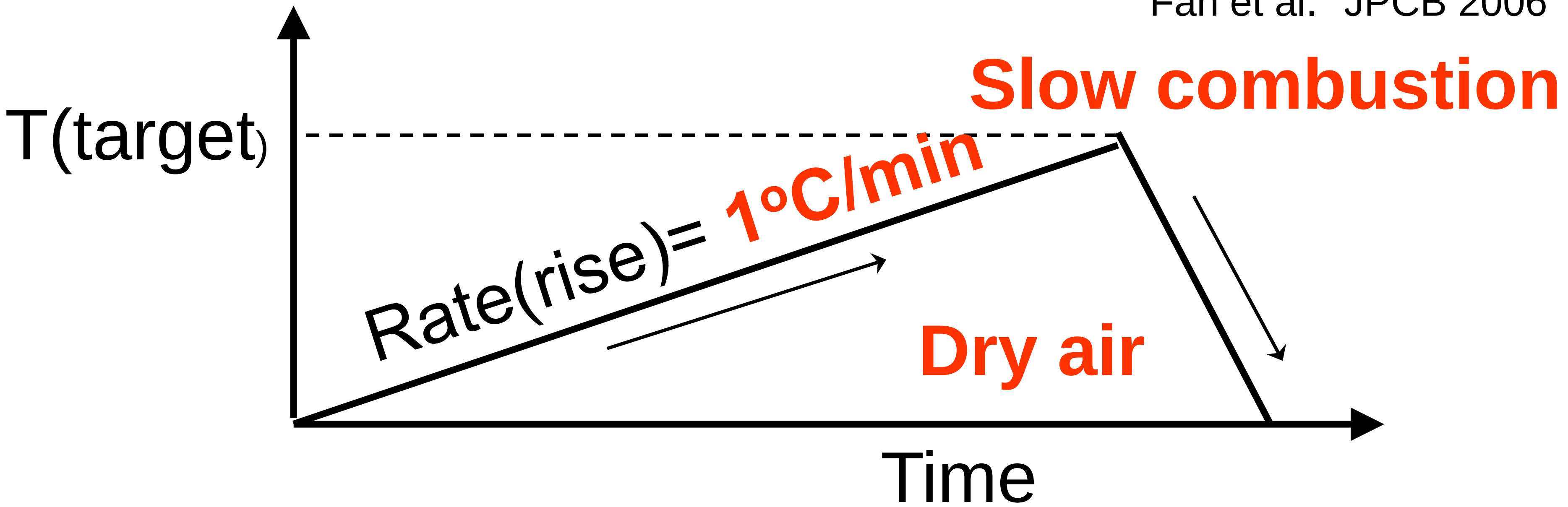
カーボンナノチューブの化学をカーボンナノチューブを使って行うのは、量が少なくて、困難。
よって、ナノホーンで、化学研究したほうが、多くのことが分かる。

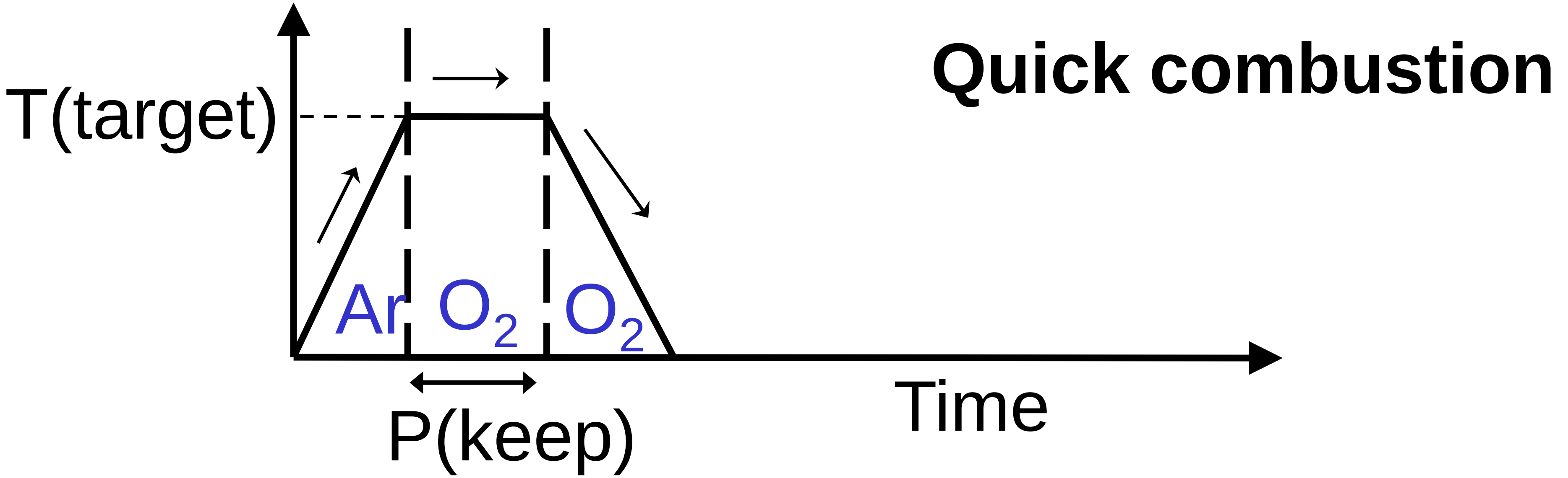
開孔方法

- 酸化
（HNO_3, H_2SO_4, H_2O_2, O_2）
- メカニカルクラッシュ

酸素中加熱で開孔

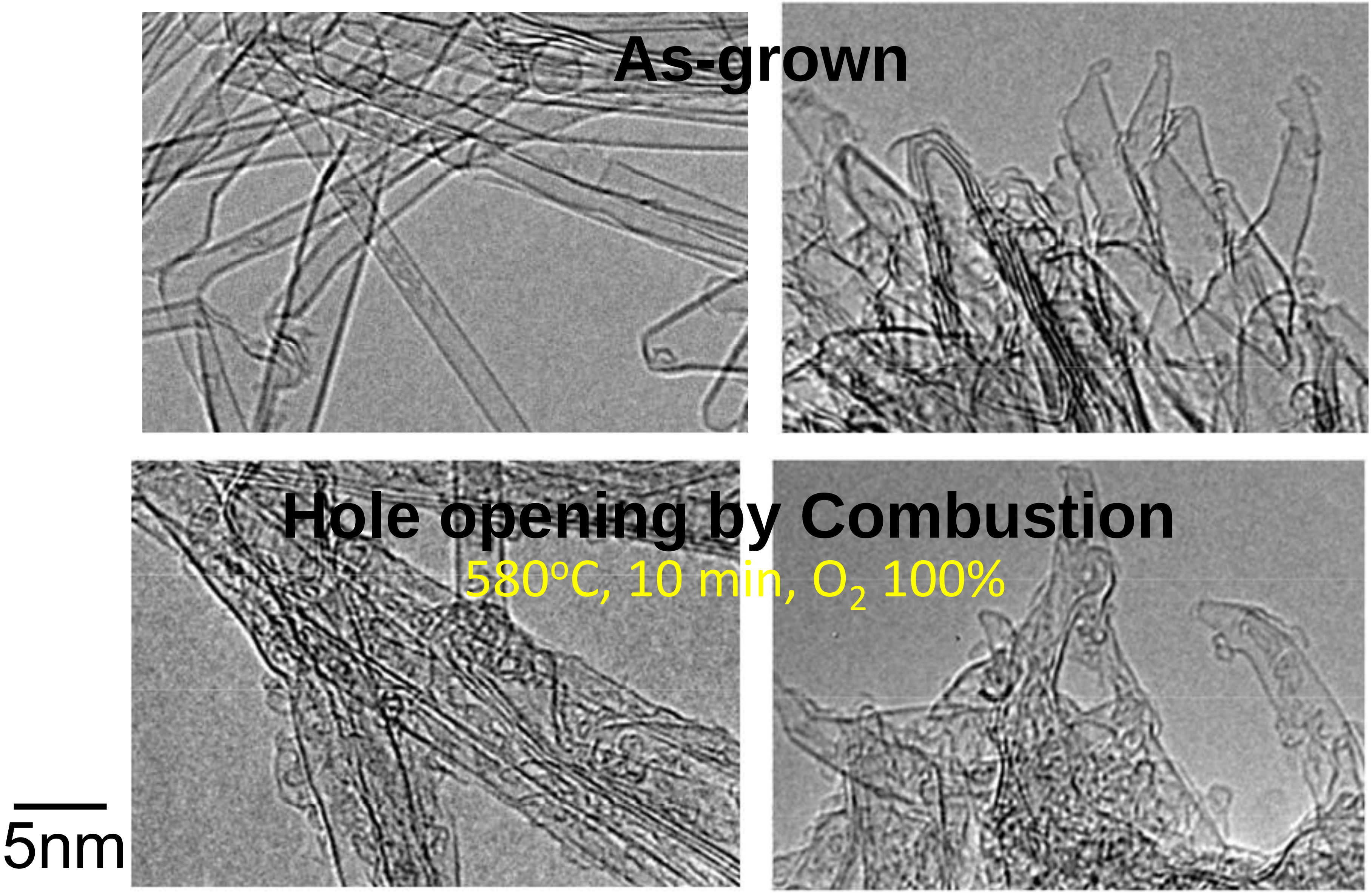
Fan et al. JPCB 2006





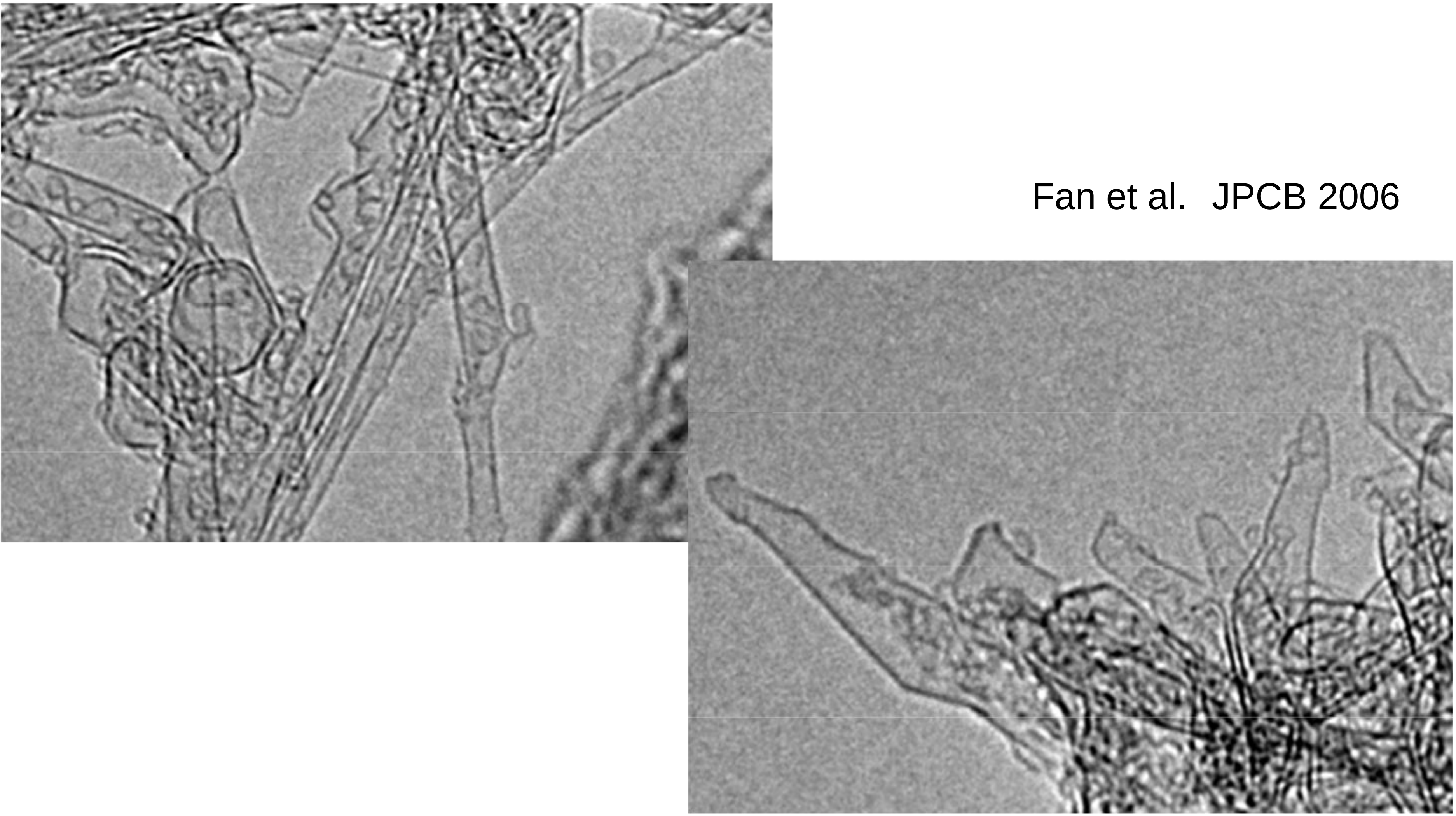
問題：酸化処理により生じる炭素ゴミ

Fan et al. JPCB 2006



解決法:炭素ゴミを取るために熱処理

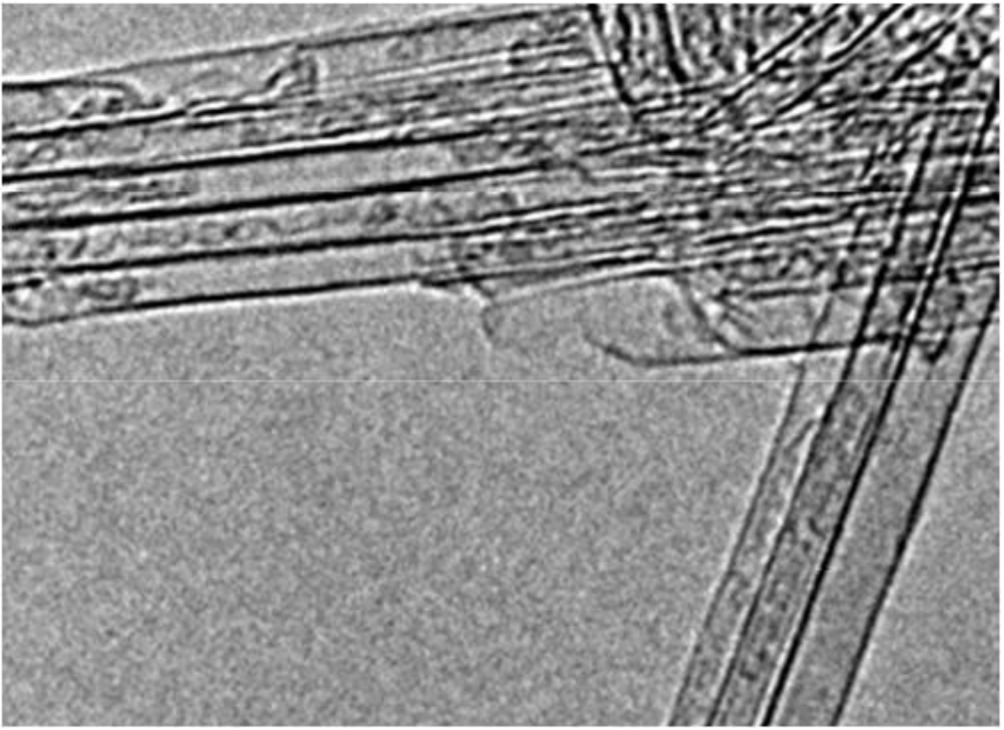
500^{o}C, 2 h, 5x10^{-6} Torr



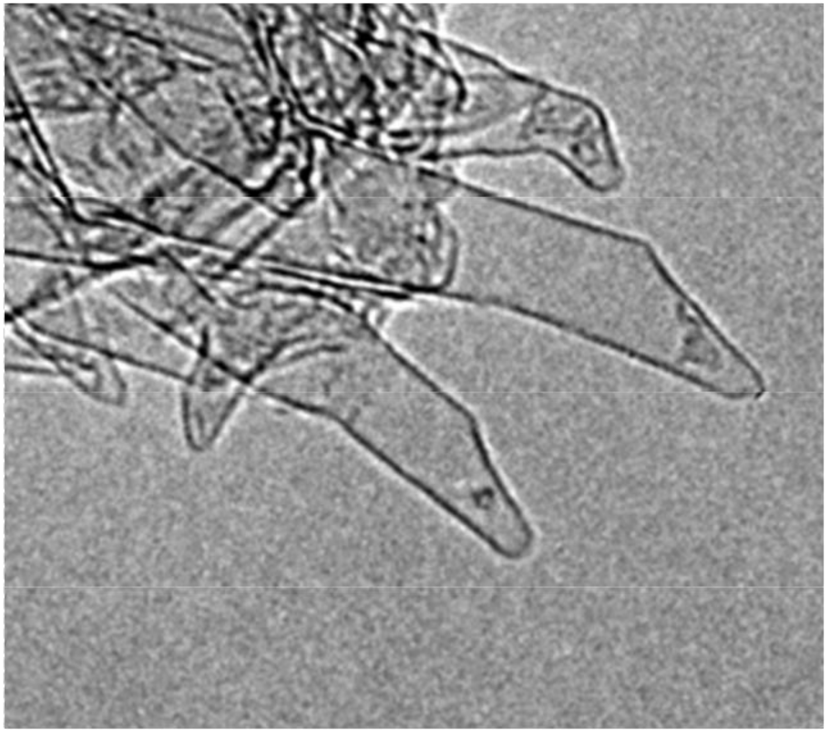
Fan et al. JPCB 2006

解決法:ゆっくり酸化（Slow　combustion）

Fan et al.　JPCB 2006



T(target): 550ºC



:炭素ゴミが少ない

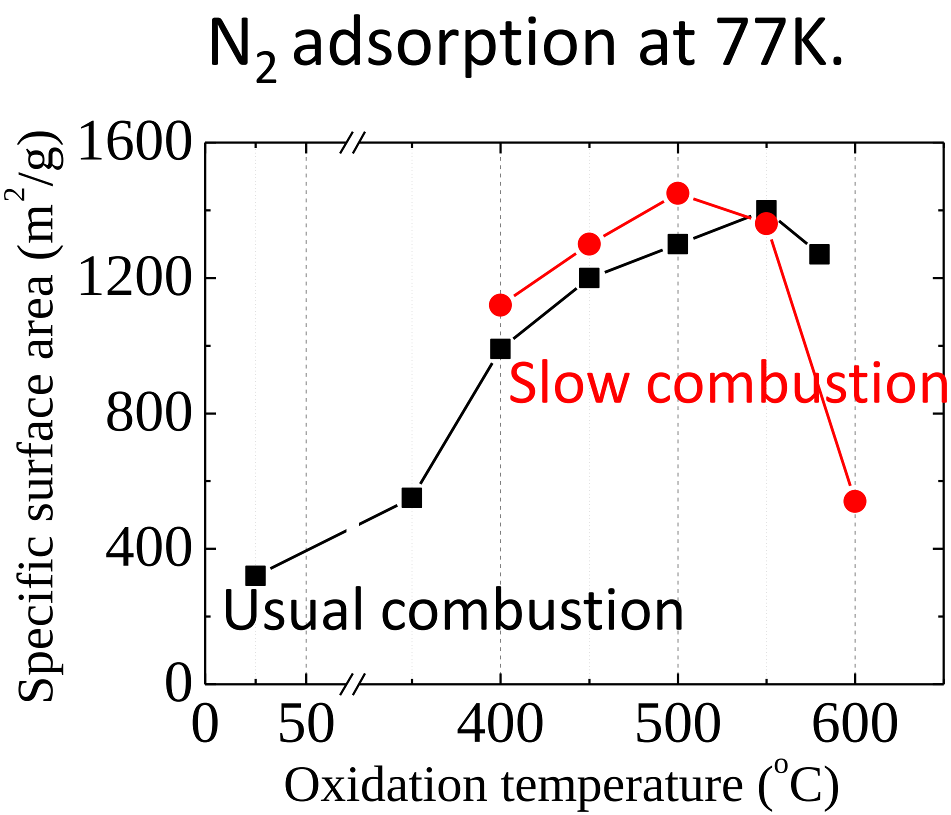
開孔した事を確認する。

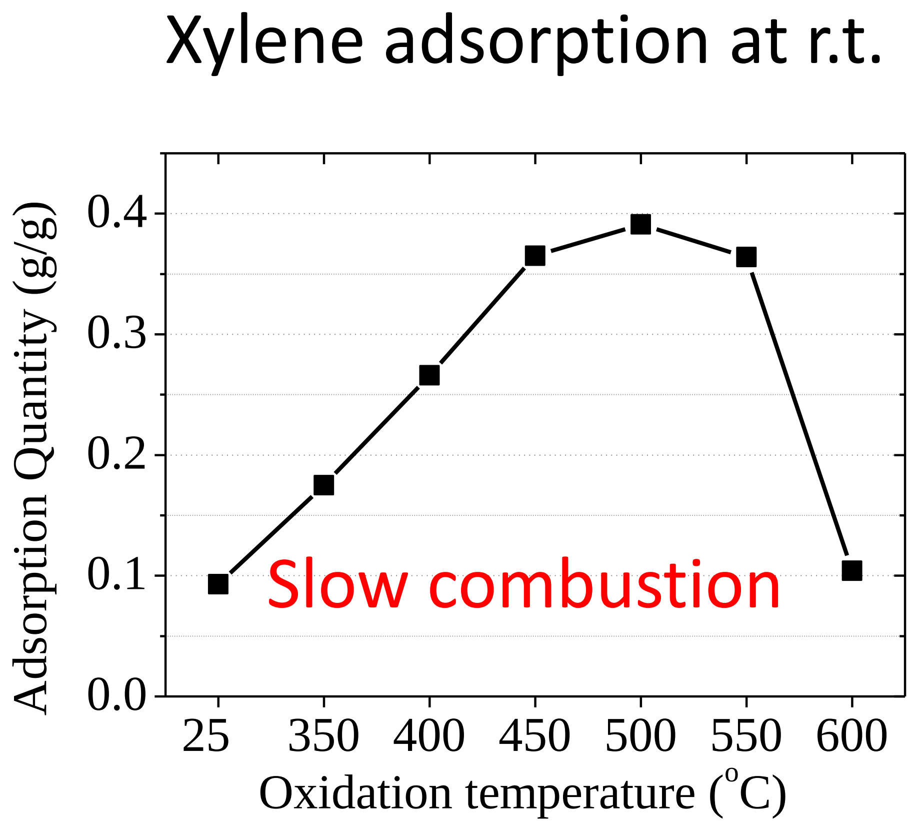
Fan et al. JPCB 2006

- 比表面積、細孔容量
- TEM
- Raman スペクトル

Specific surface area

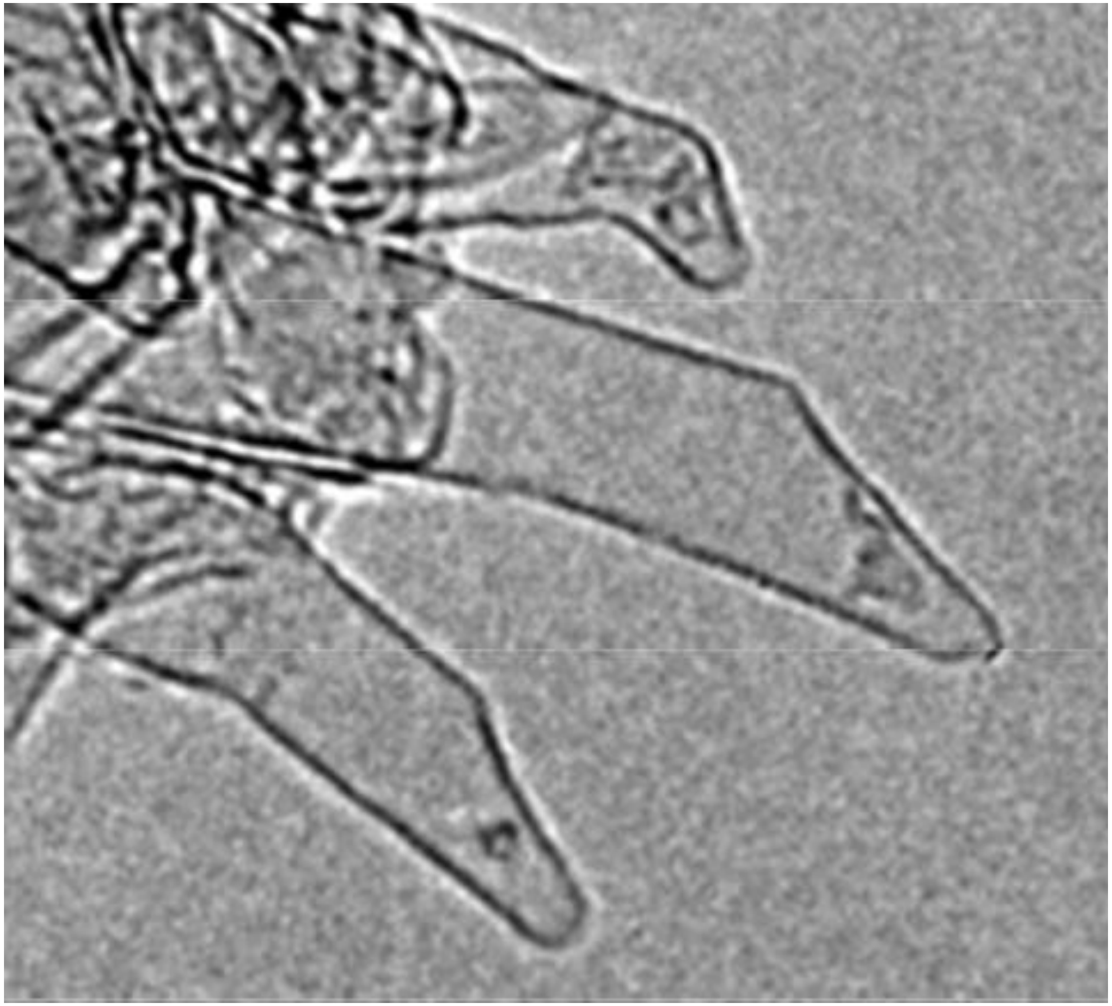
Fan et al. JPCB 2006





BET吸着等温式（Brunauer,Emmett、Teller）

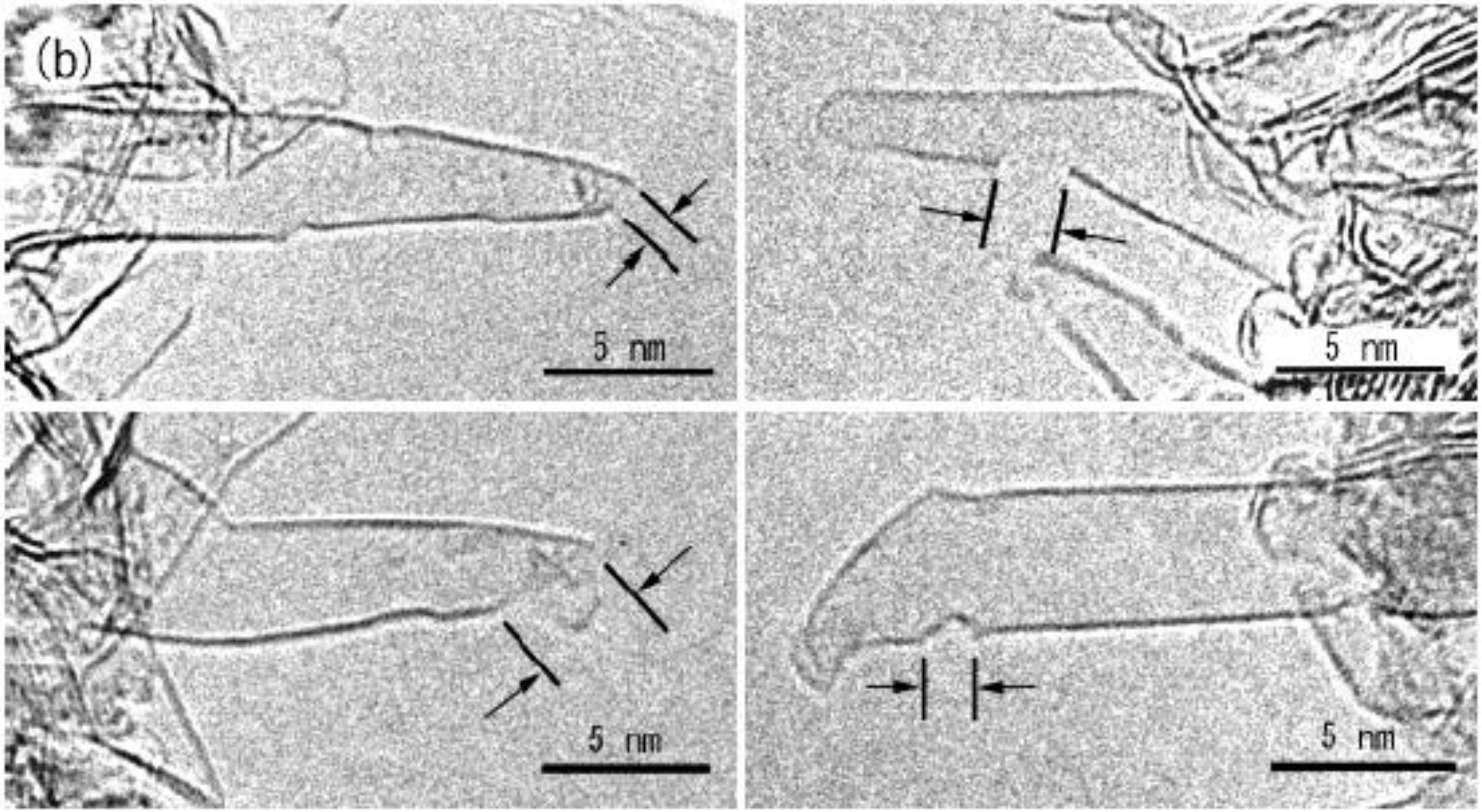
孔？



Holes in graphene walls

SWNHox

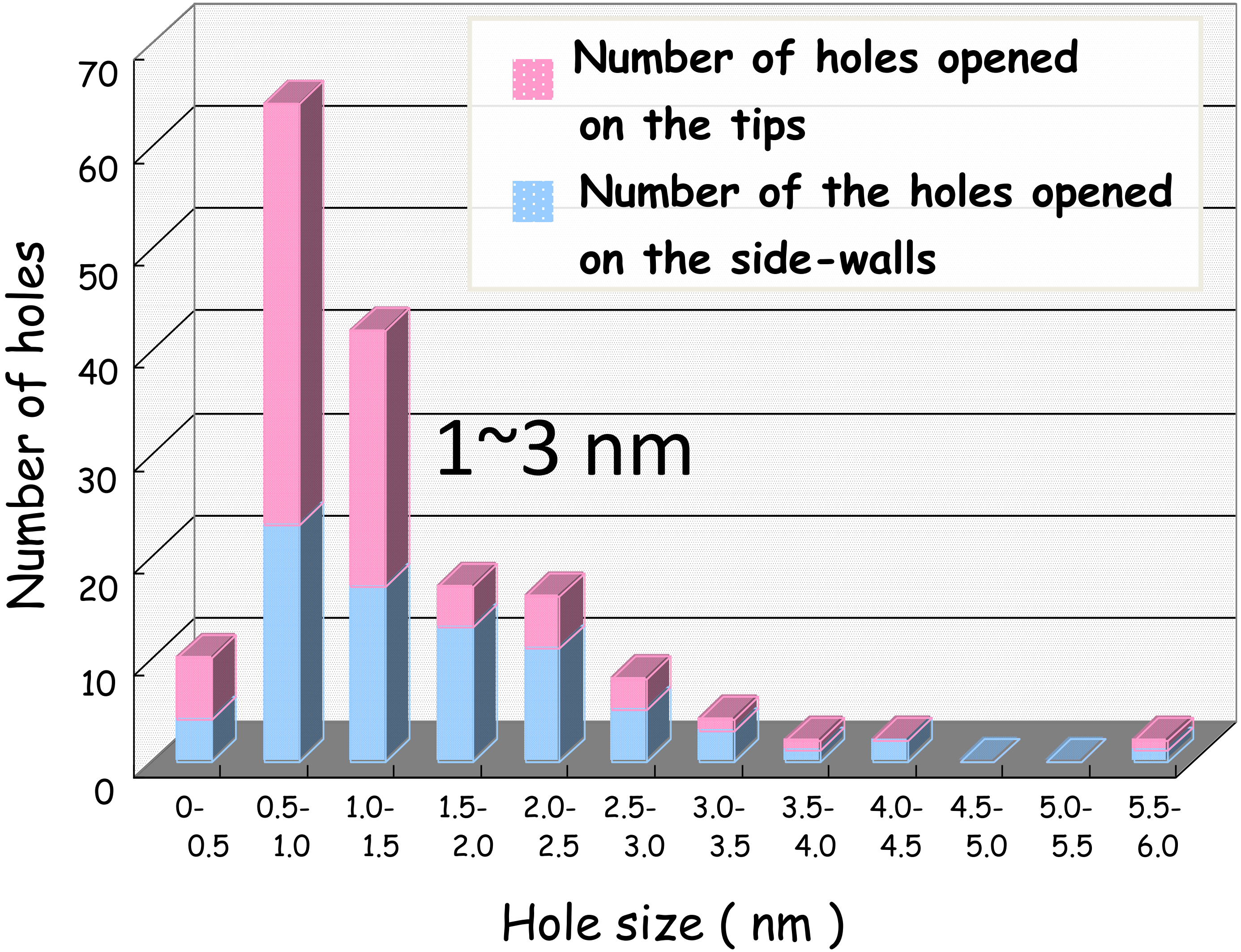
O_2, 570°C, 15 minutes + HT in vac.

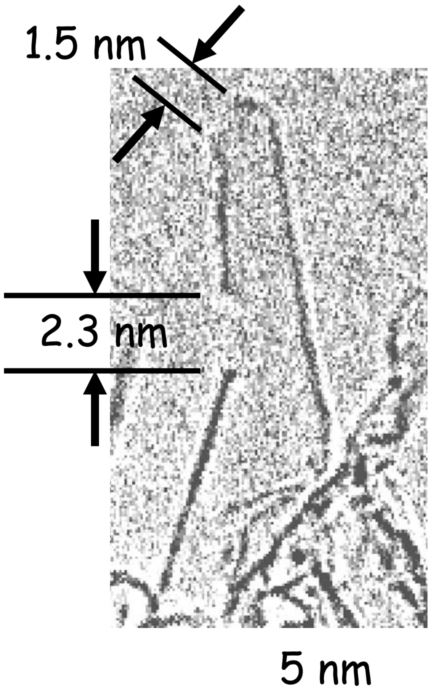


Ajima et al. Adv. Materials, 16 (2004) 397.

Distribution of Hole Sizes.

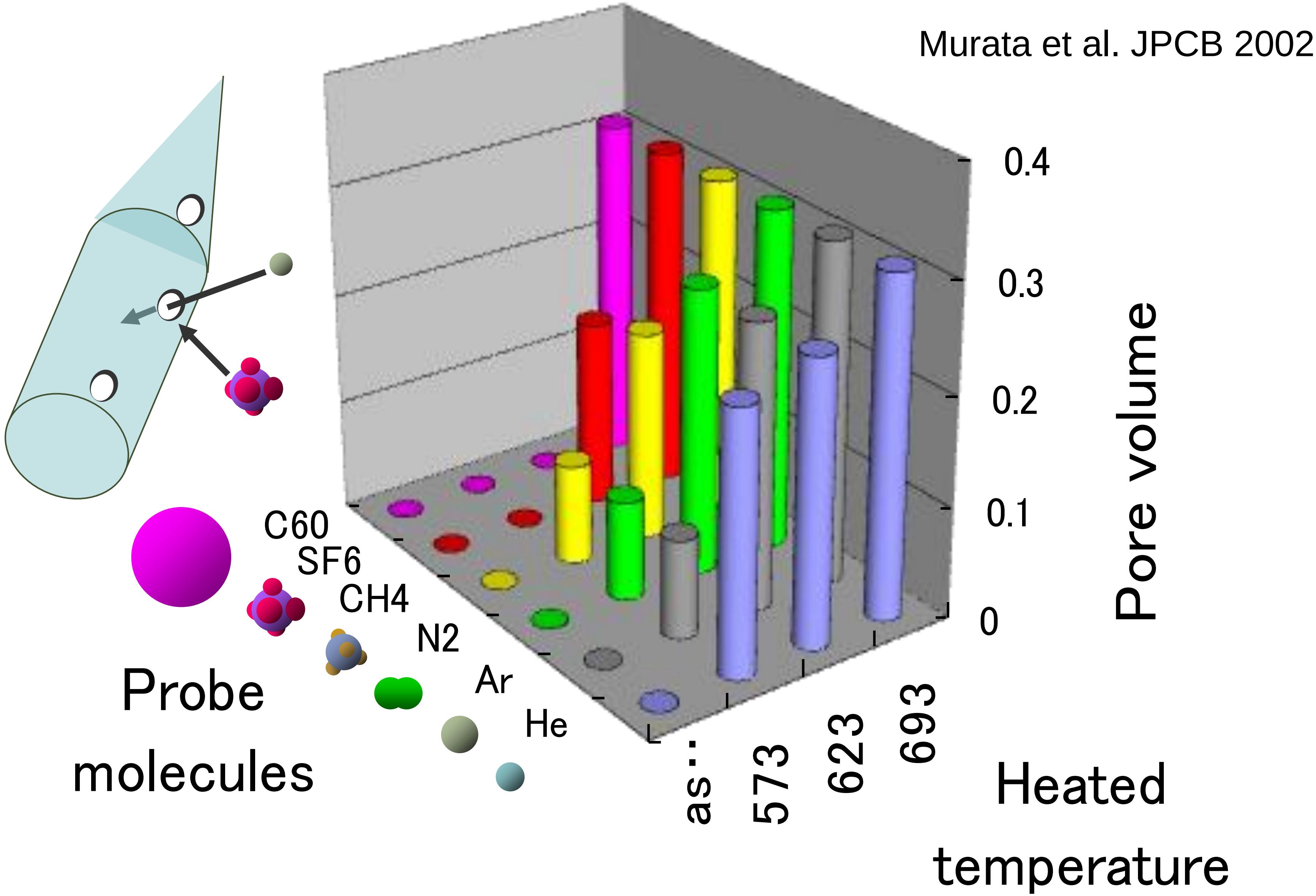
O_2, 570^oC, 15 minutes



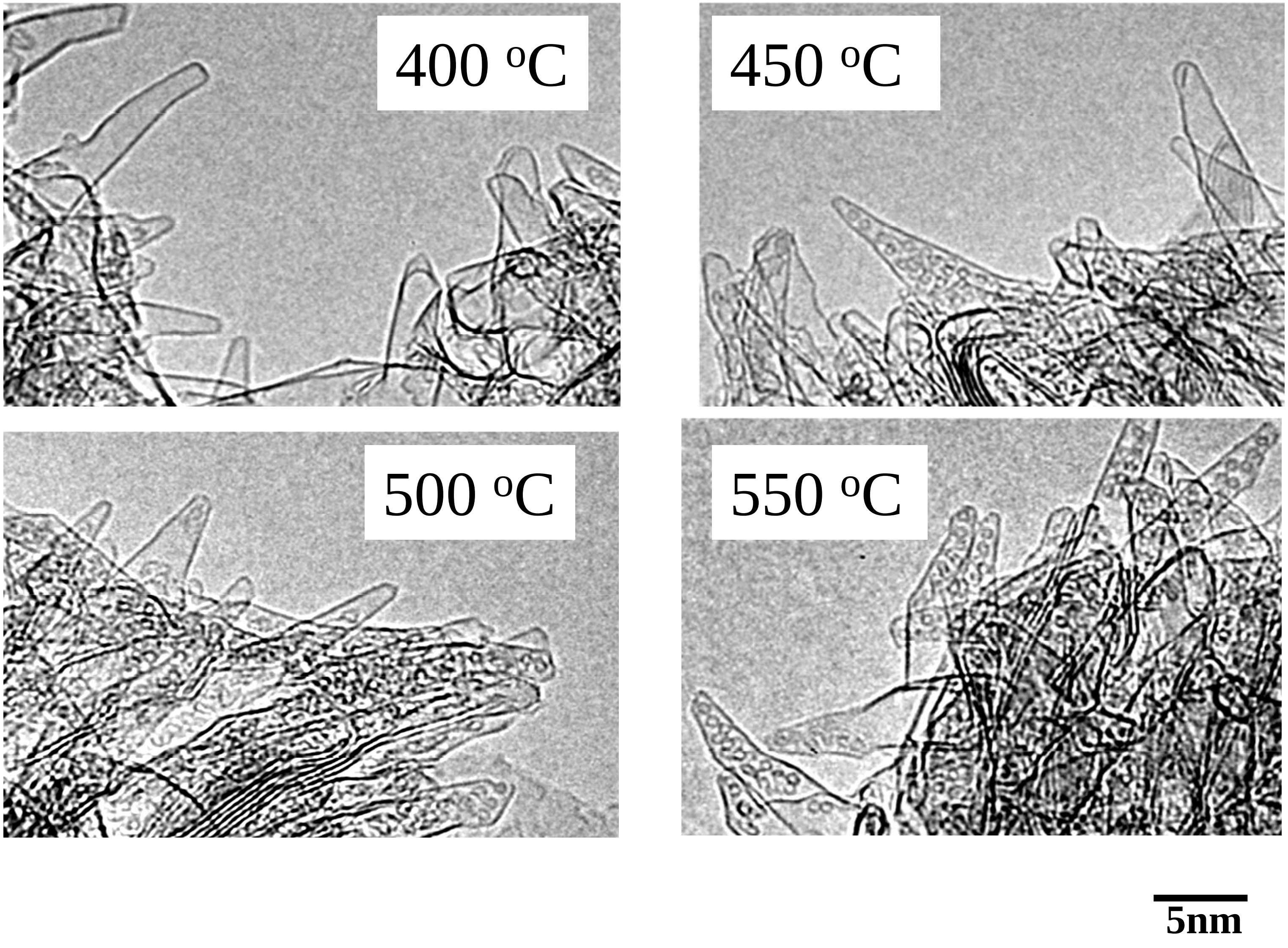


Ajima et al. Adv. Materials, 16 (2004) 397.

Hole sizes depending on oxidation temperature

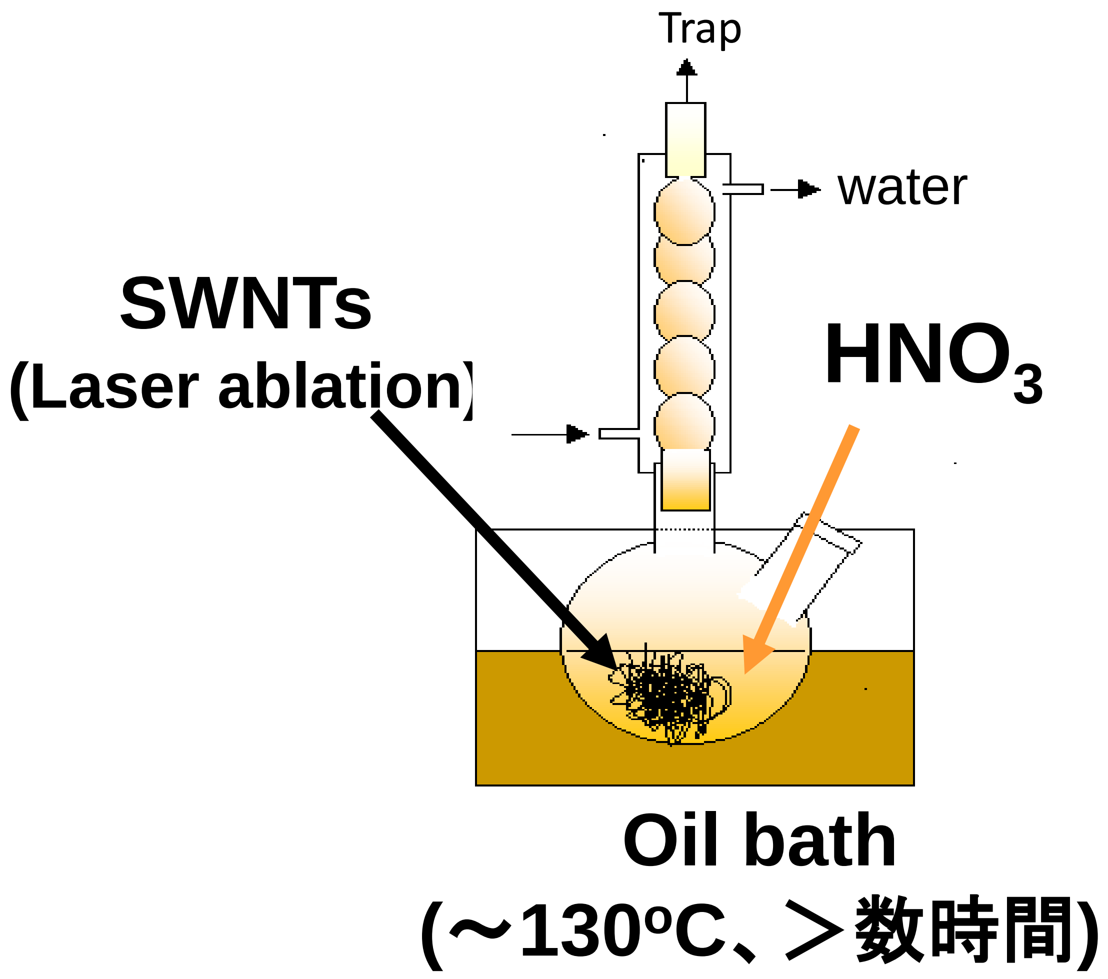


C_{60}が入れる大きさの孔



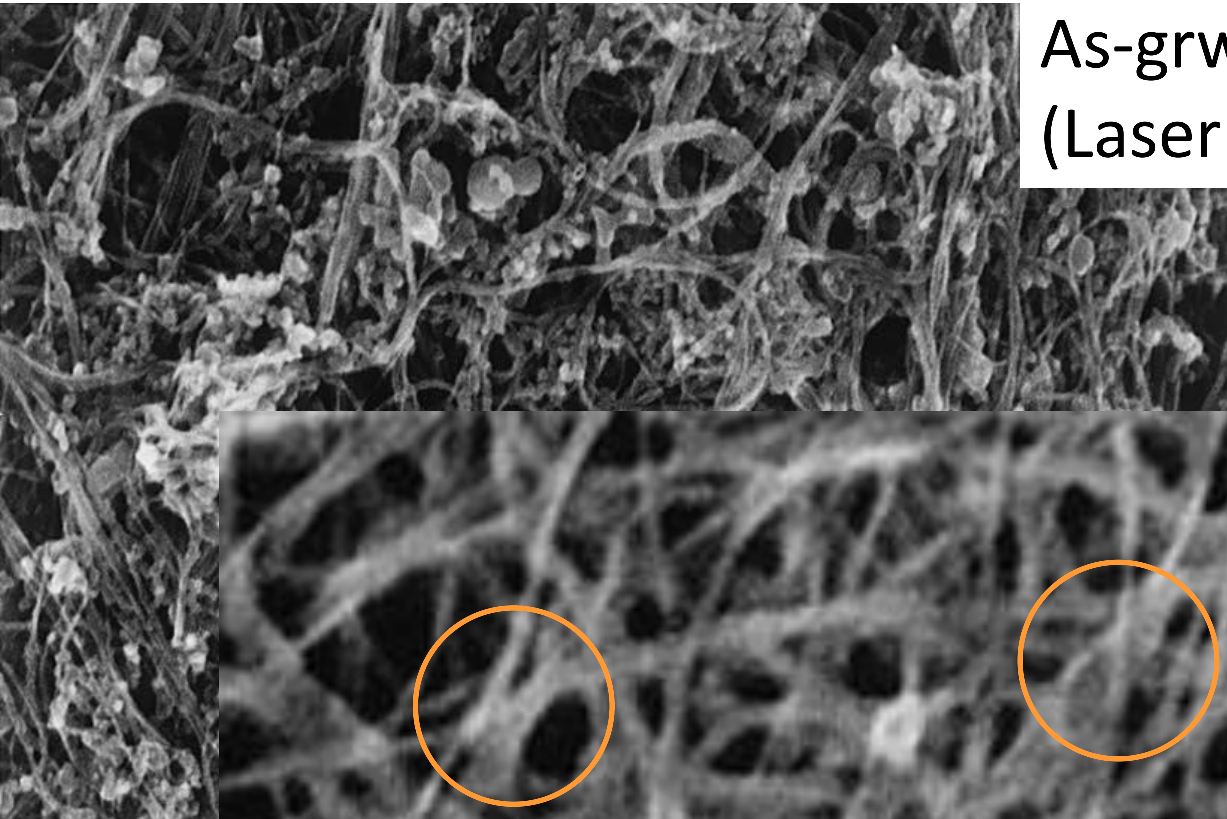
Yudasaka et al

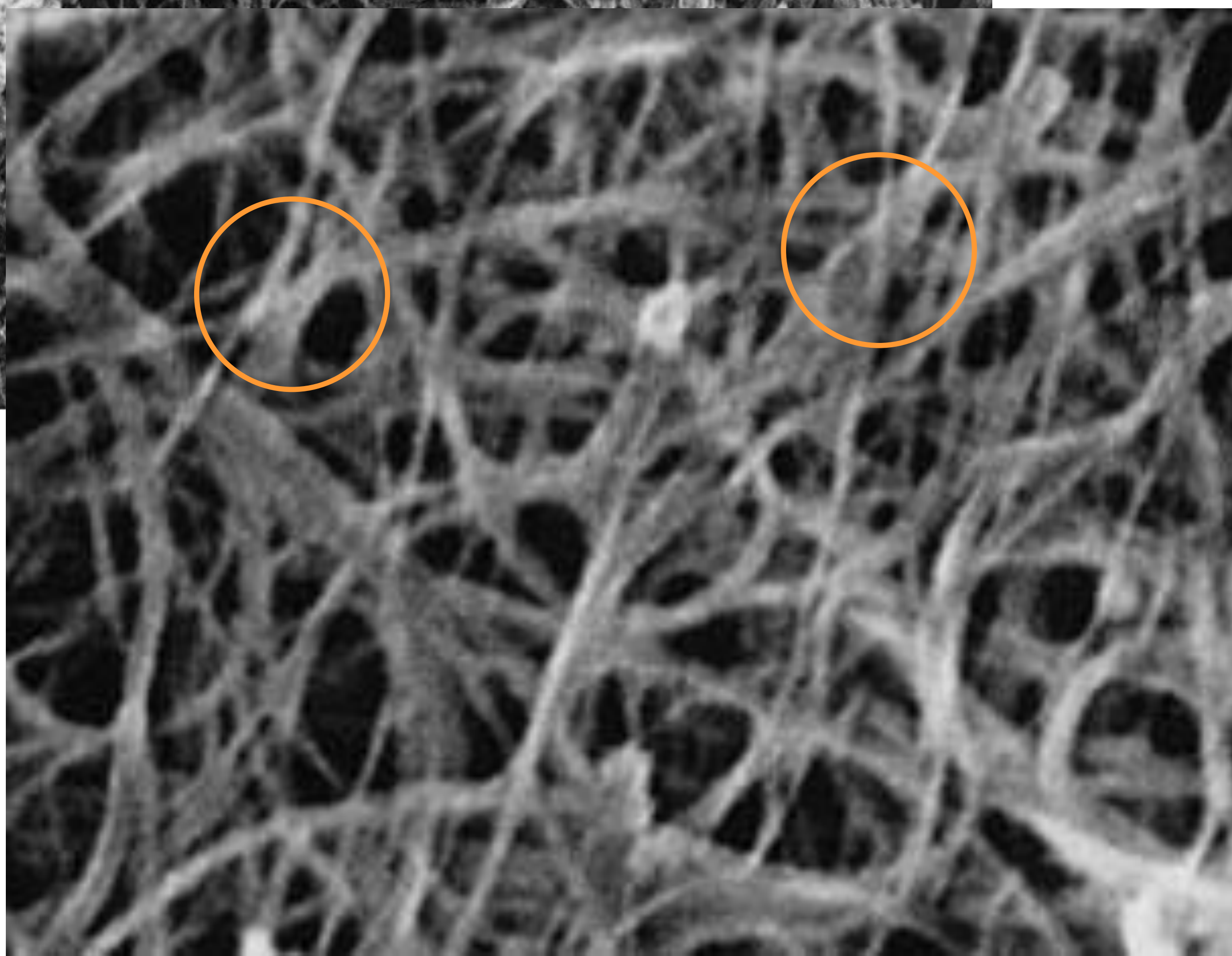
酸を用いた開孔
硝酸



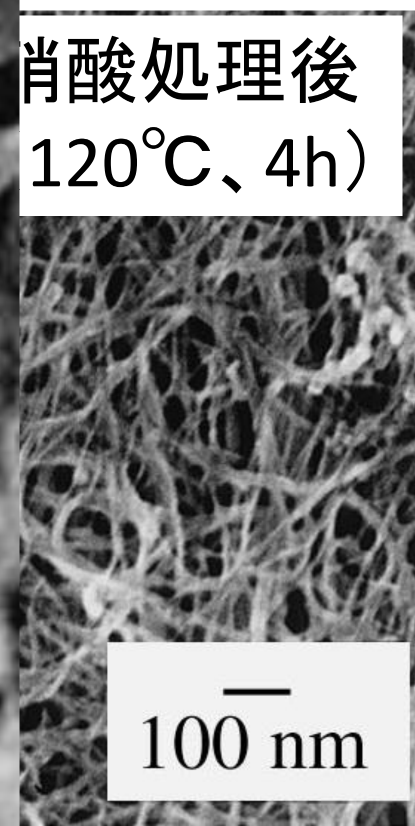
As-grwon SWNTs
(Laser ablation)

Nagasama et al. CPL 2000

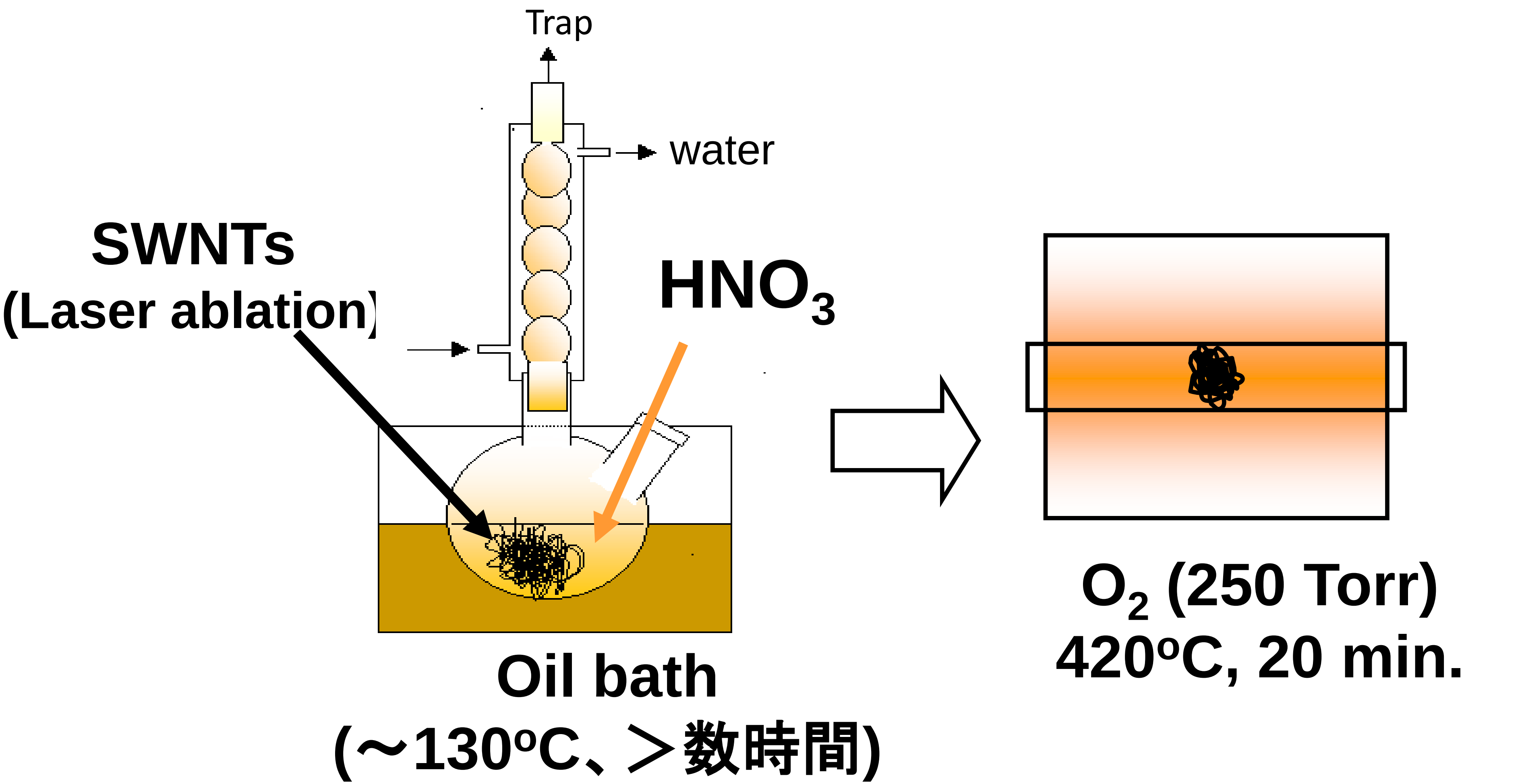




硝酸処理後
120℃、4h）



酸化性酸を用いた開孔
硝酸



開孔縁の官能基

開孔縁にある官能基

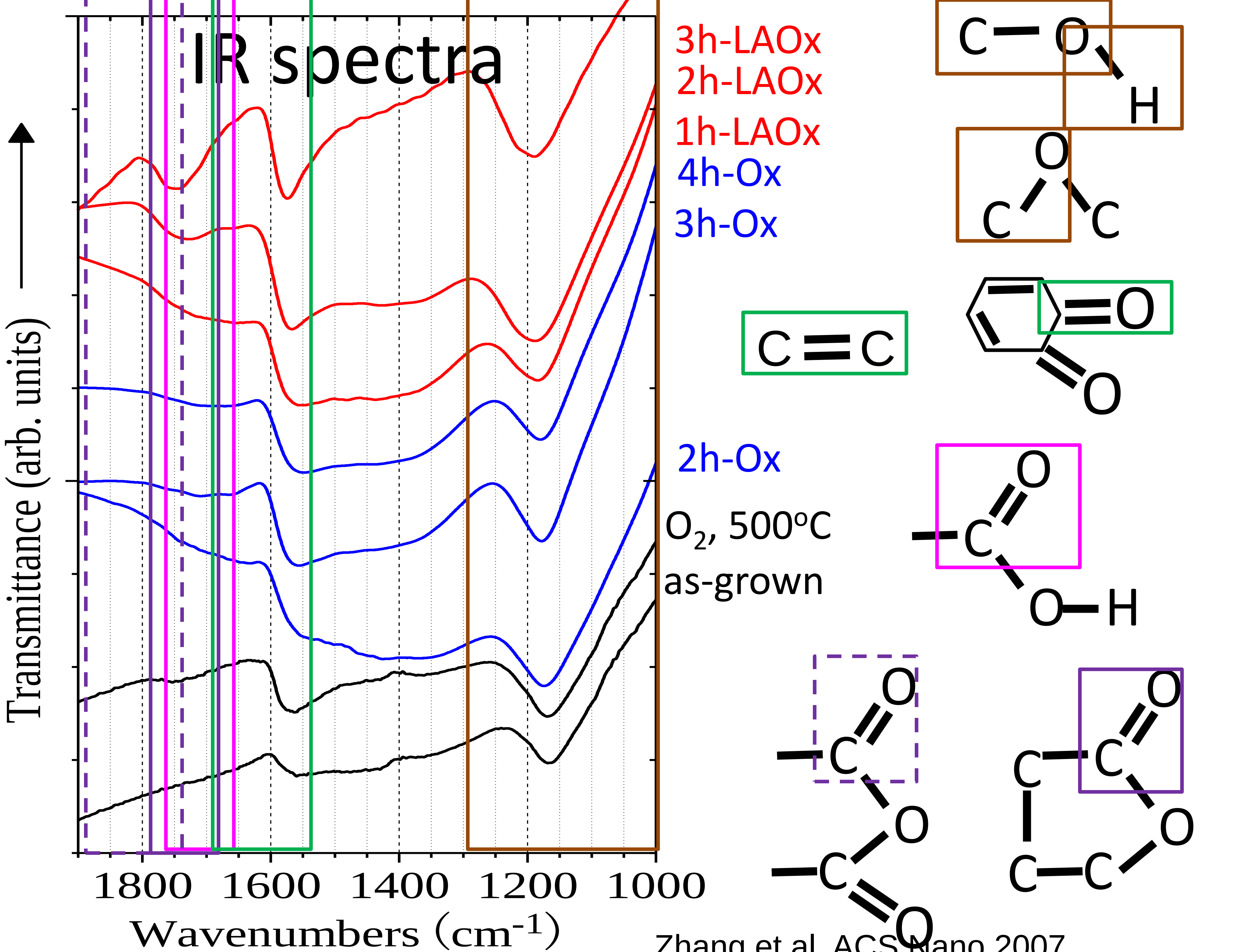
化学修飾に使えるもの

分析方法

- 定性：IR
- 定性：TPD-MS
- 定量：TGA

可視化

- 染色→TEM



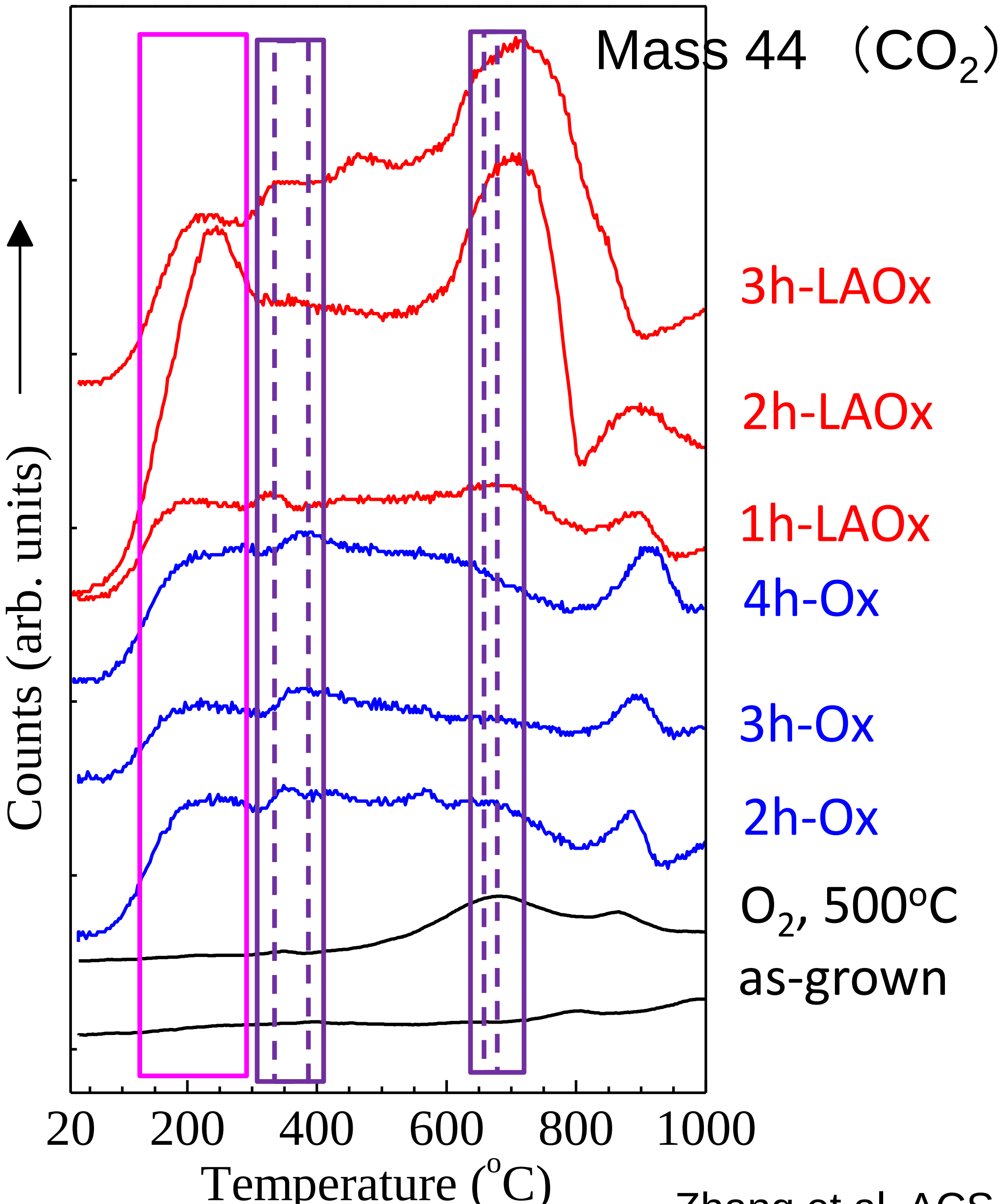
Zhang et al. ACS Nano 2007

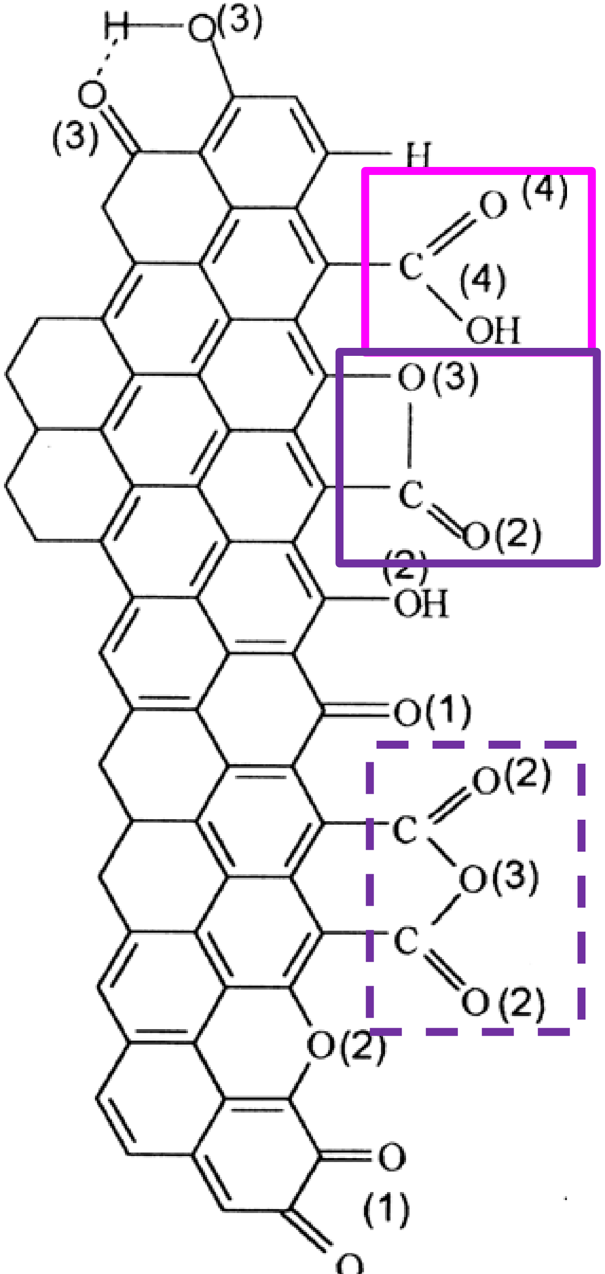
IR assignments of functional groups on carbon surfaces

Fanning PE, Vannice MA. Carbon 1993;31:721.

C–O in ethers (stretching)	1000–1300		
Alcohols	1049–1276		3200–3640
Phenolic groups:			
C–OH (stretching)	1000–1220		
O–H	1160–1200		2500–3620
Carbonates; carboxyl-carbonates	1100–1500	1590–1600	
C=C aromatic (stretching)		1585–1600	
Quinones		1550–1680	
Carboxylic acids	1120–1200	1665–1760	2500–3300
Lactones	1160–1370	1675–1790	
Carboxylic anhydrides	980–1300	1740–1880	
C–H (stretching)			2600–3000

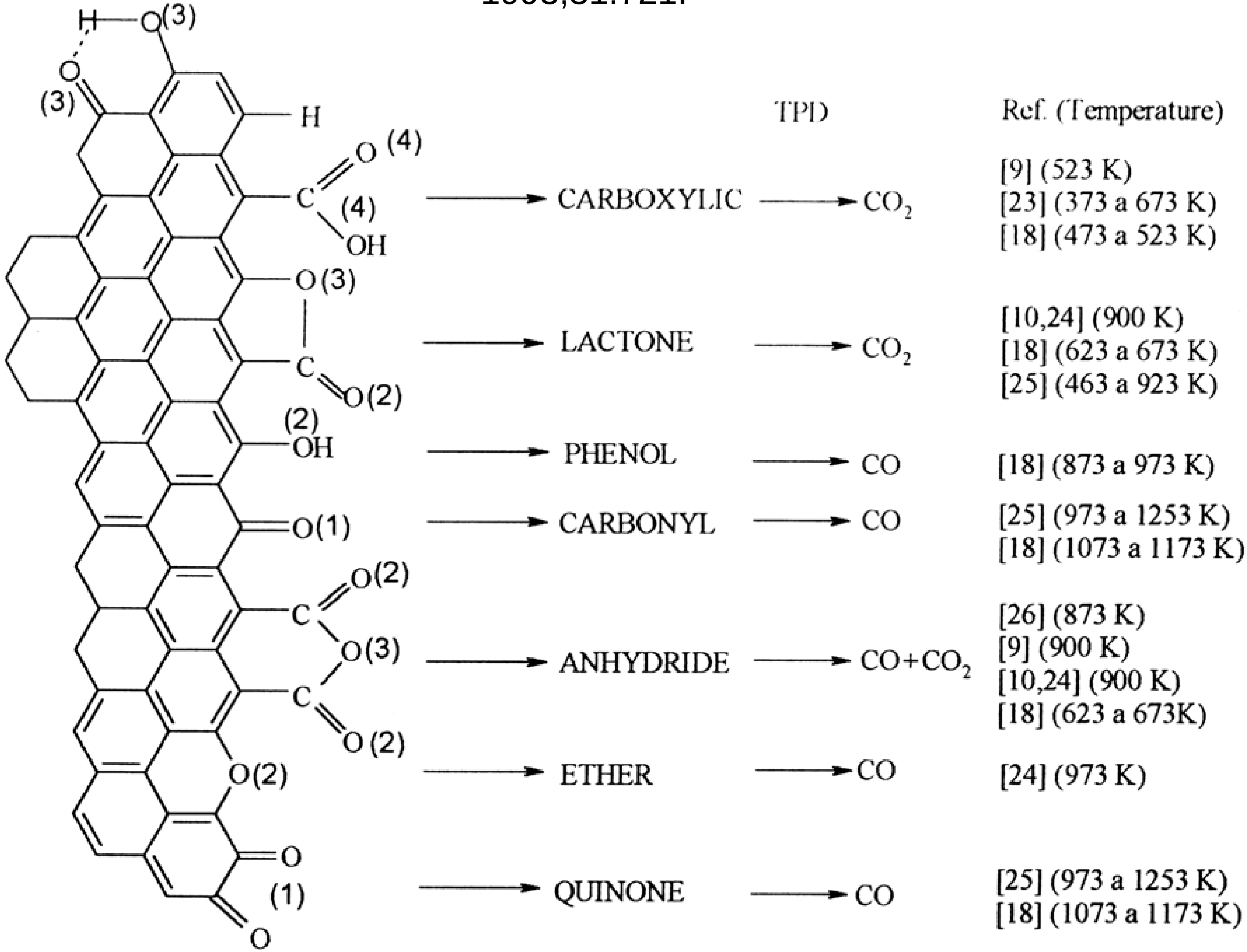
TPD-MS



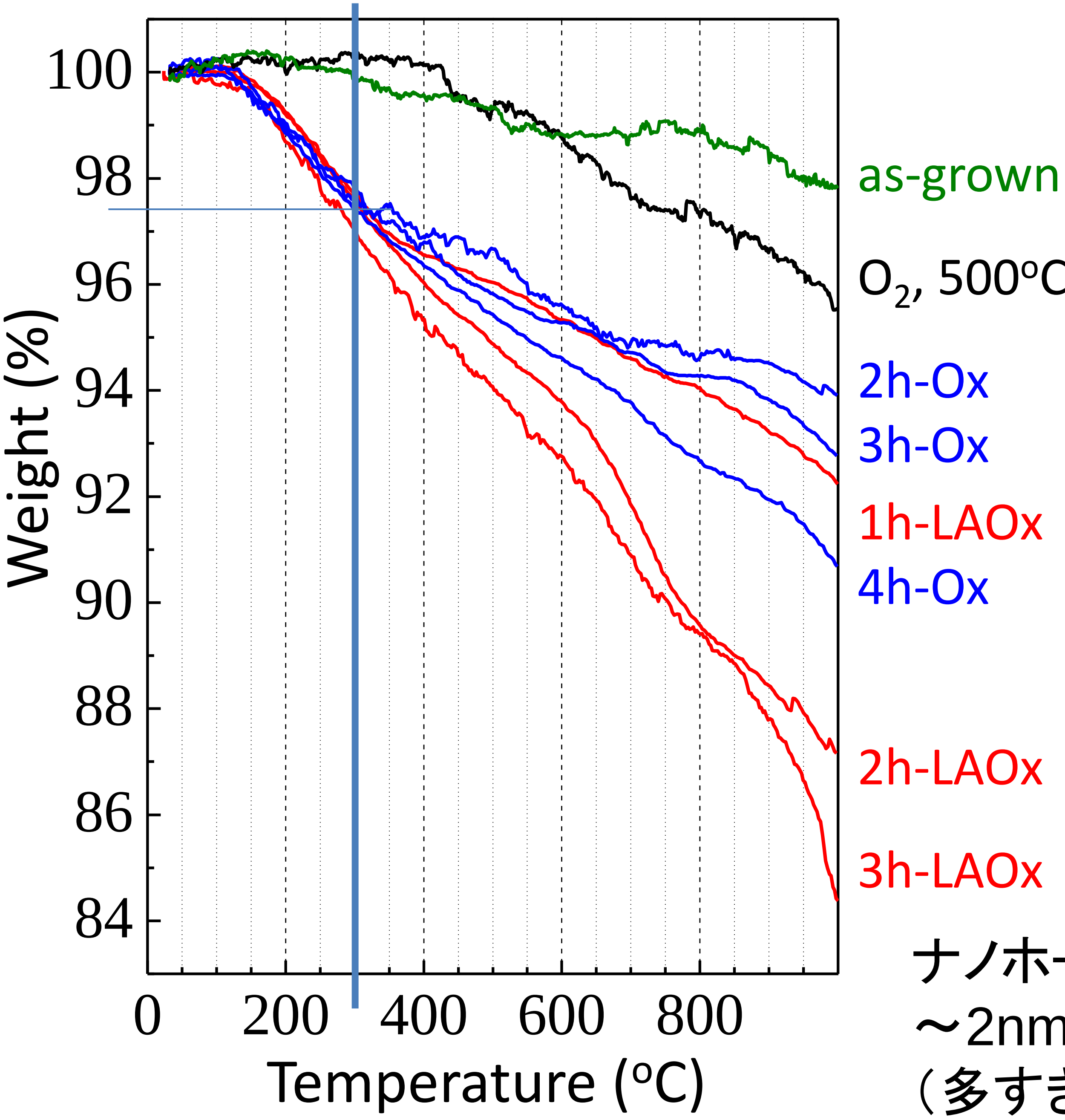


Zhang et al. ACS Nano 2007

Fanning PE, Vannice MA. Carbon 1993;31:721.



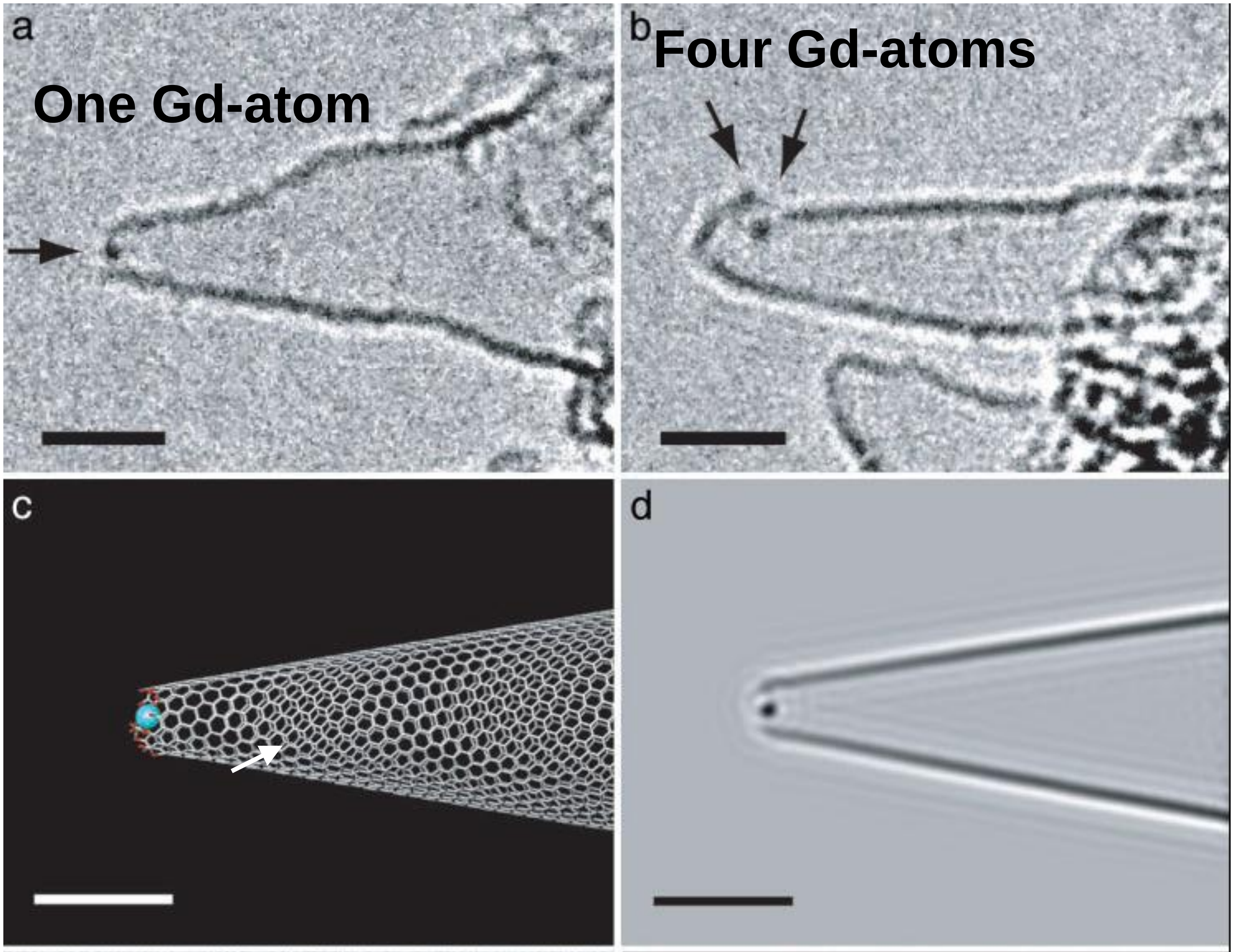
カルボキシル基の数を推定　TGA (He)



ナノホーン1本あたりの孔（直径～2nm）の数・・・・5個程度。（多すぎる。）

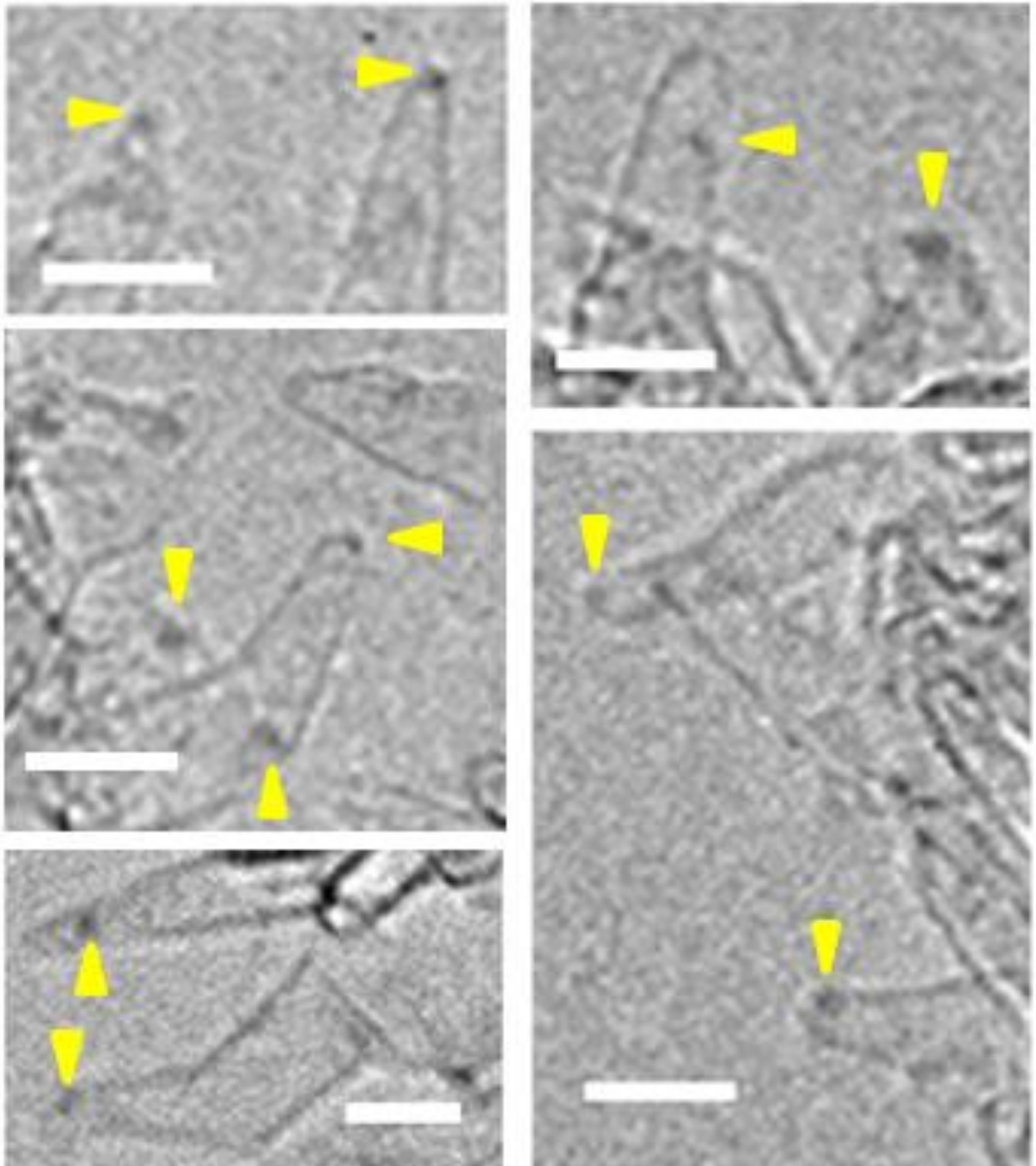
カルボキシル基の可視化

Hashimoto et al. *PNAS* **101**(2004)8527.



Gd(CH3COO)3
を使ってキレート
結合でエッジに
つける。

可視化 (Site localization)

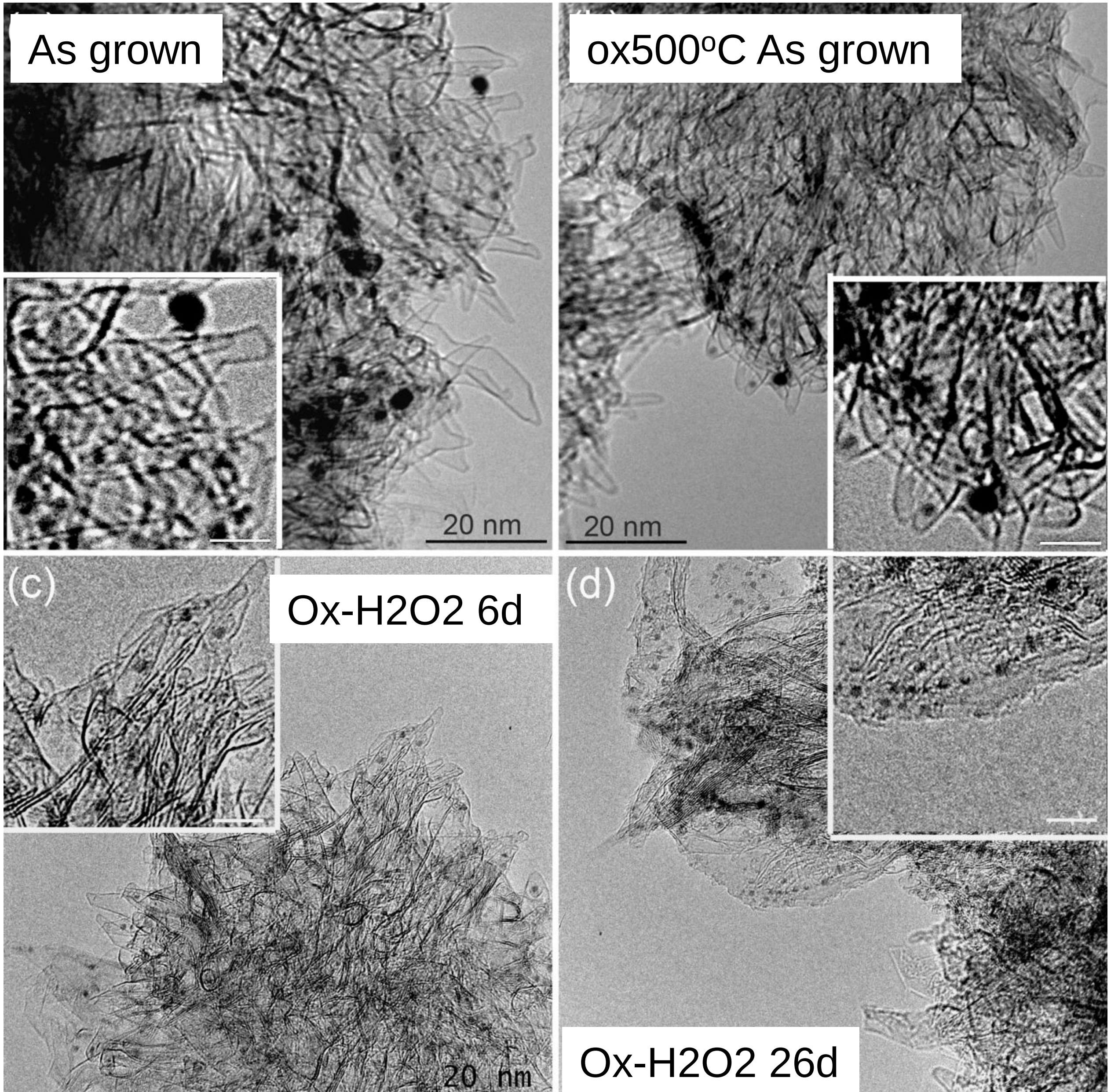


$-COOH + Pt(NH_3)_6(OH)_4 \rightarrow$

$\left\{ \begin{array}{l} -CO\text{-}O\text{-}NH_2\text{-}Pt(NH_3)_5(OH)_4 \\ -COO^- \ Pt(NH_3)_5(OH)_4 \ (NH_4)^+ \end{array} \right.$

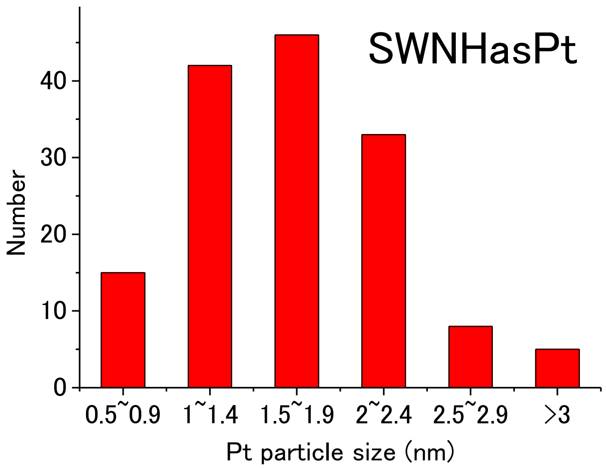
Xu et al. APA 2010

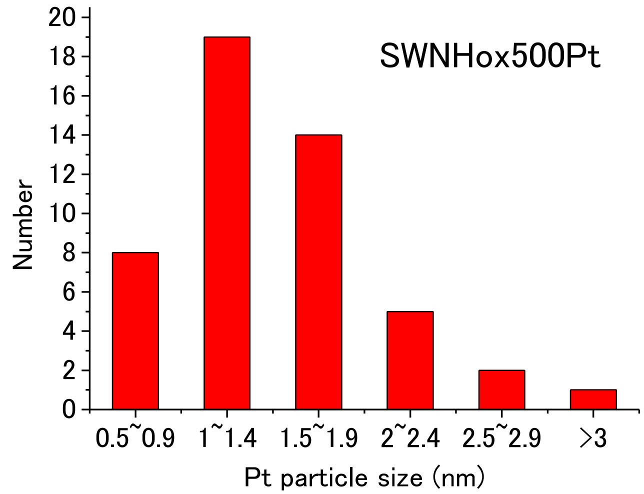
Pt 化合物付着の様子と一COOHの有無

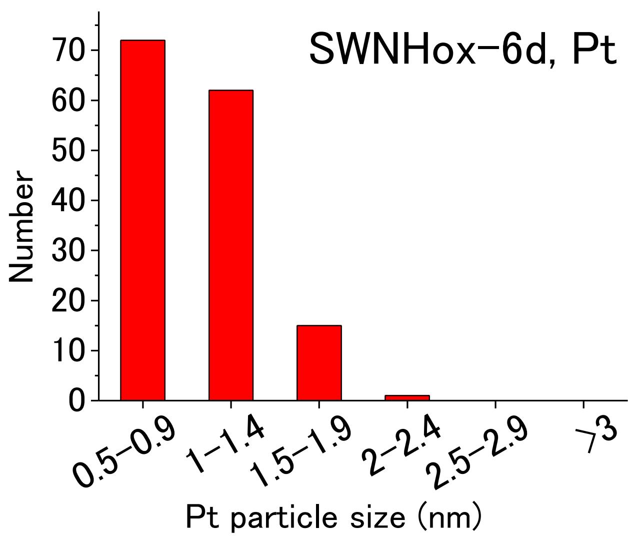


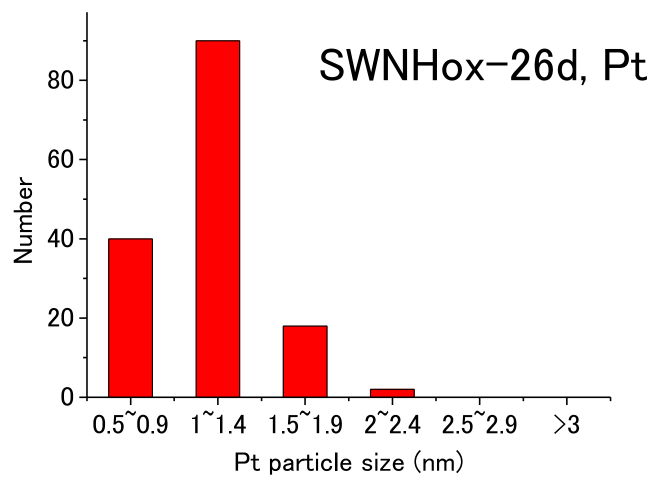
Xu et al. APA 2010

Pt complex particles: Size distribution

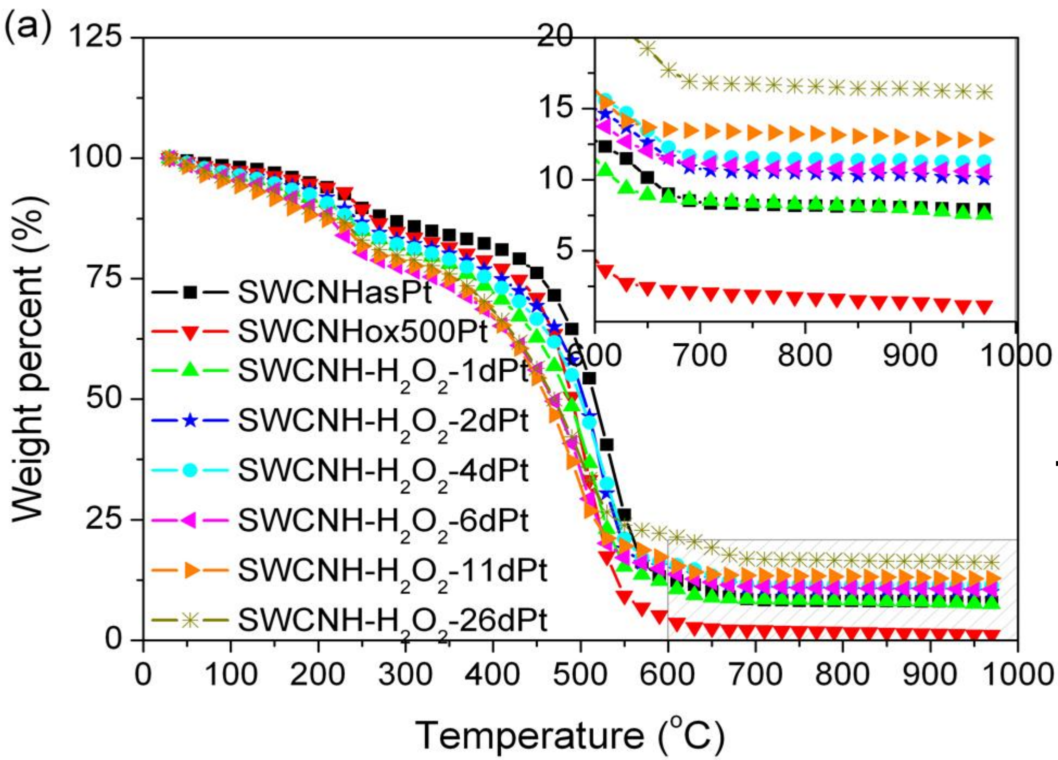








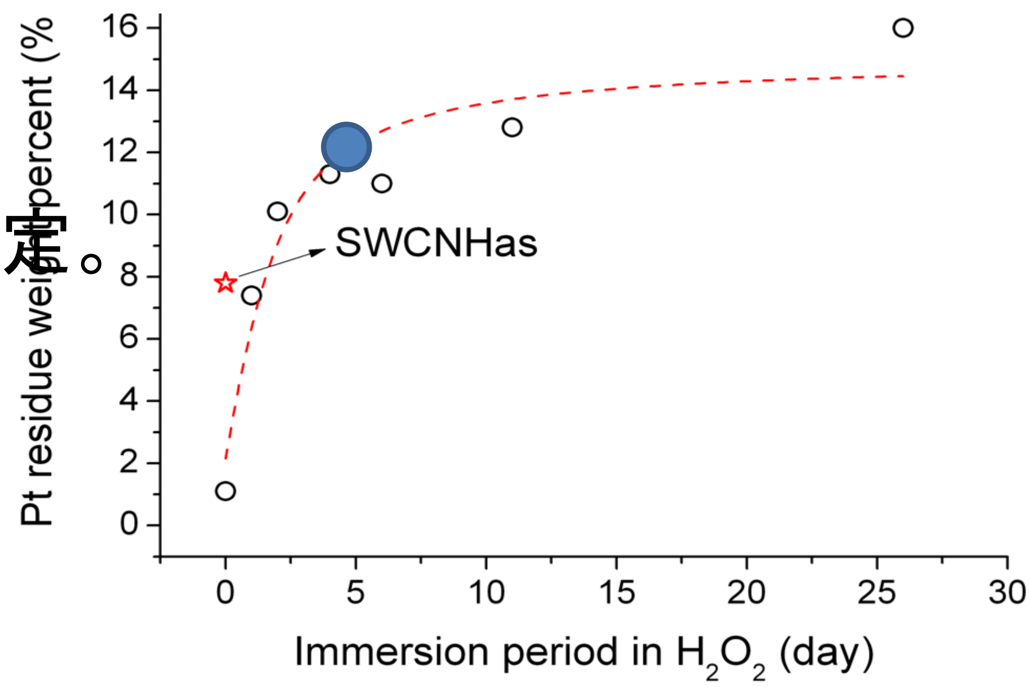
Xu et al. APA 2010



Ptの量を測定できる。

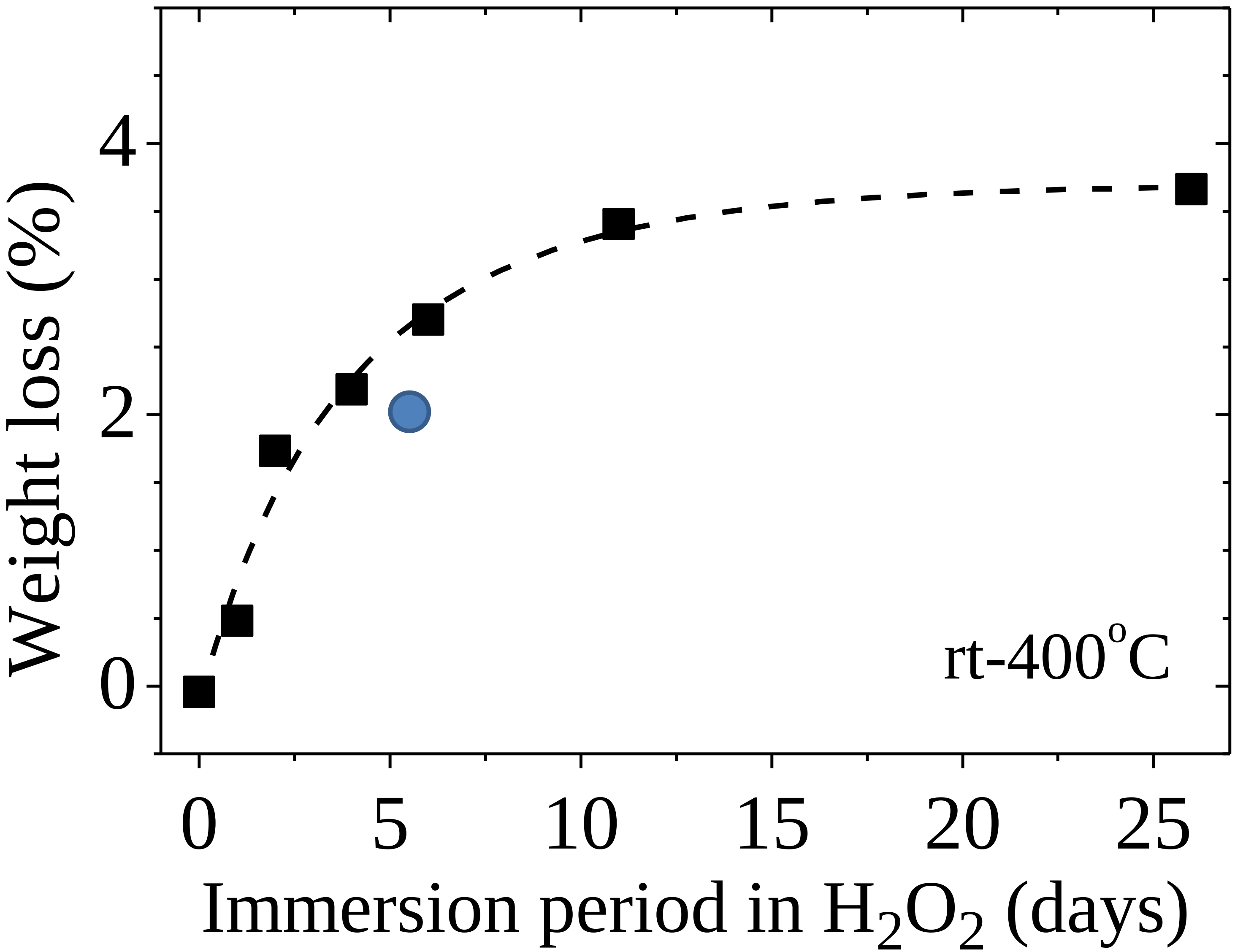
TGA（酸素）

Ptの量からCOOH量を推定。



Ptの量は、COOHの量と相関。

Xu et al. APA 2010



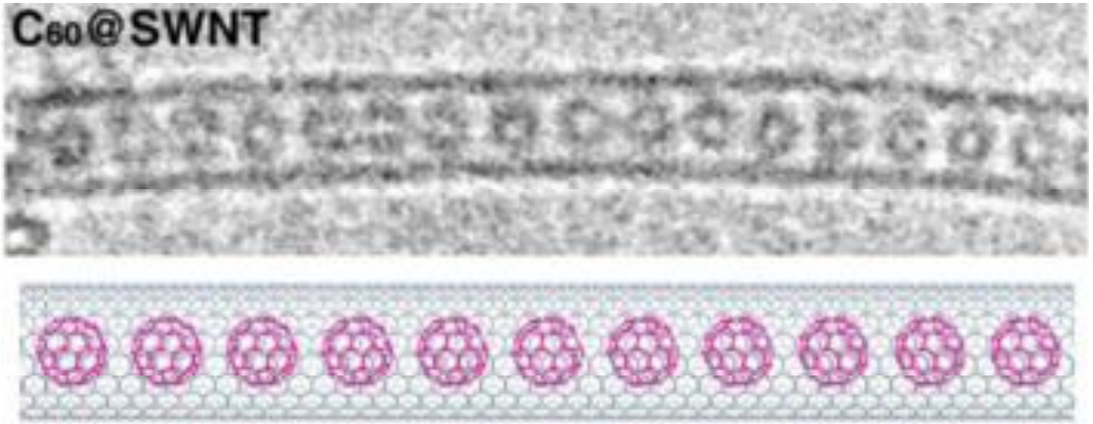
内包

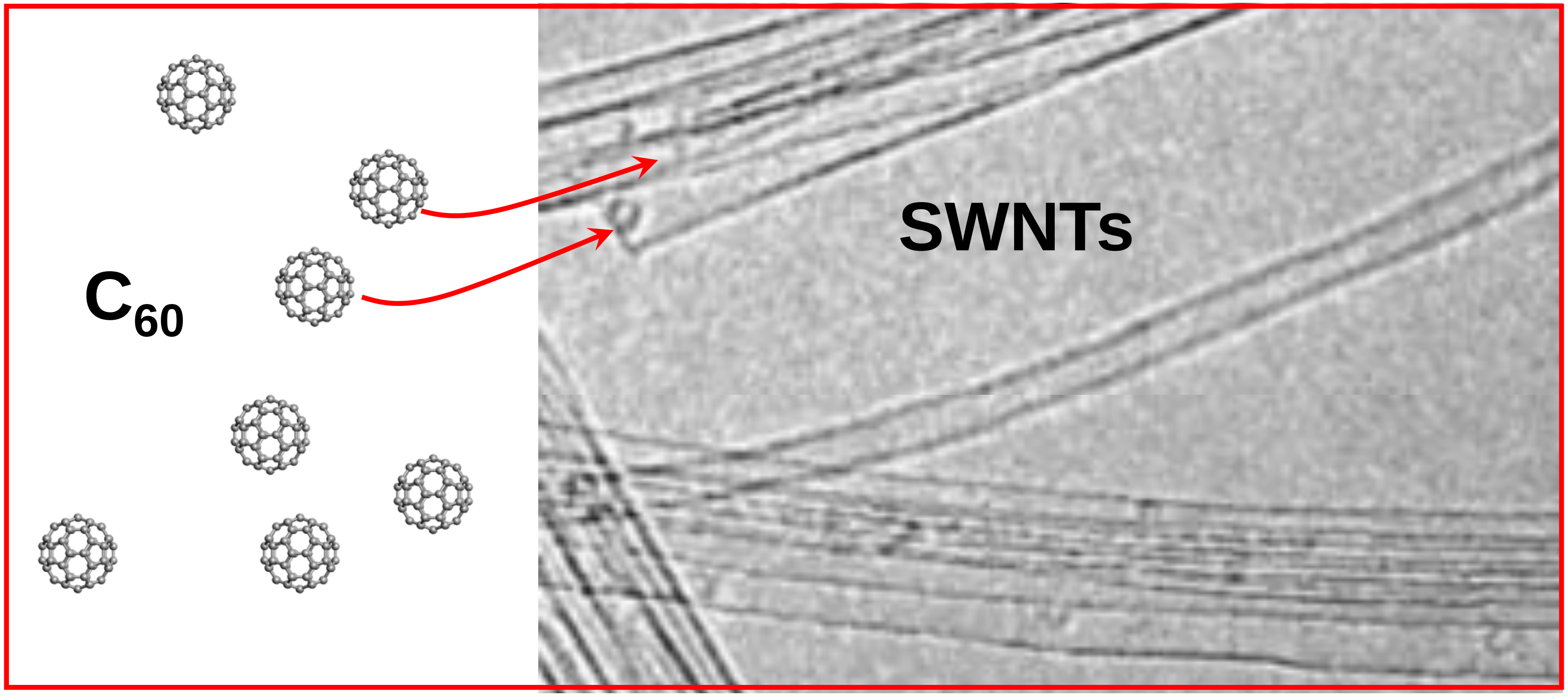
１．気相（昇華法）
２．液相
３．吸着サイト
４．内包物質の反応

Hirahara et al. *Phys. Rev. Lett. 85*, 5384, **1999**

$(C_{60})_n$@SWNT (Peapod)

1. *Open SWNT tips by Oxidation.*
2. *Expose to C_{60} Vapor at 400 ^oC.*

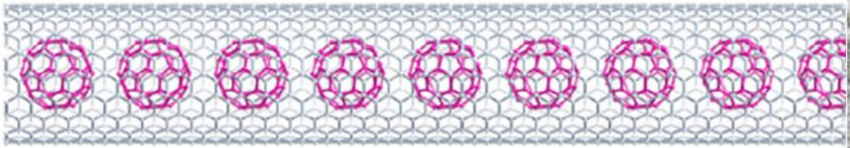


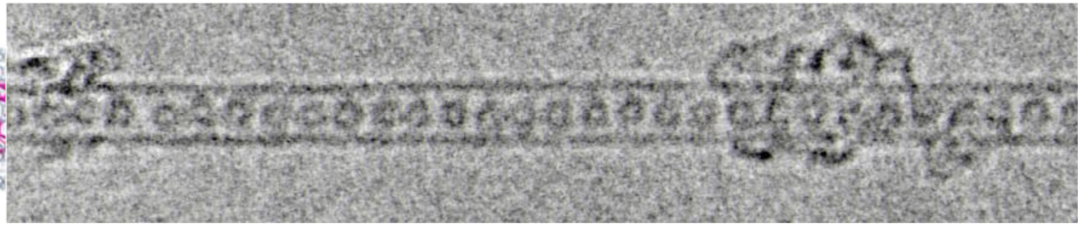


C_{60}@SWNTs → Double-walled carbon nanotubes

Bandow et al. *Chem. Phys. Lett. 337*, 48, **2001**

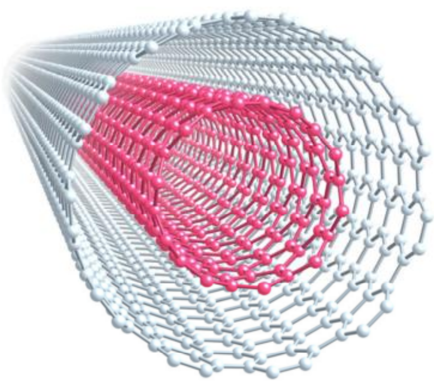
C_{60}@SWNT

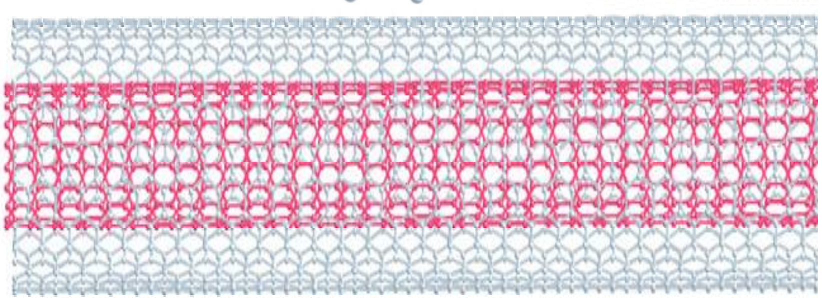


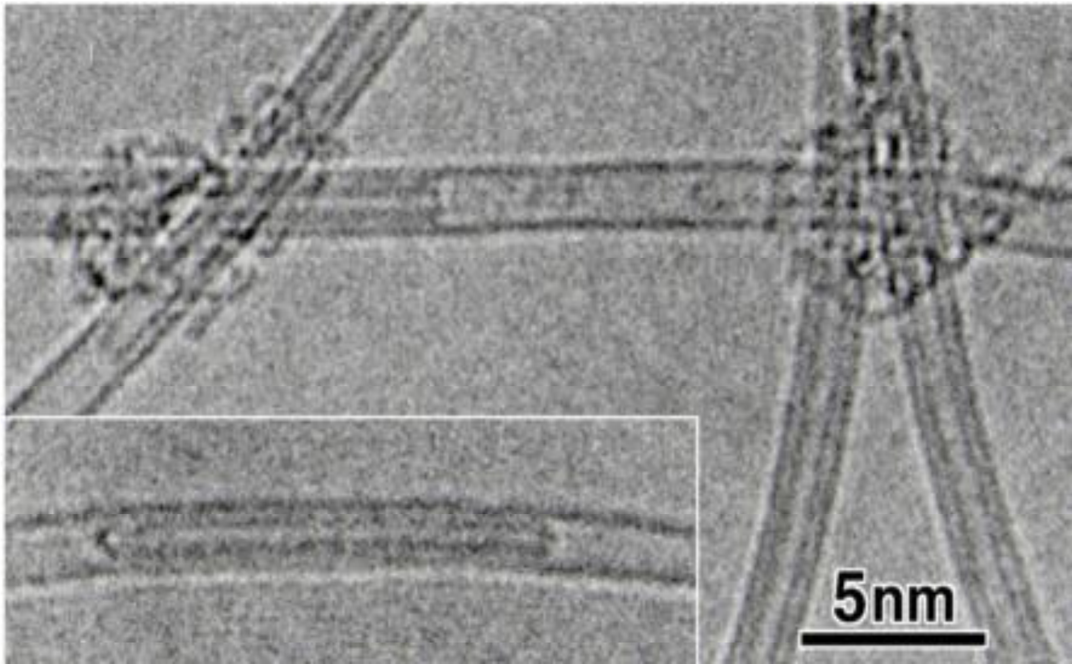


Heat treatment at 1200 ^{o}C

Double-wall carbon nanotubes

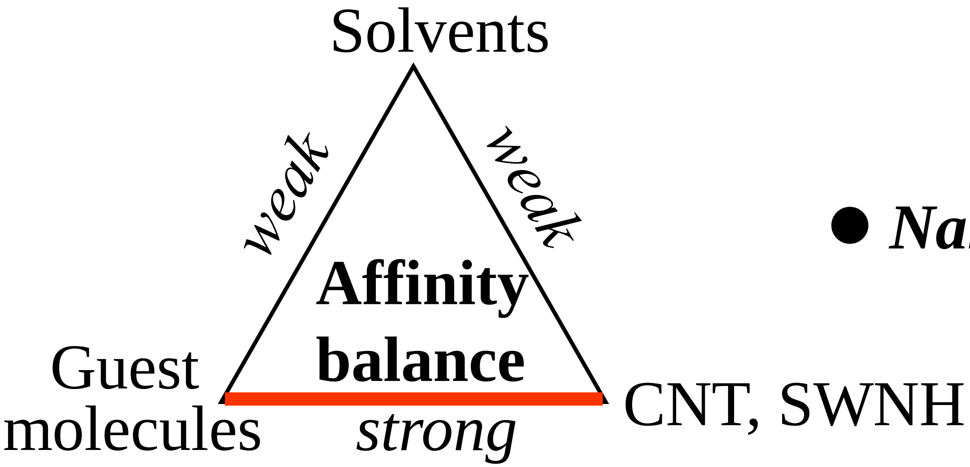




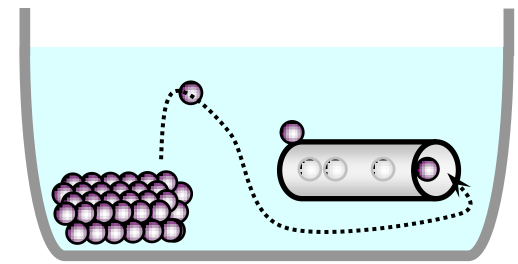


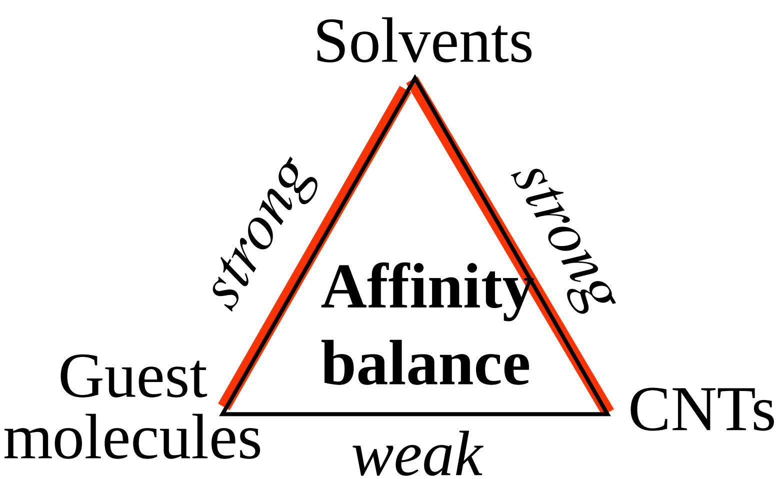
Incorporation in liquid phase at room temperature.

Yudasaka et al. Chem. Phys. Lett. 2003.
Yuge et al, J. Phys. Chem. B 2005.

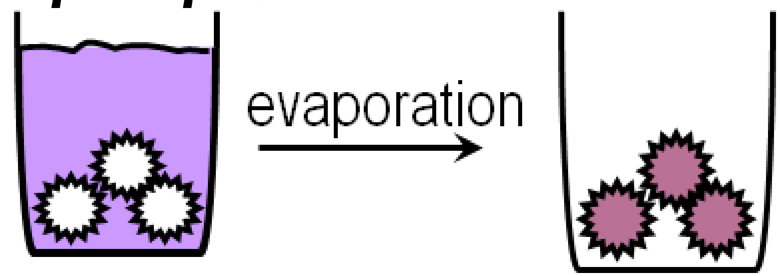


- ***Nano-Extraction***

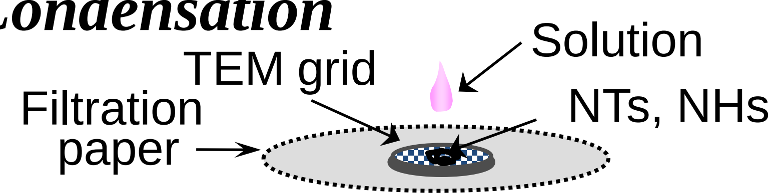




- ***Nano-precipitation***



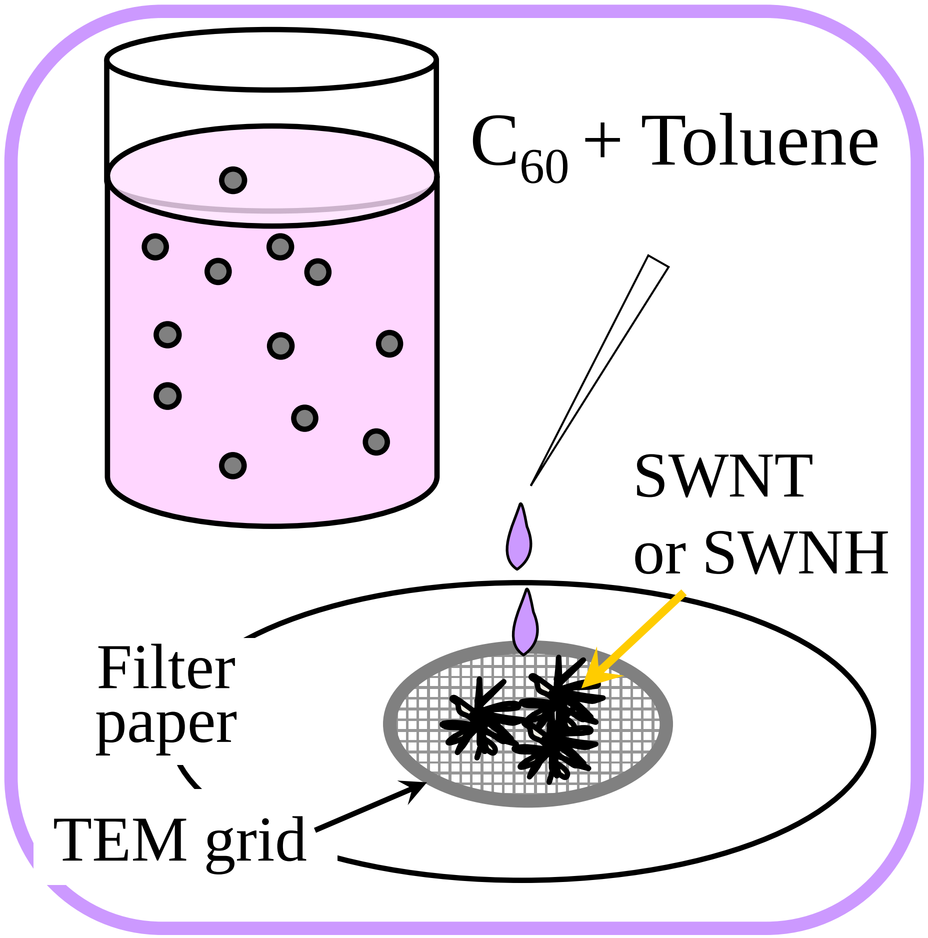
- ***Nano-Condensation***



- ***Nano-Titration, etc.***

Incorporation Methods：Non-equilibrium methods of C_{60} in Liquid Phase at Room Temperature

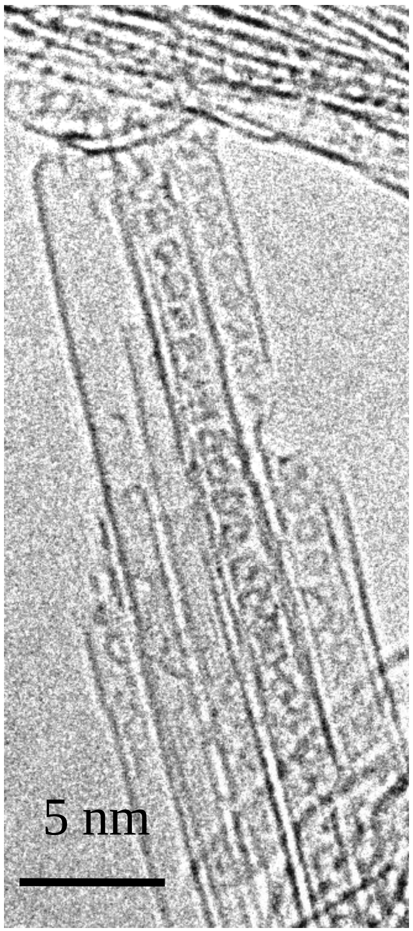
Nano-Condensation



M.Yudasaka et al., Chem. Phys. Lett., 380, 42 (2003).
Ajima et al. Adv. Materials, 16 (2004) 397.

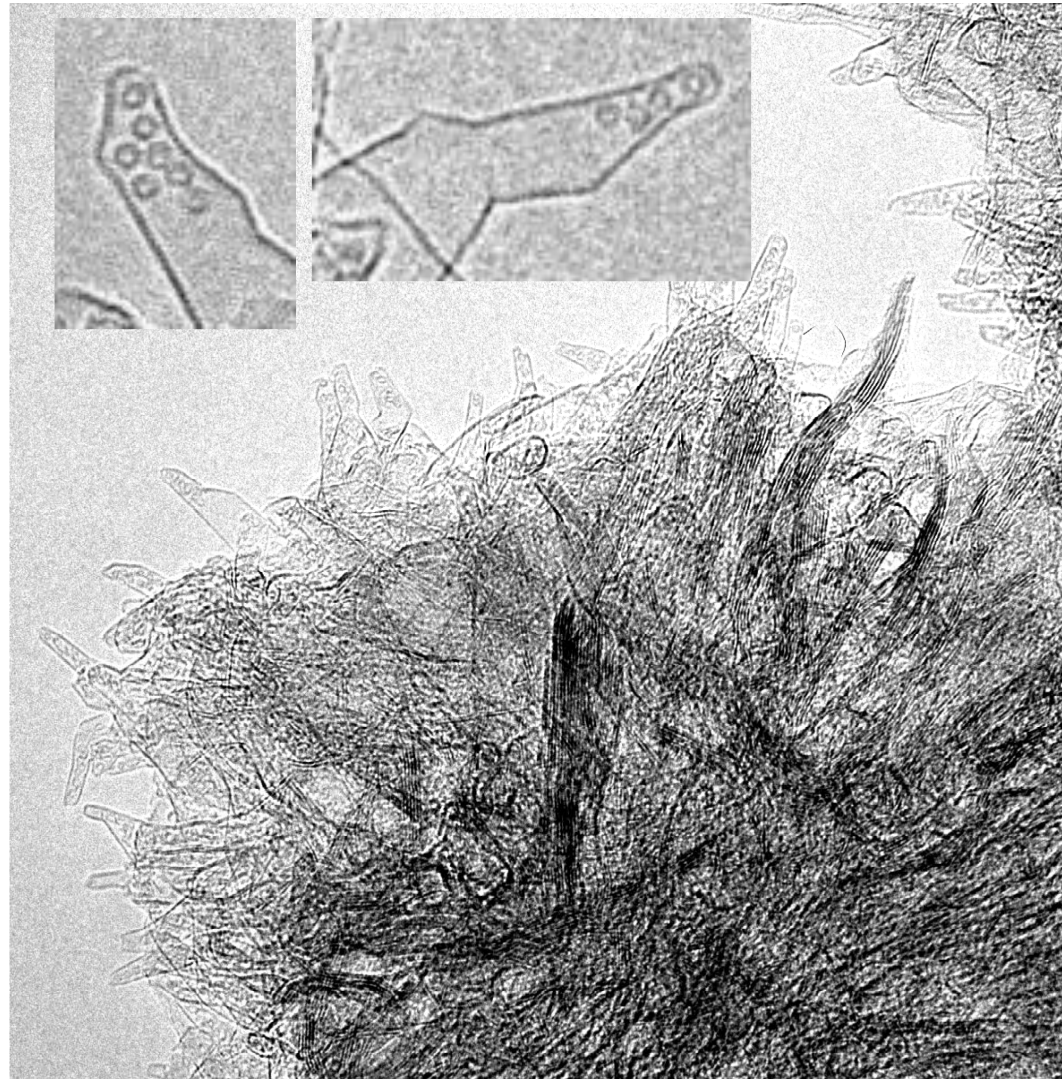
C_{60} @ SWNTs

M.Yudasaka et al., Chem. Phys. Lett., 380, 42 (2003).

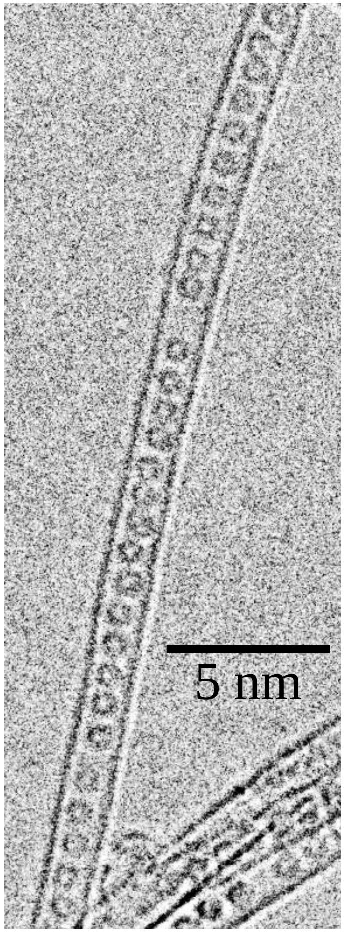


C_{60} @ SWNHs

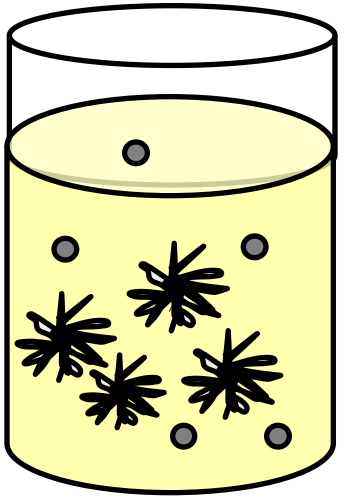
Ajima et al. Adv. Materials, 16 (2004) 397.



Incorporation Methods：Non-equilibrium methods of C_{60} in Liquid Phase at Room Temperature



Nano-Extraction

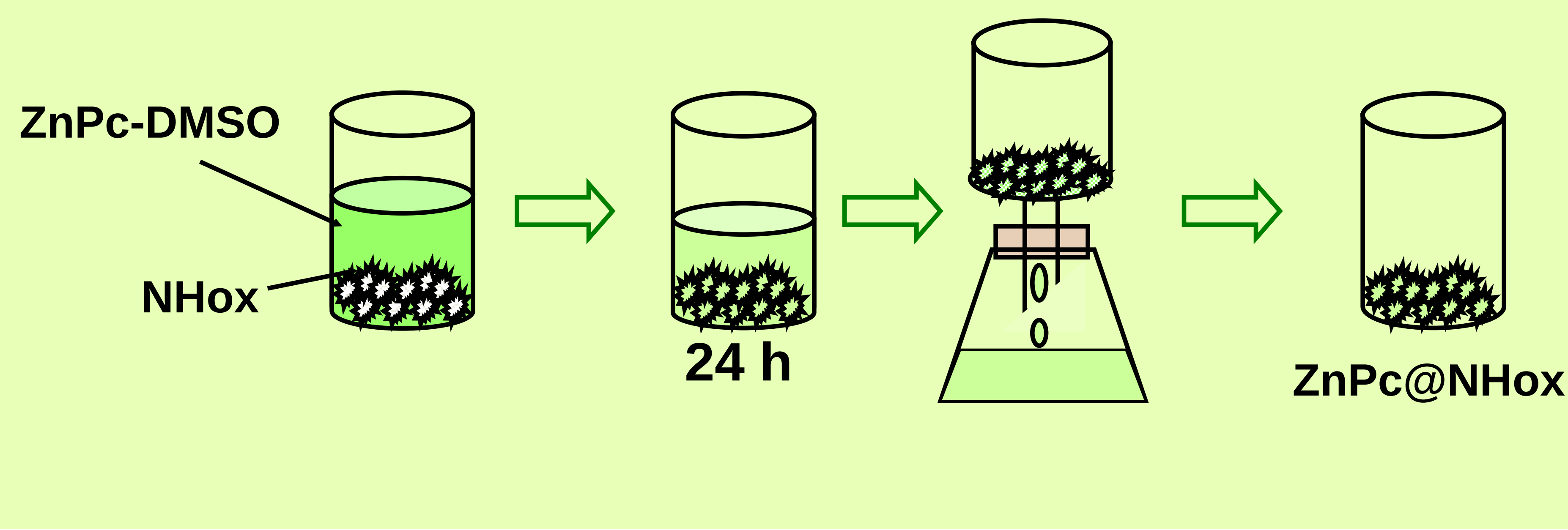


C_{60} + EtOH + SWNT/ SWNH

M.Yudasaka et al., Chem. Phys. Lett., 380, 42 (2003).
Ajima et al. Adv. Materials, 16 (2004) 397.

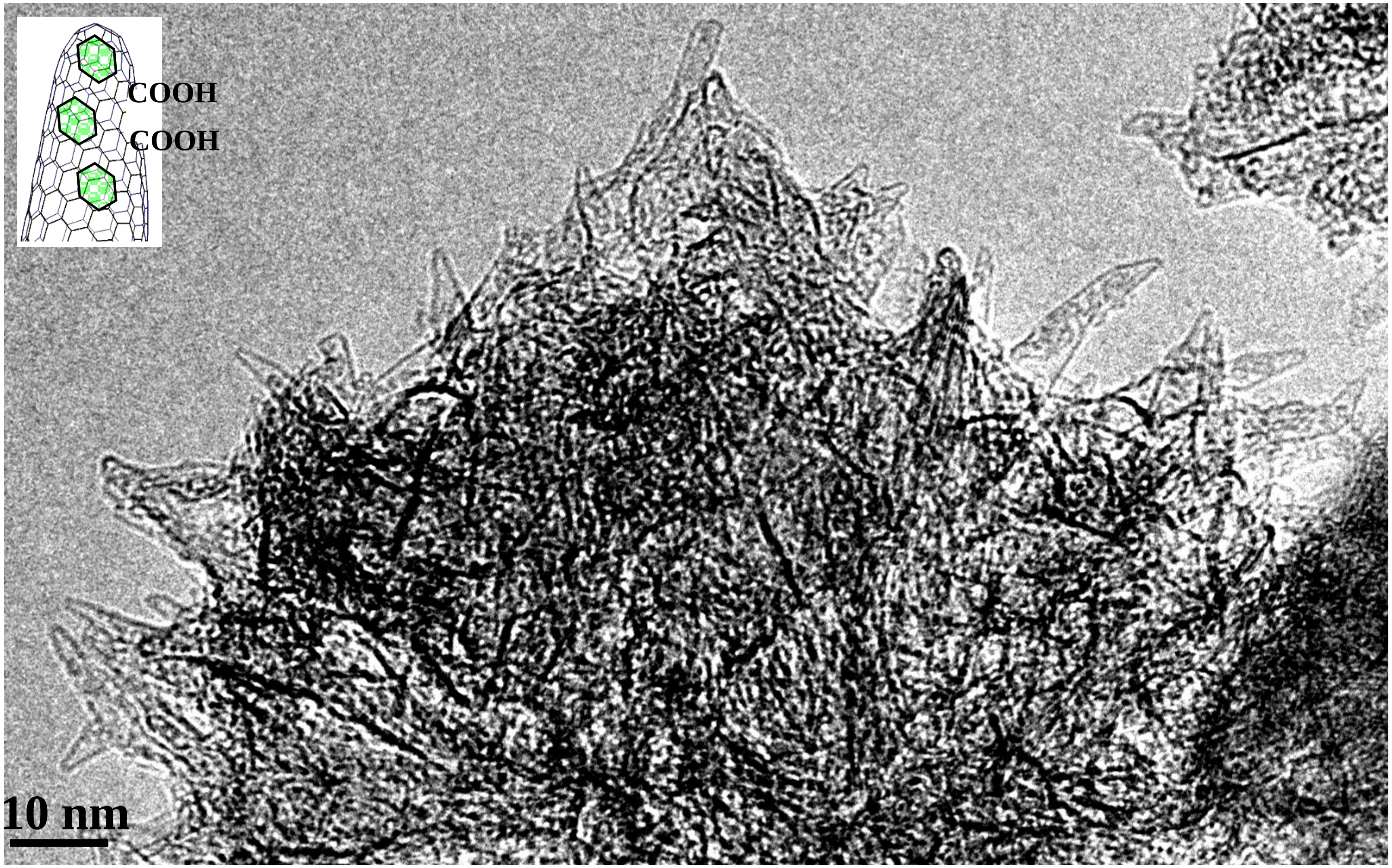
Incorporation of ZnPc into SWNHs (NHox)

SWNHox was dispersed in DMSO-Ethanol solution of ZnPc → SWNHox was immersed in ZnPc-DMSO – EtOH for 24 h → Filtration, and washing with ethanol → Dried in N_2 flow at r. t.



Zhang et al PNAS 2008

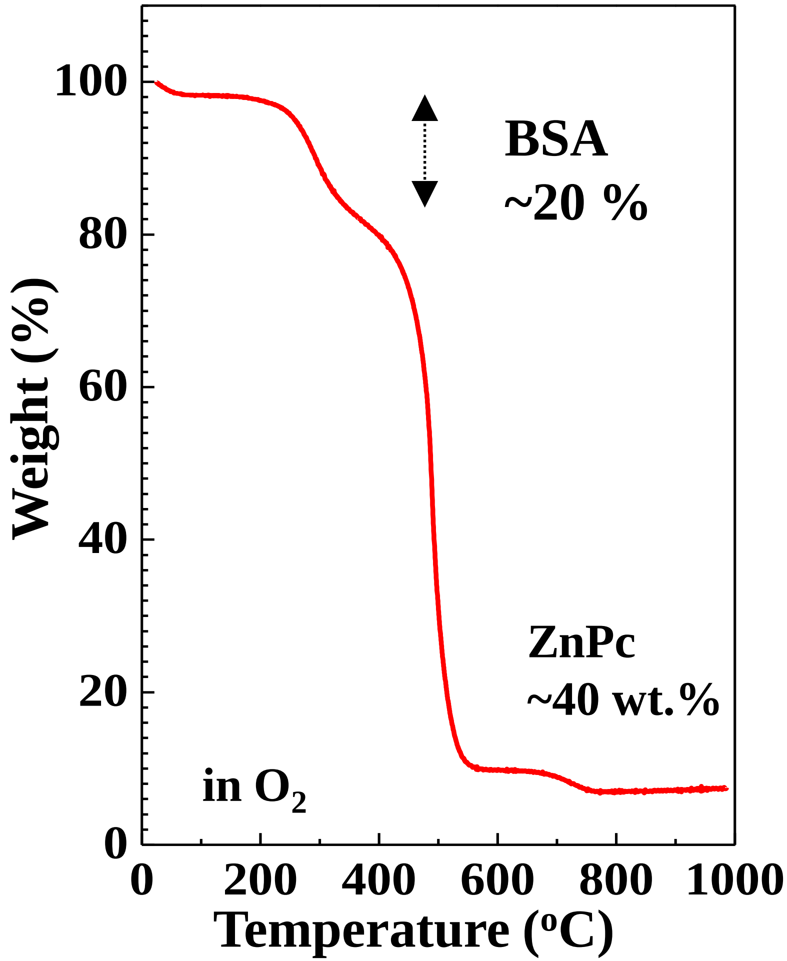
TEM image of ZnPc-SWNHox

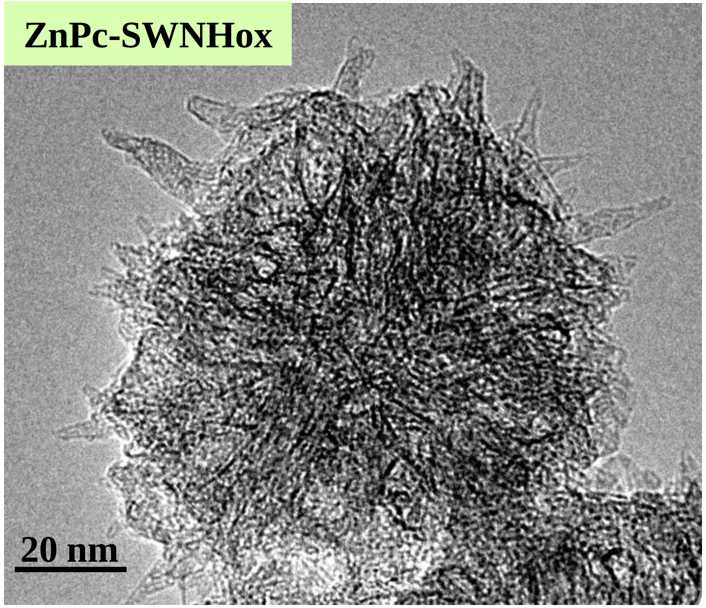


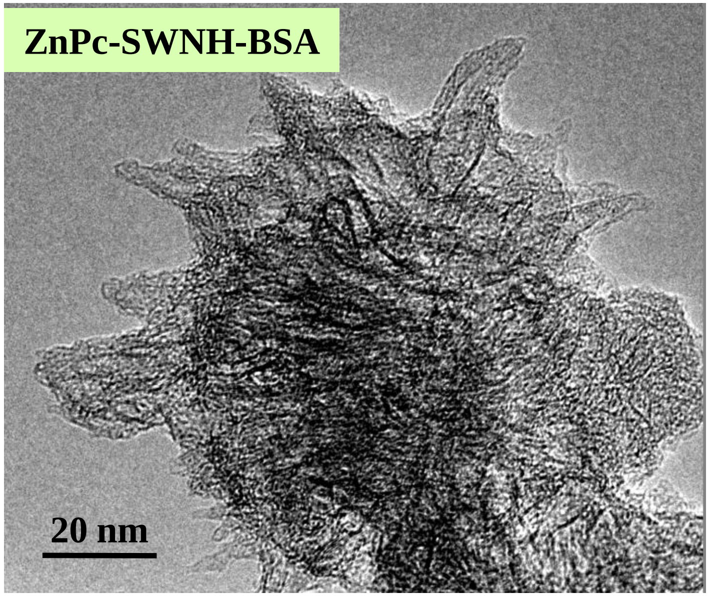
Zhang et al PNAS 2008

Chemical Modification of ZnPc-SWNHox with BSA protein

TGA results





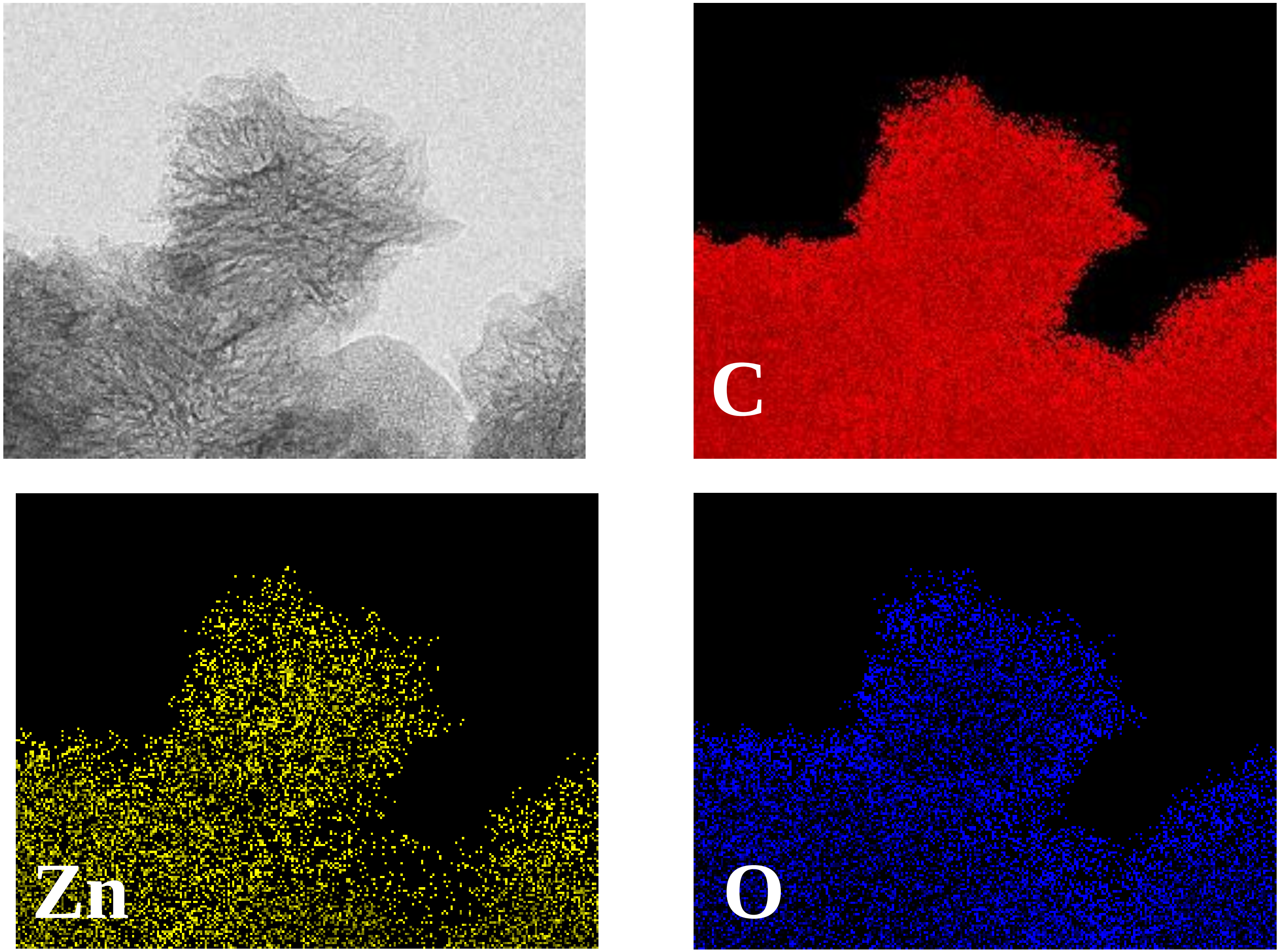


The content of ZnPc in SWNHox did not change after modification with BSA.

Zhang et al PNAS 2008

Zhang et al PNAS 2008

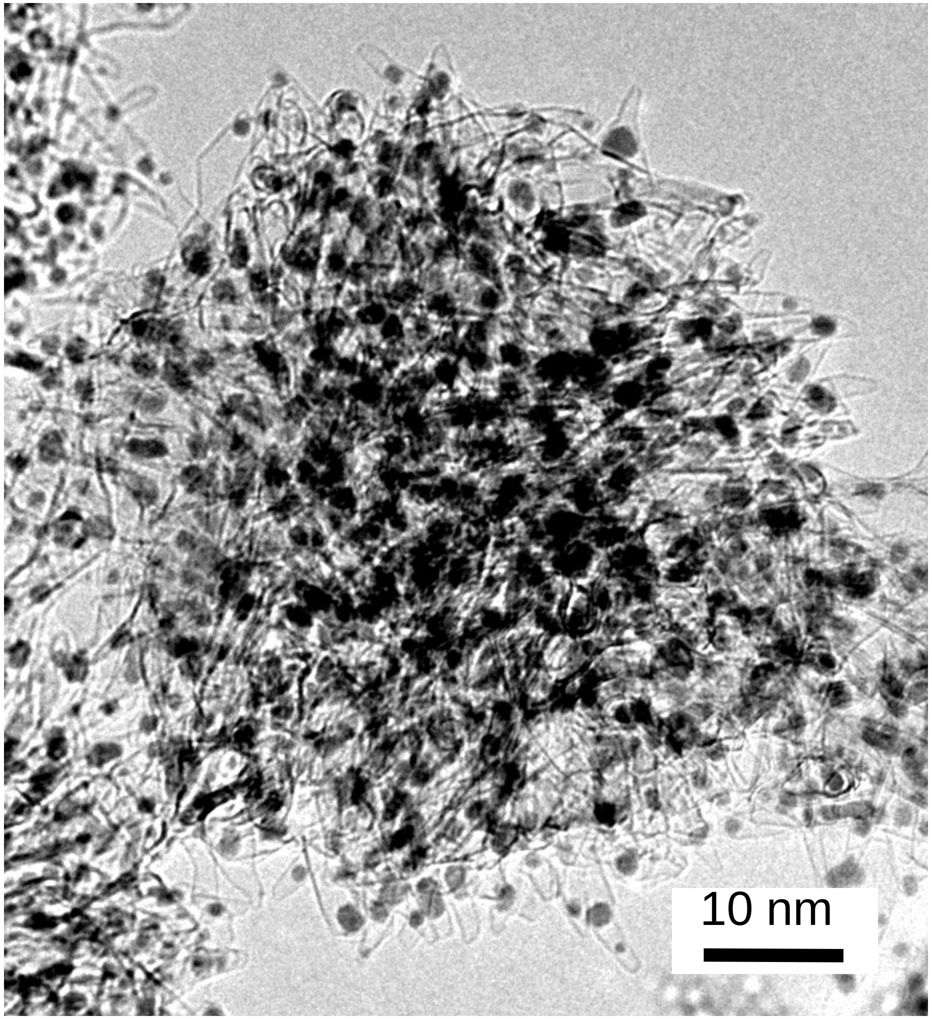
元素マッピング（EELS）

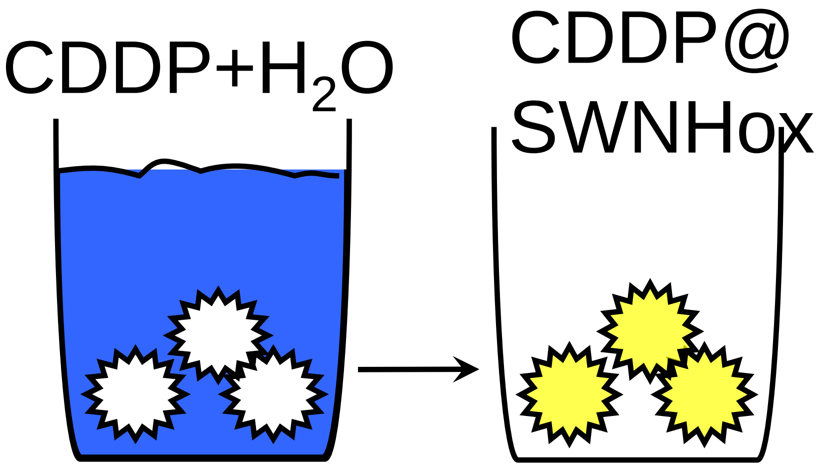


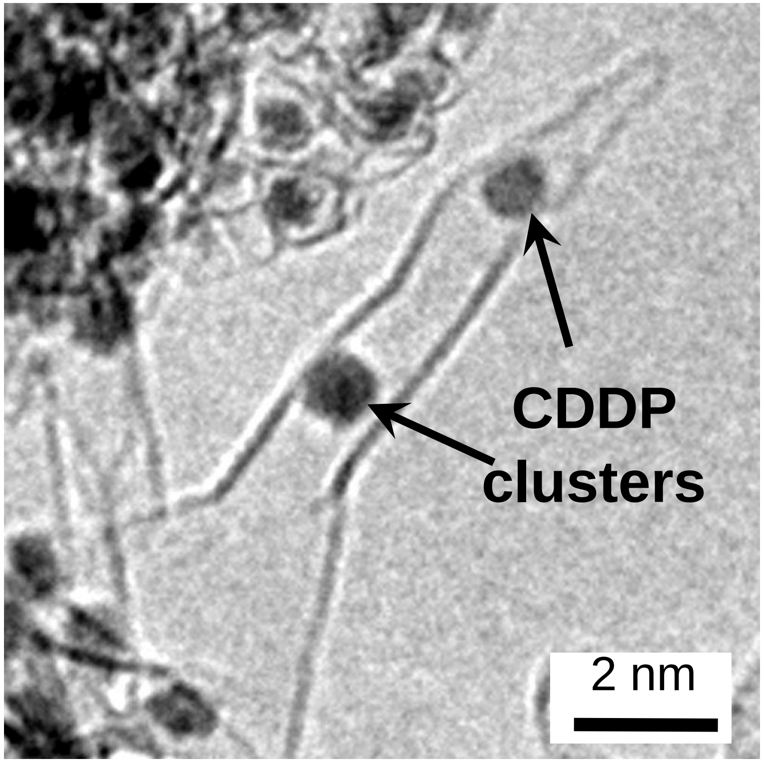
Cisplatin (CDDP)@SWNHox

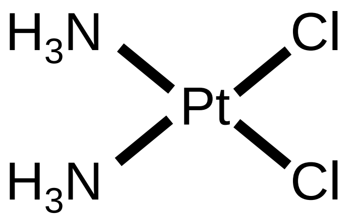
Ajima, et al. ACS Nano 2008

- Abundant incorporation :
  CDDP 50 wt%
- Slow release : 4days



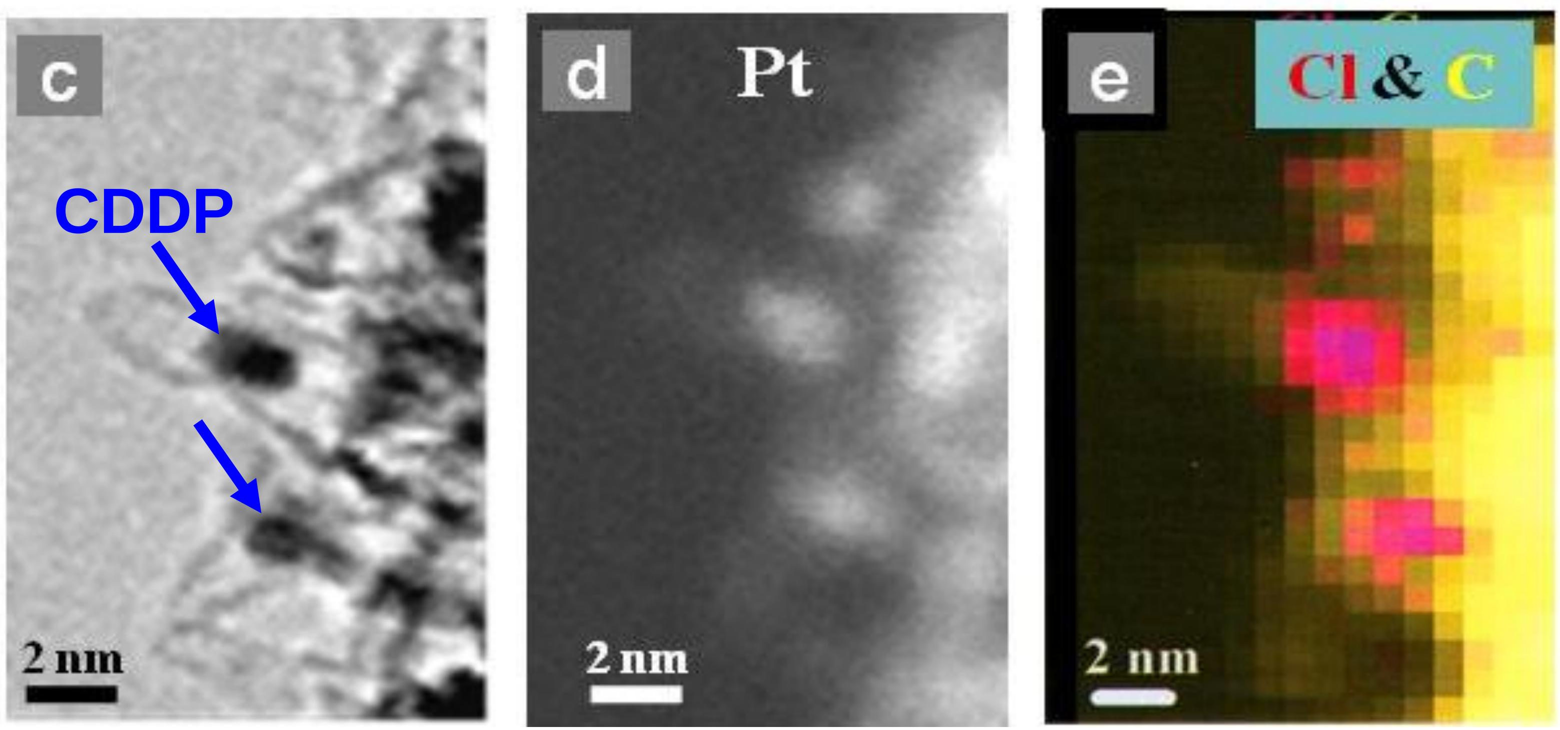






Molecular structure confirmation for CDDP in CDDP@SWNHox

ICP analysis → Pt:Cl= 1:2



STEM image

Z-contrast image

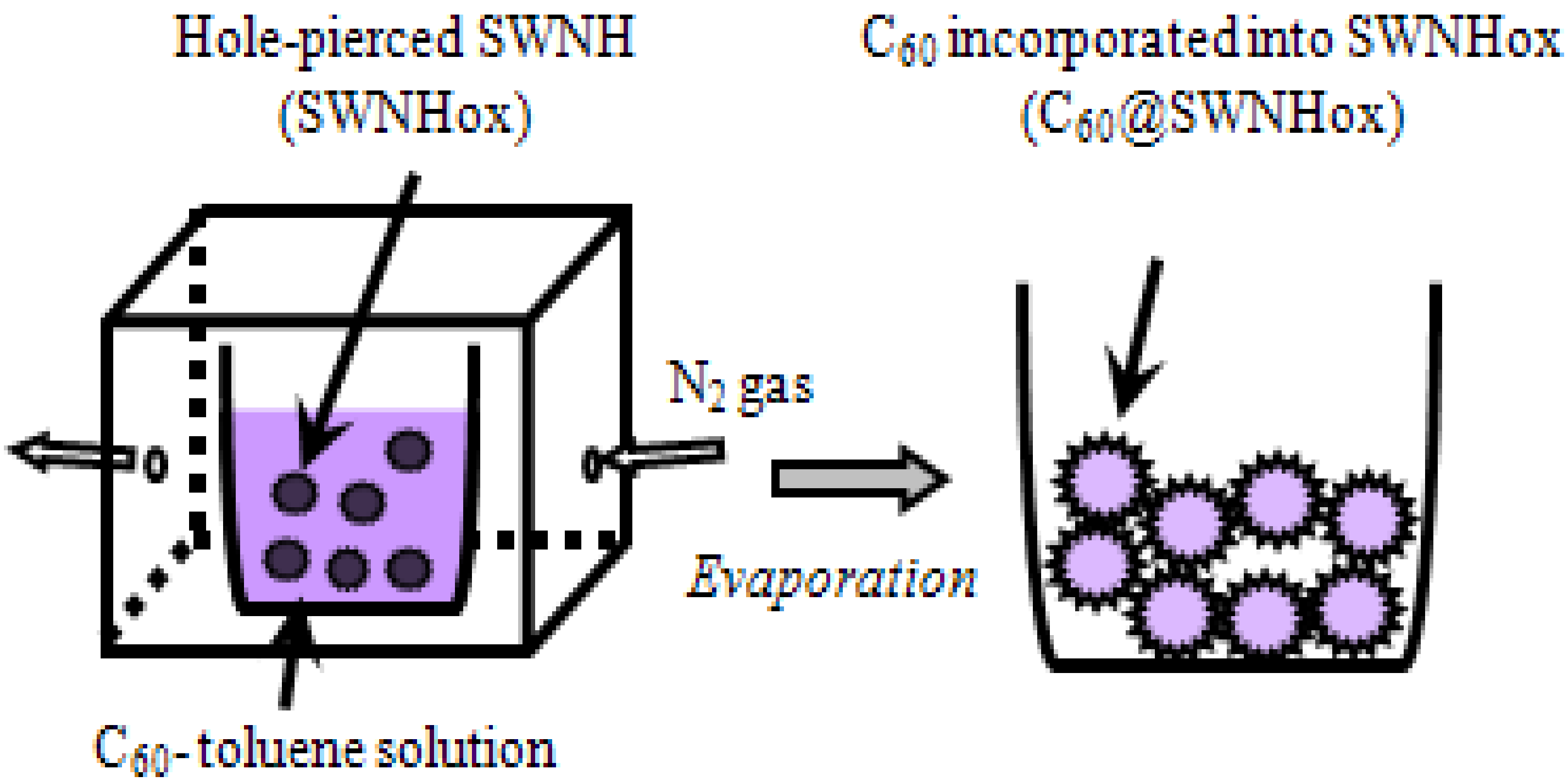
Pt: Bright spots

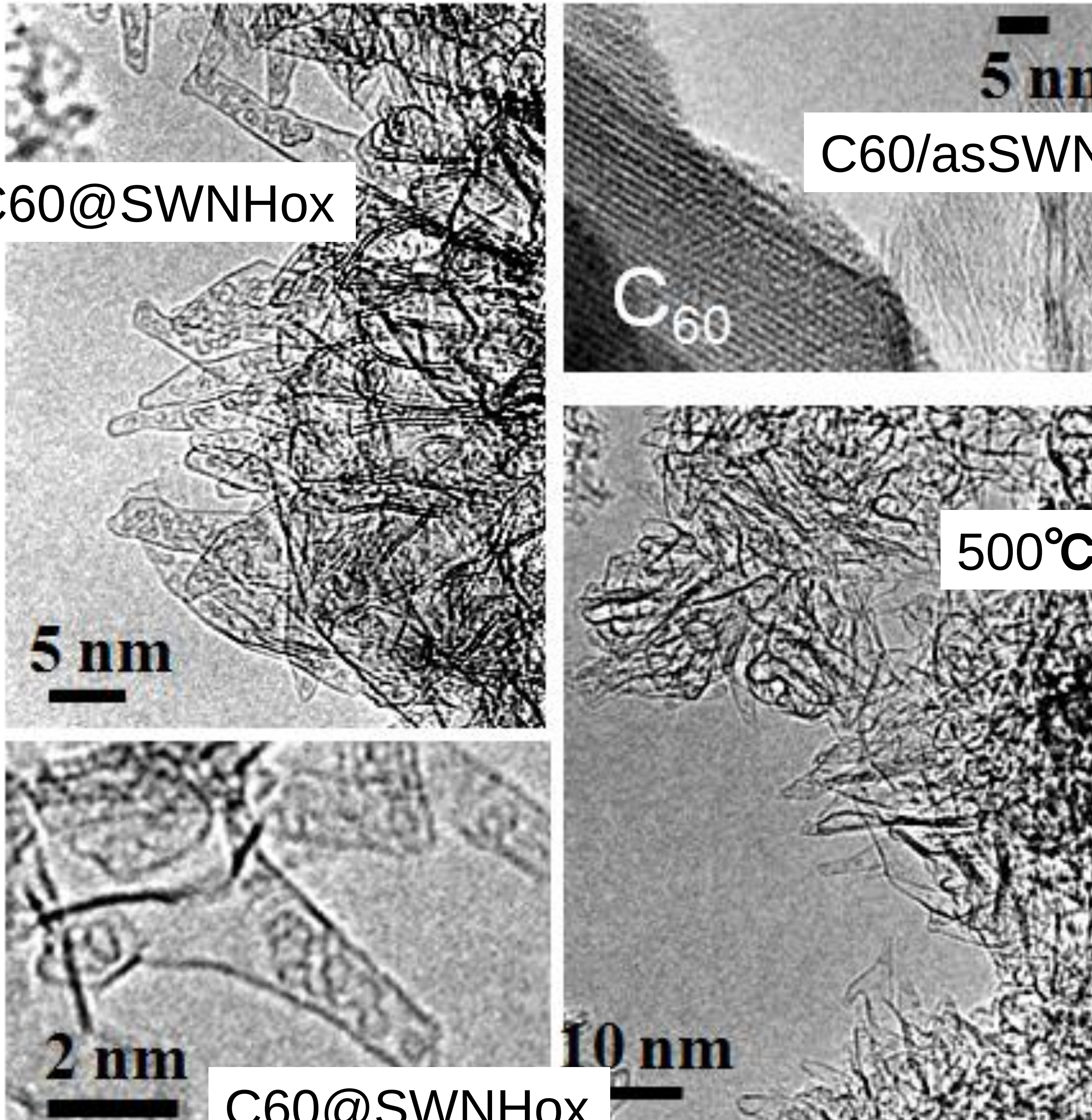
EELS

Cl and C mapping

Ajima, et al. ACS Nano 2008

内包量の評価は、金属（あるいは、SとかFとか）がない場合は簡単ではない。



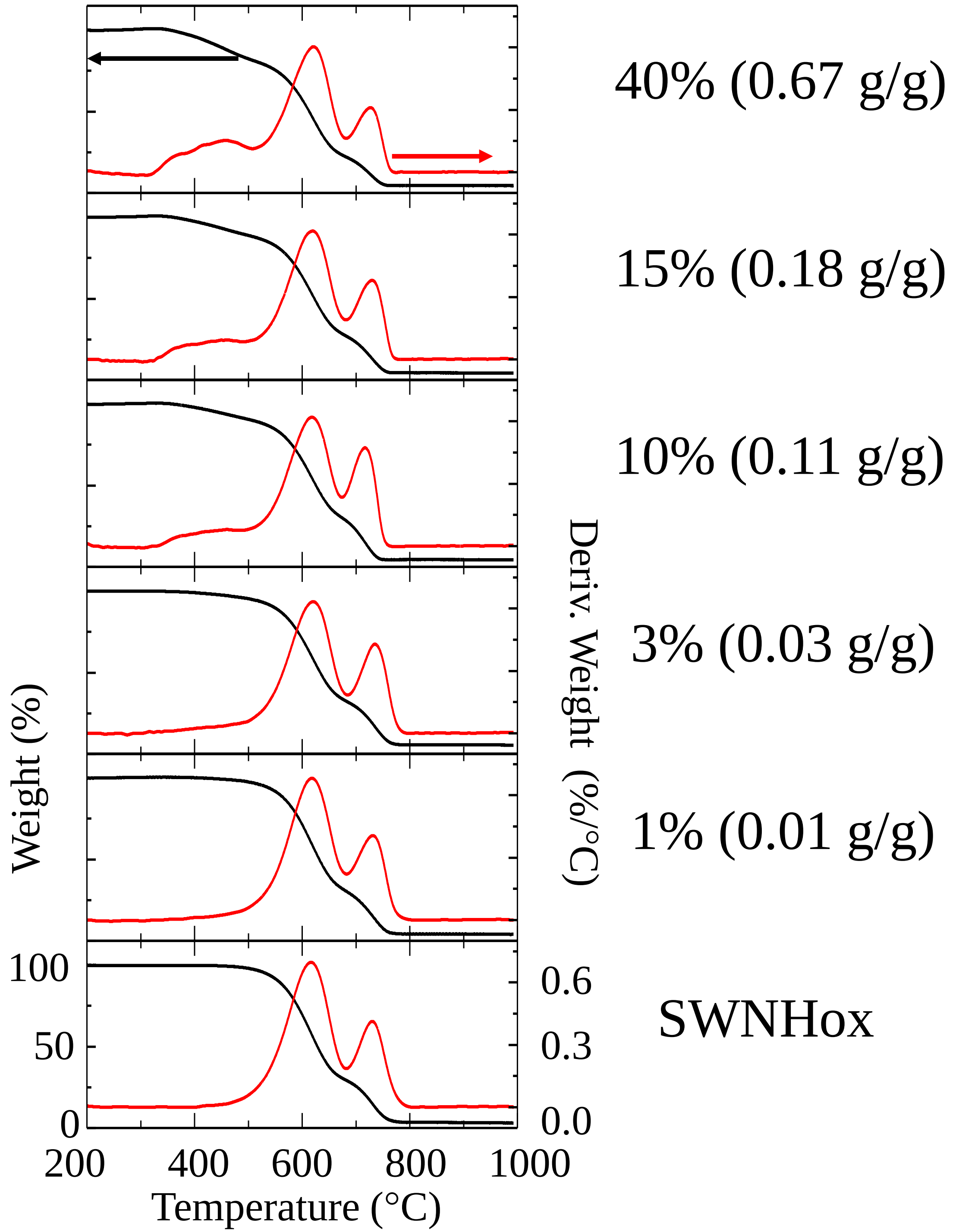


Yuge et al. JPCB 2005

ɛM images of
͵@SWNHox prepared by
ıo-precipitation (b and c),
l C_{60} crystal (indicated by
ɔw) deposited on as-grown
/NHs (d). TEM image of
idue obtained by stopping
measurement of 15%-
͵@SWNHox at 500°C,
icating most of C_{60} was
ninated by combustion with
(e).

Raman spectra

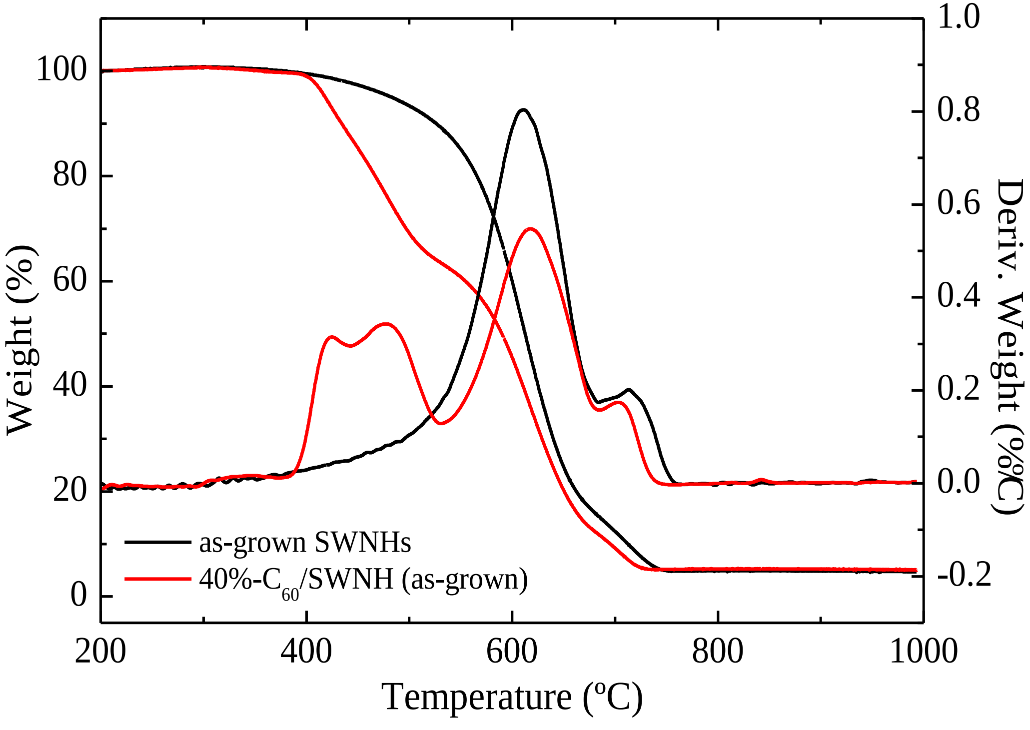
C_{60}@SWNHox



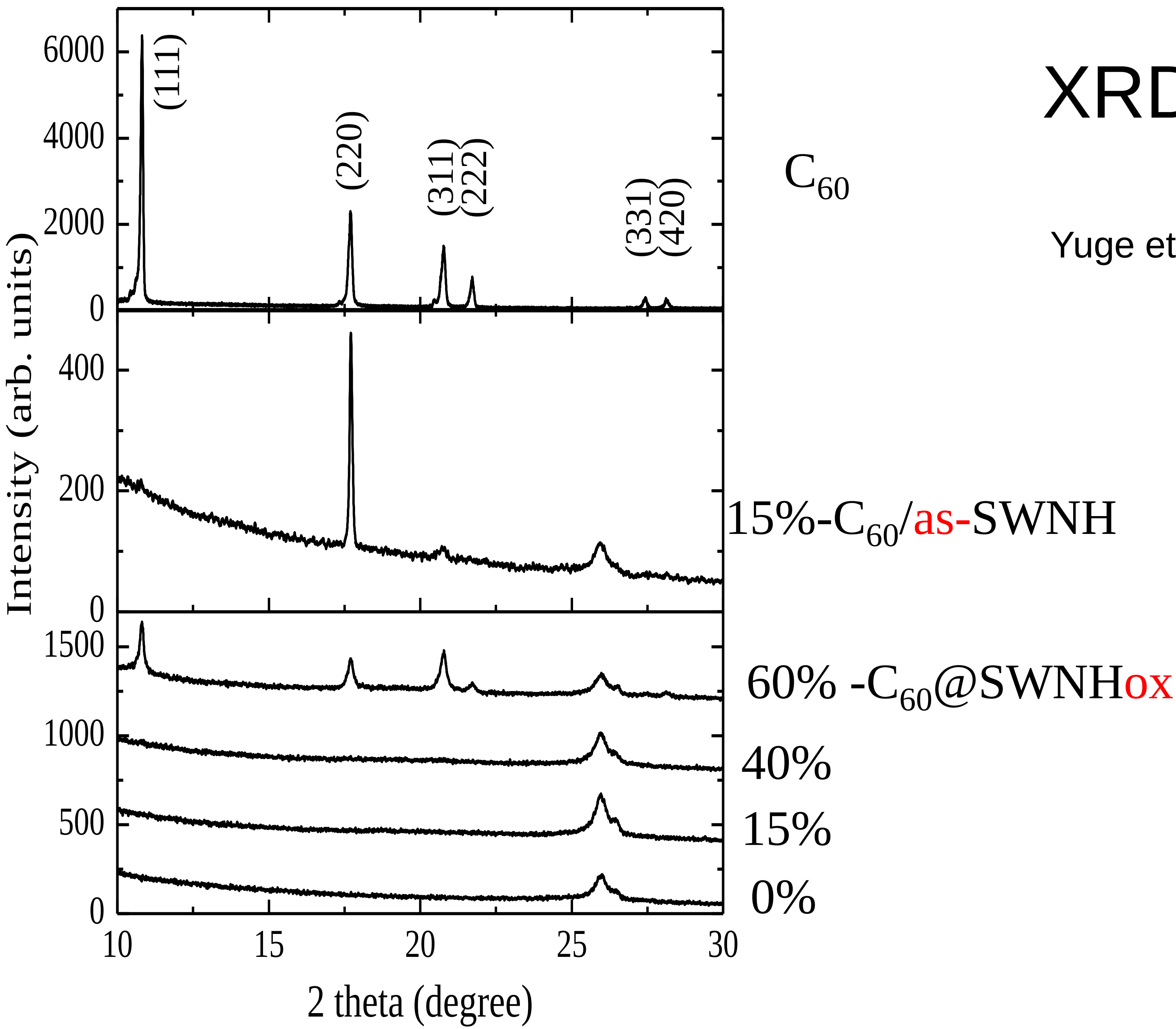
Yuge et al. JPCB 2005

Raman spectra

C_{60}@as-SWNH

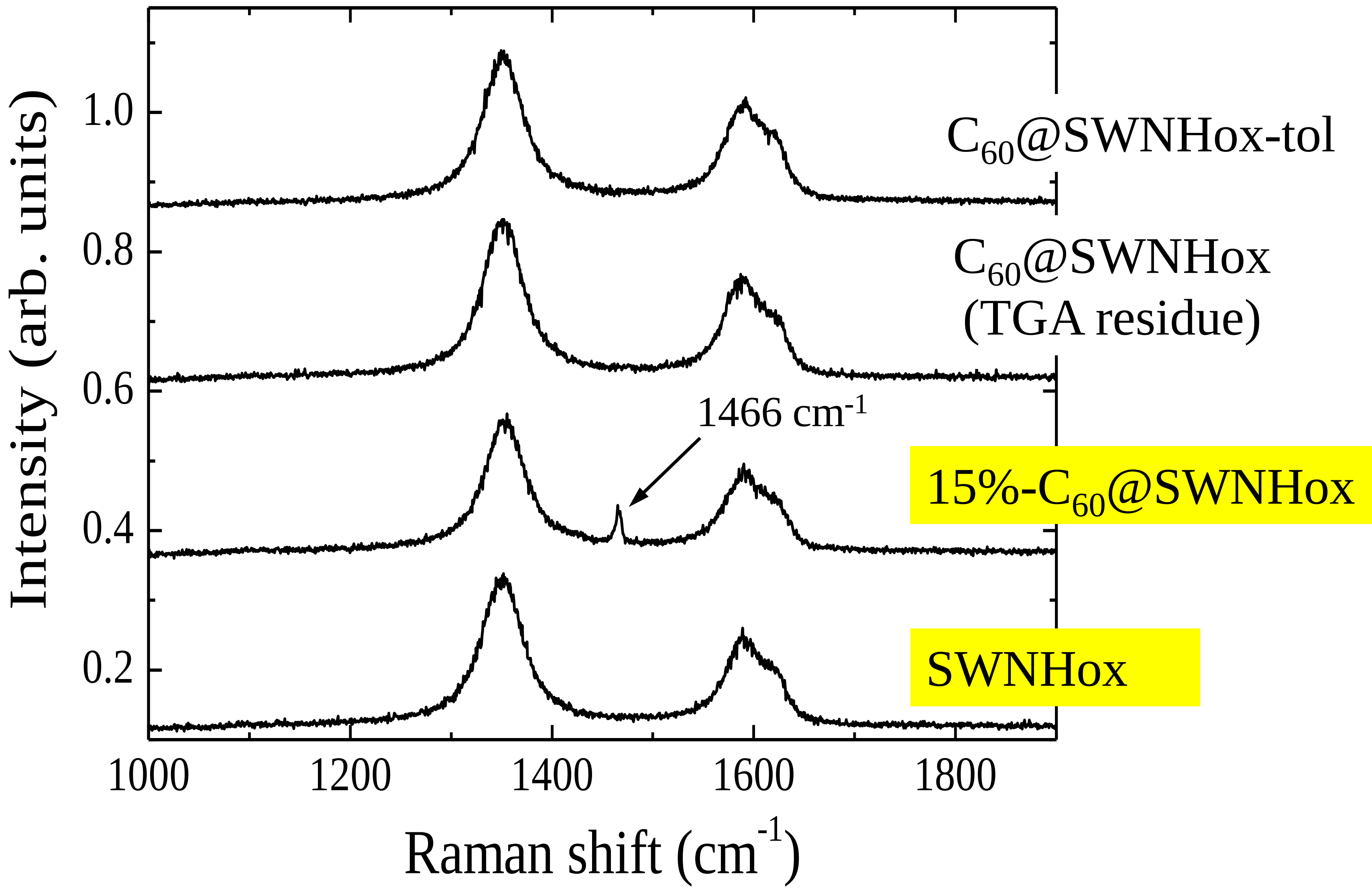


XRD

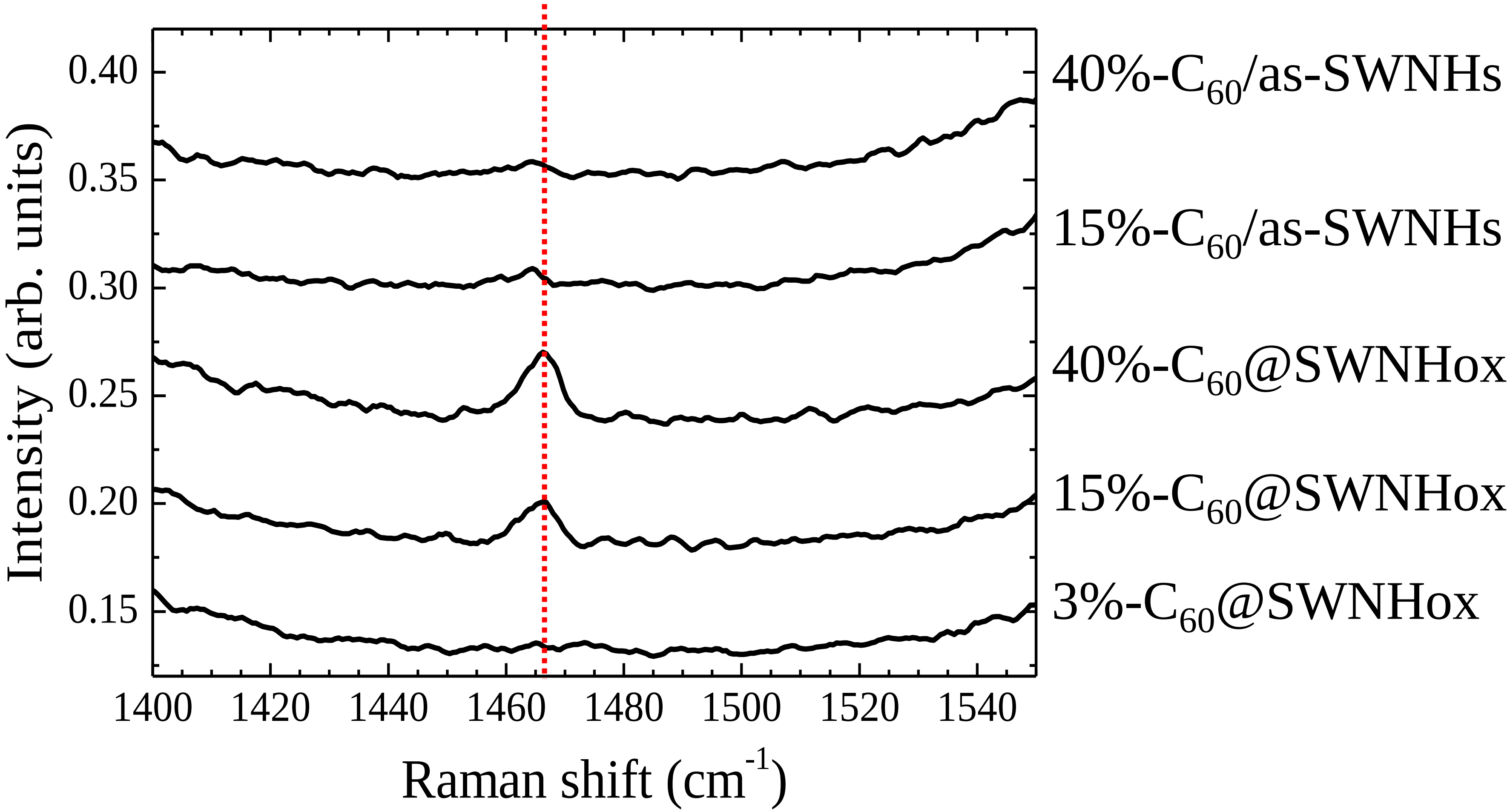


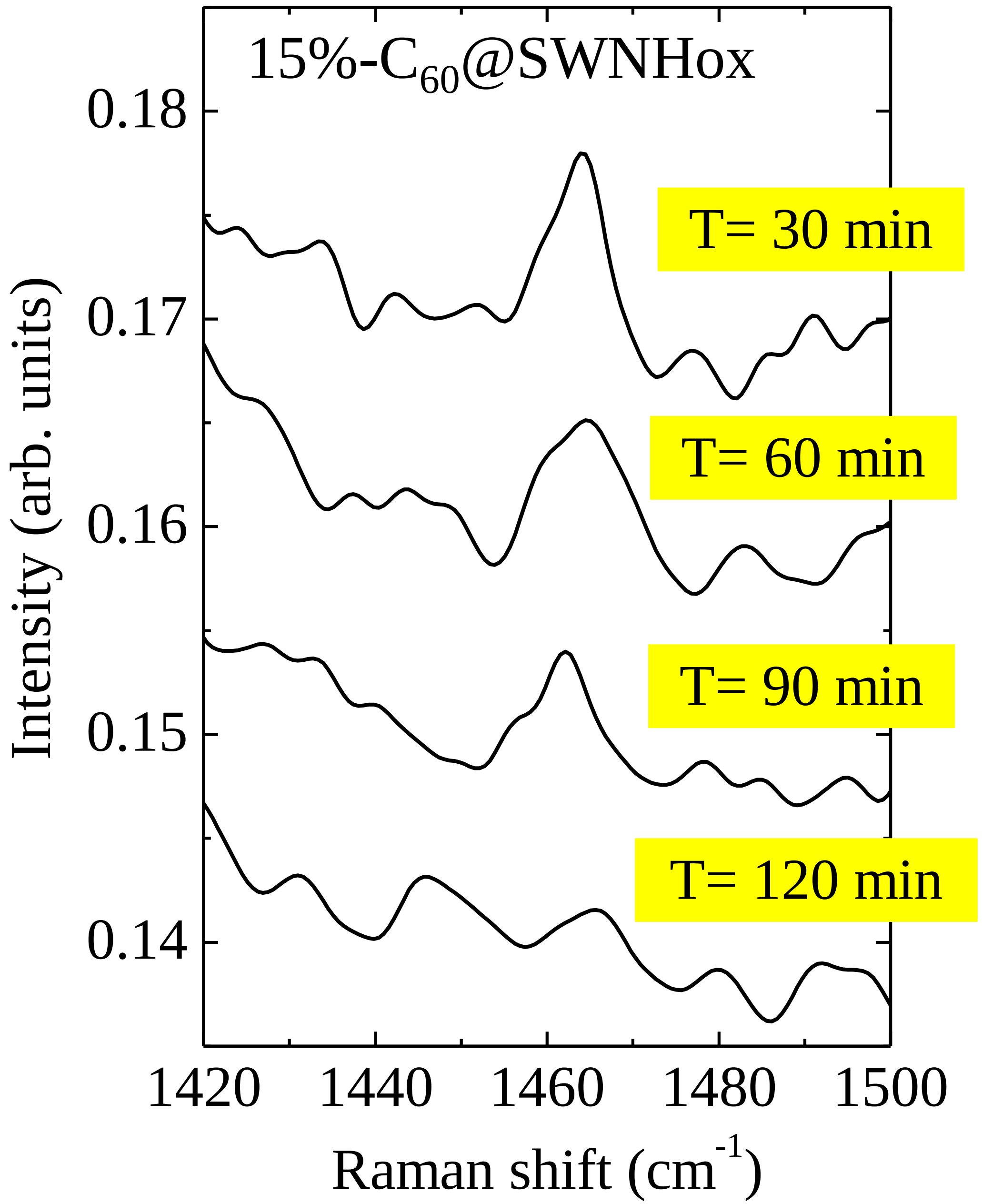
Yuge et al. JPCB 2005

Raman spectra



Raman spectra





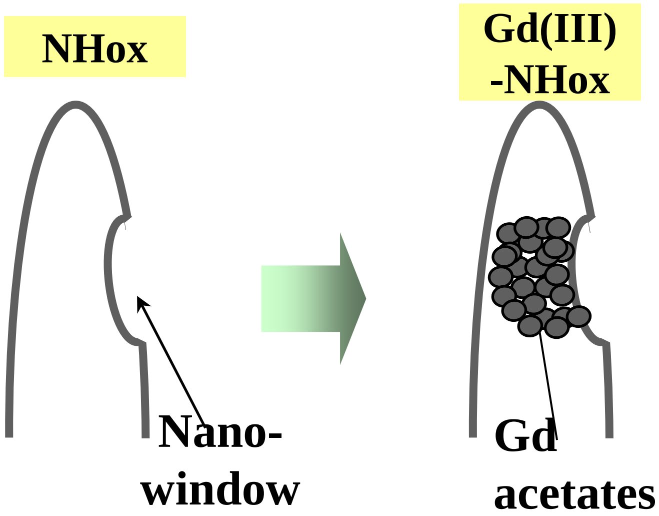
Raman spectra
(レーザー照射によるC60ラマンピーク強度の減衰。SWNHox内部にあると減衰速度は遅くなる。）

- SWNH外部にはC_{60}がいないことを確認。
  ➔ TGAからC_{60}量を見積もった。
- 内包量は、仕込み量で制御できる。

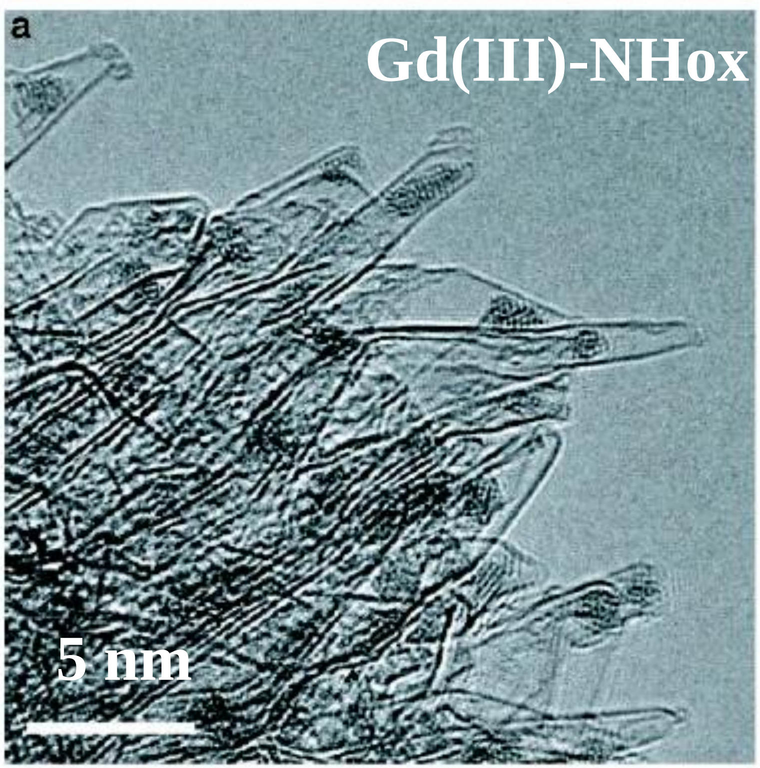
	%	1	3	10	15	40	60
Starting quantity of C_{60} in the initial mixture of C_{60}, SWNHox, and toluene	g/g	0.01	0.03	0.11	0.18	0.67	1.50
	vol/vol	0.02	0.05	0.17	0.28	1.06	1.65
Ratio of incorporated C_{60} and SWNHox in the end products of C_{60}@SWNHox	g/g	0	0.03	0.09	<u>0.11</u>	0.22	**
	vol/vol	0	0.05	0.15	0.19	0.36	**

In calculating C_{60} quantities in units of vol/vol, the density of the C_{60} crystal (1.68 g cm^{-3}) and the pore volume of the inside space of the SWNHox (0.36 ml g^{-1})[13] were applied.

カギになる元素がいない場合には、量の計測が容易ではない。

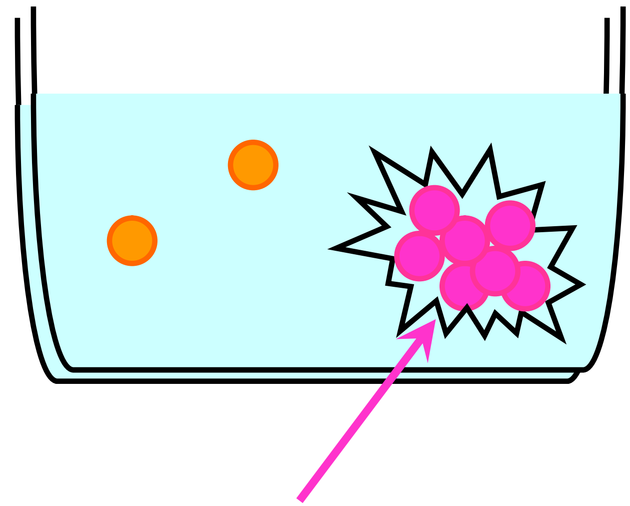


Hashimoto, A. et al.,
Proc. Natl. Acad. Sci. USA, (2004).



Equilibrium methods for preparing Gd-acetates@SWNHox

SWNHox and **$Gd(OAc)_3$・4H_2O** are immersed in **EtOH** at room temperature.



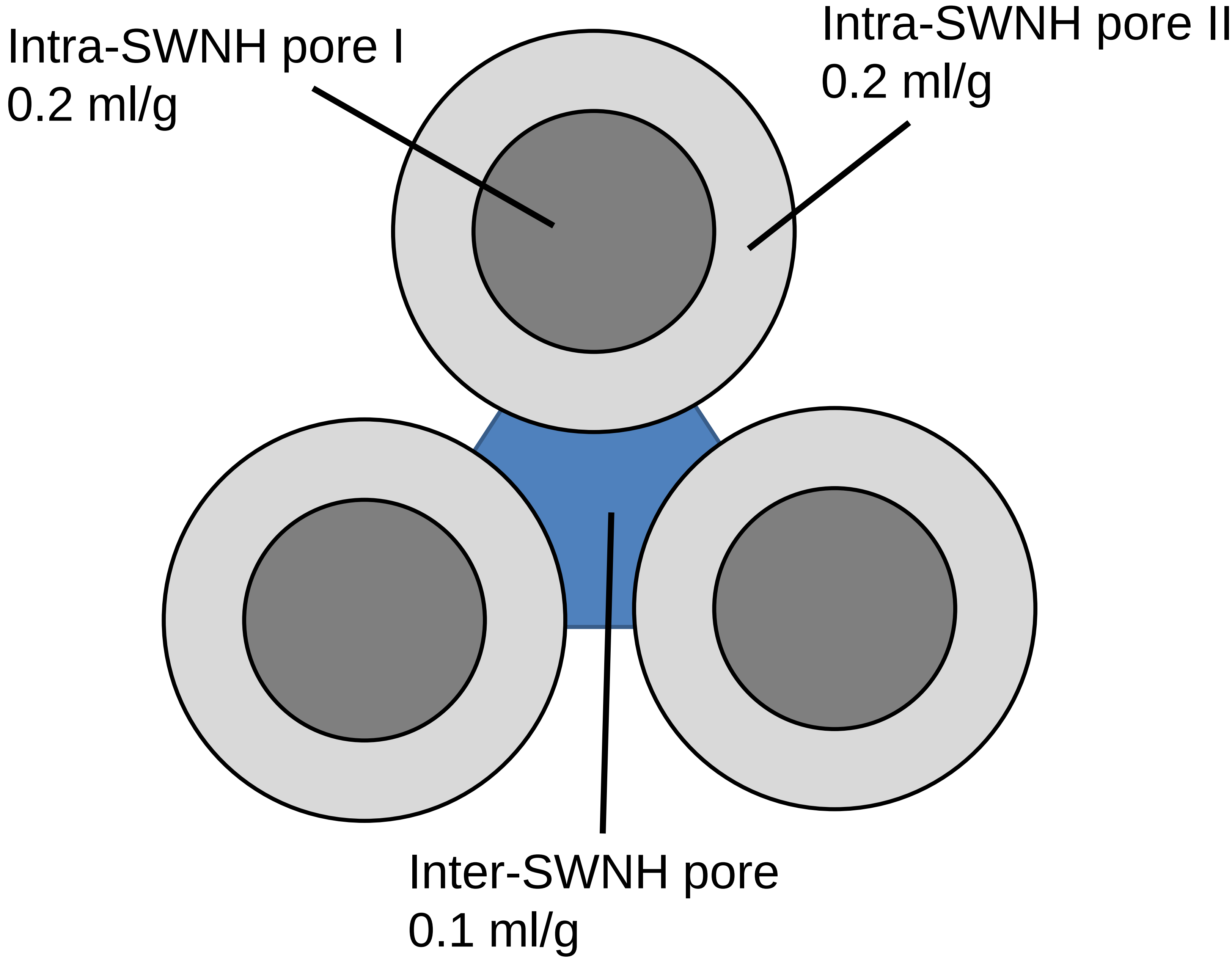
Gd(OAc)・0.5H_2O

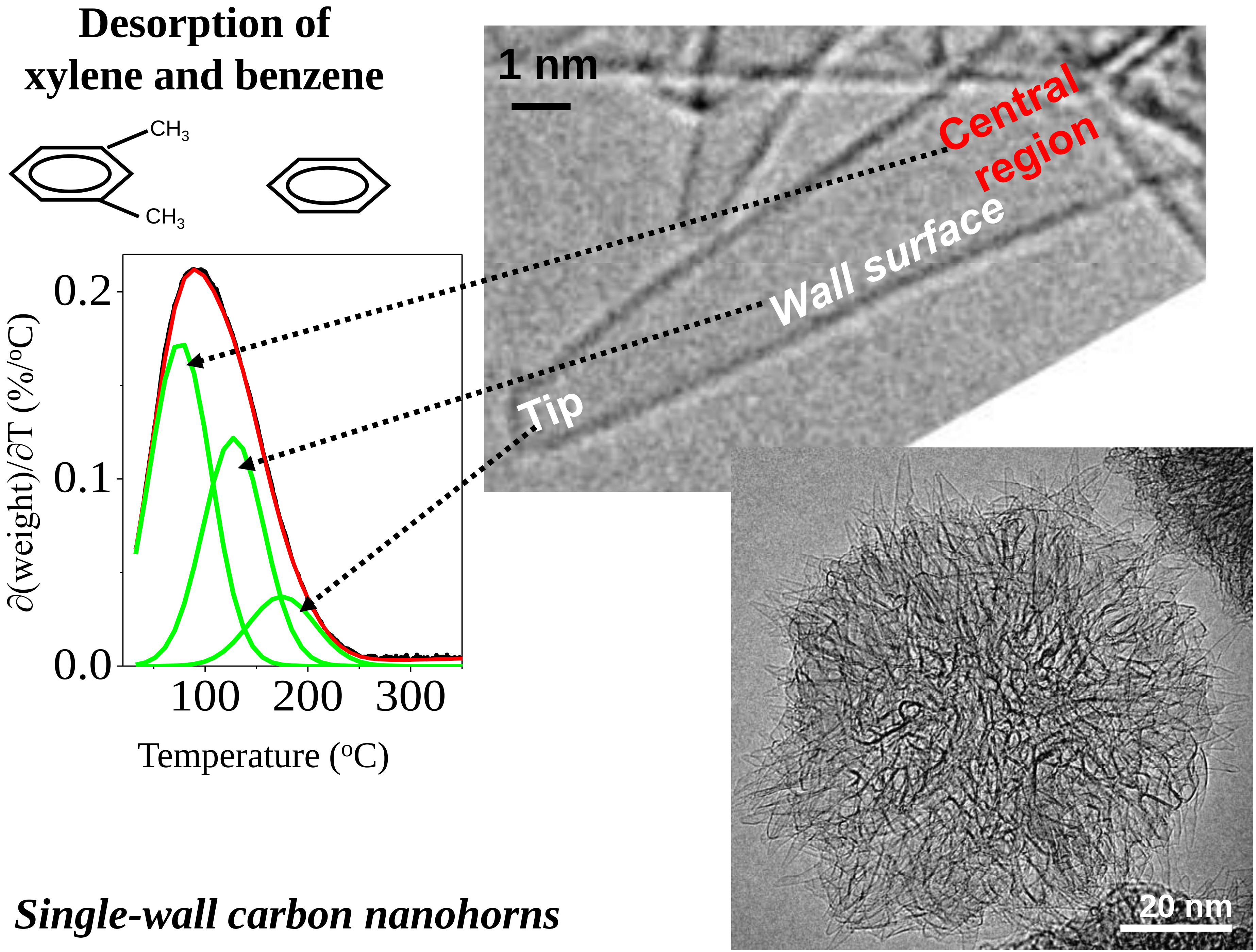
(From TG-MS and IR)

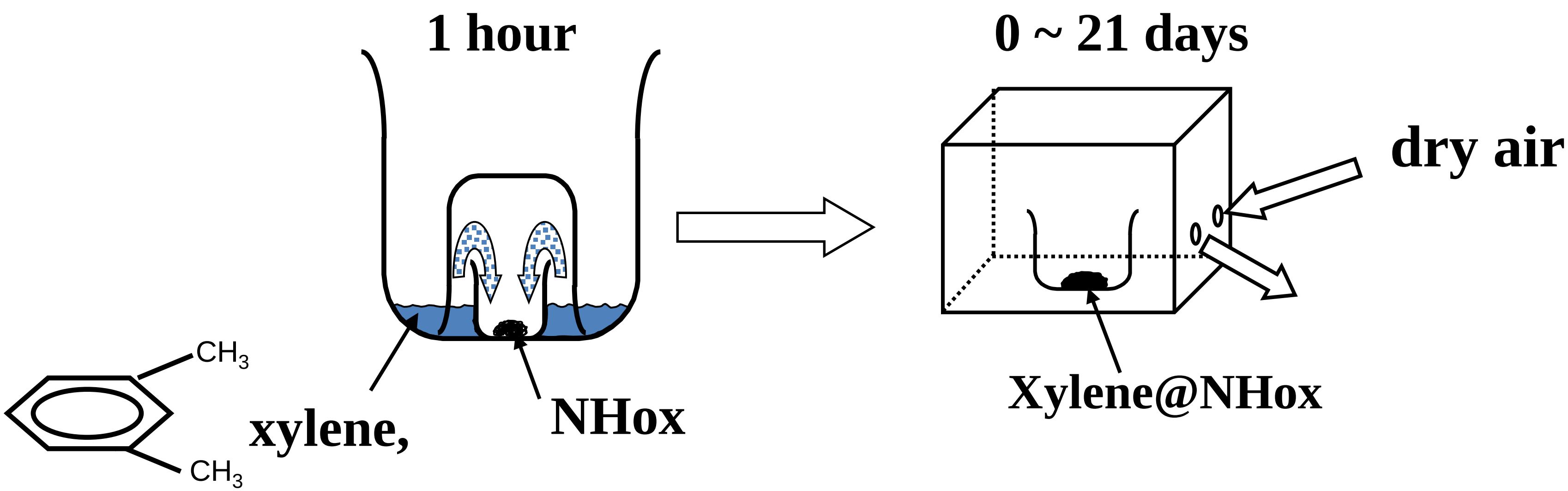
($Gd(OAc)_3$・4H_2O was changed.)

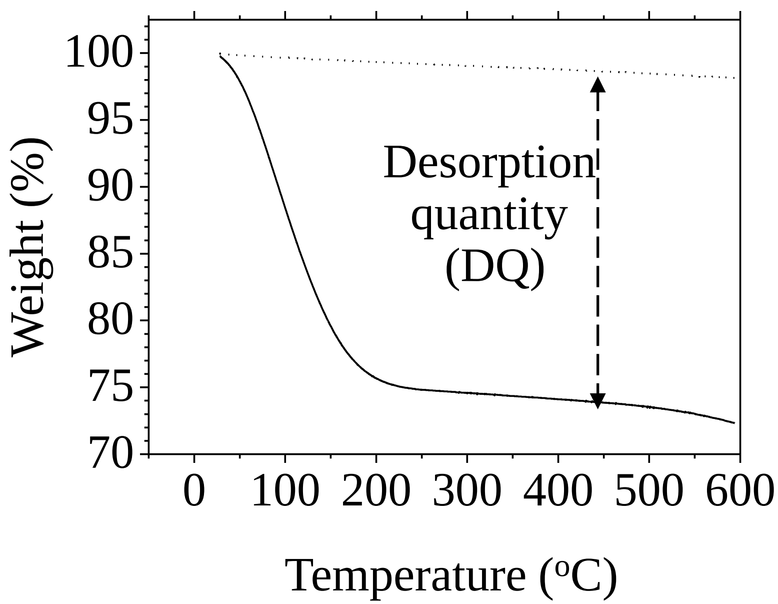
1. Stirring of NHox and $Gd(OAc)_3$・4H_2O in EtOH for 24 hrs at r.t.
2. Filtration
3. Sonication in EtOH for 20 sec
4. Filtration
5. Vacuum drying

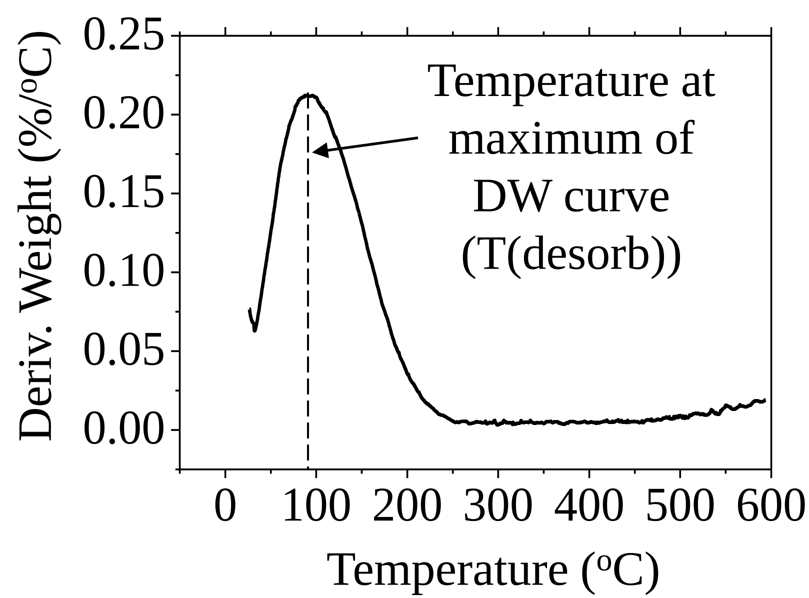
吸着サイト


Intra-SWNH pore I
0.2 ml/g
Intra-SWNH pore II
0.2 ml/g
Inter-SWNH pore
0.1 ml/g


Desorption of
xylene and benzene
CH3
CH3
∂(weight)/∂T (%/°C)
0.2
0.1
0.0
100
200
300
Temperature (°C)
1 nm
Central
region
Wall surface
Tip
20 nm
Single-wall carbon nanohorns

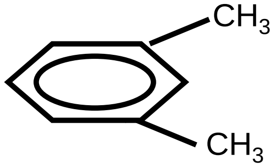


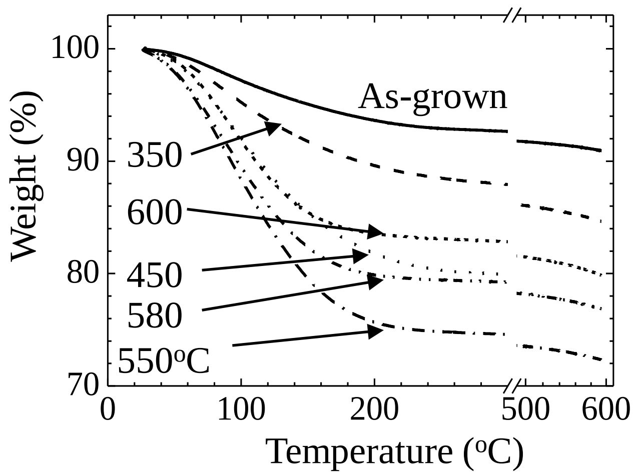


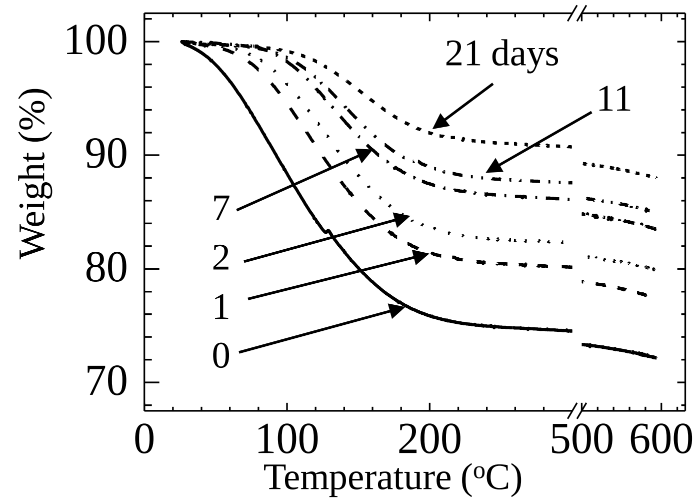


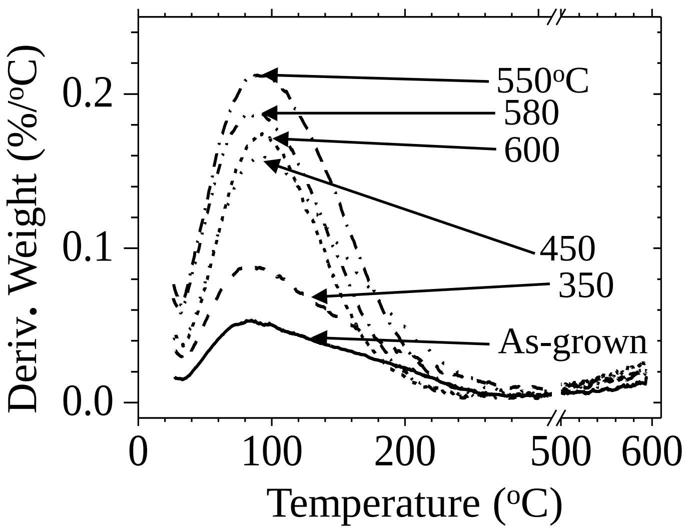
Yudasaka et al. JPCB 2005 Fan CPL 2004

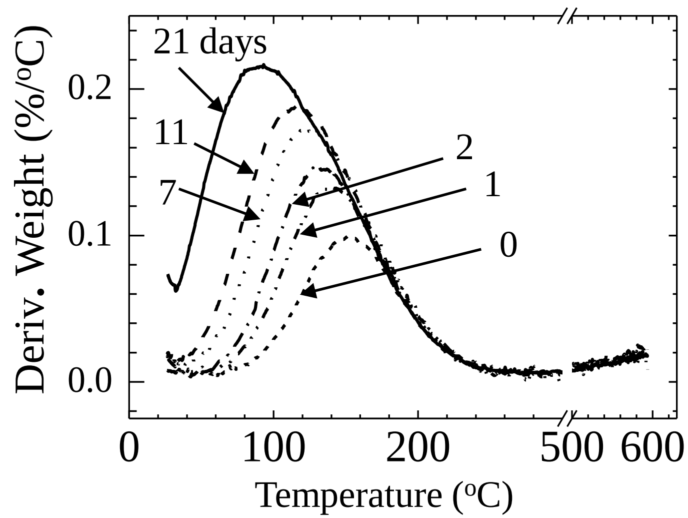
Xylene adsorption quantity depended on hole-opening temperatures. Adsorbed xylene was released slowly.



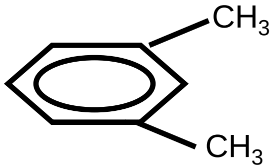


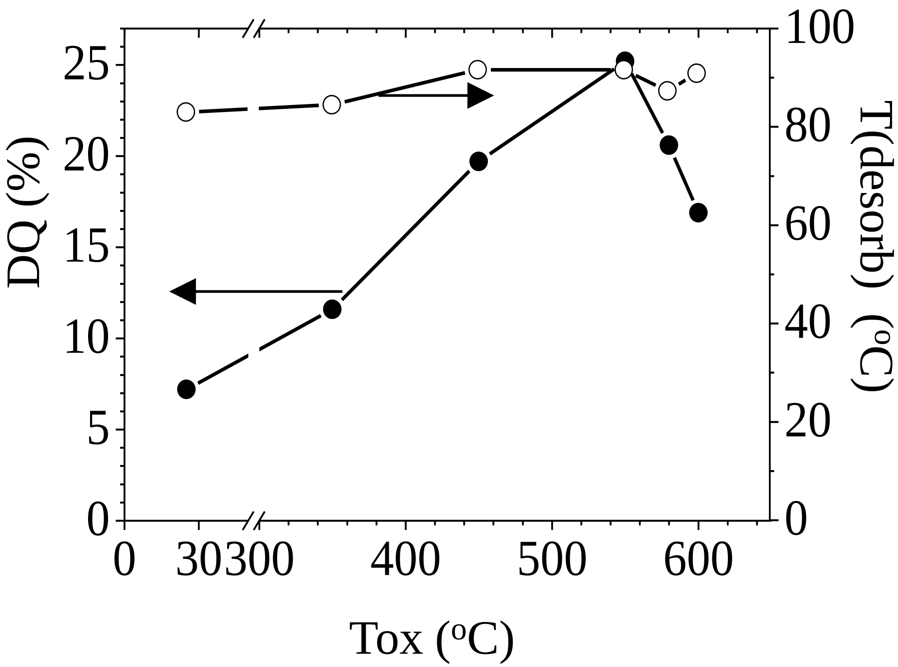


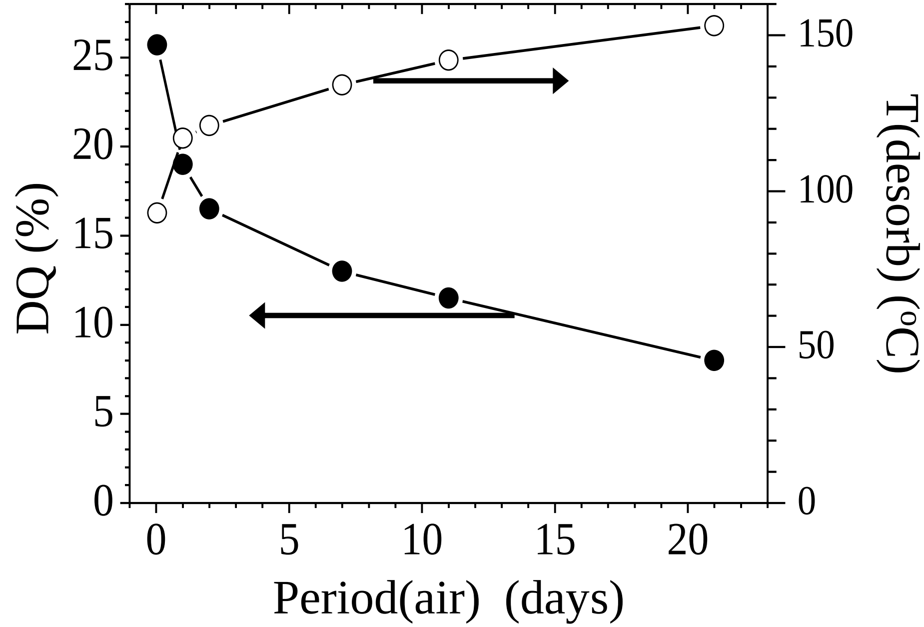




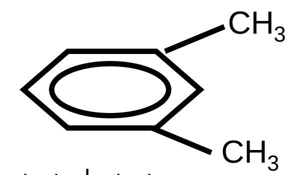
Xylene adsorption quantity depended on hole-opening temperatures. Adsorbed xylene was released slowly.

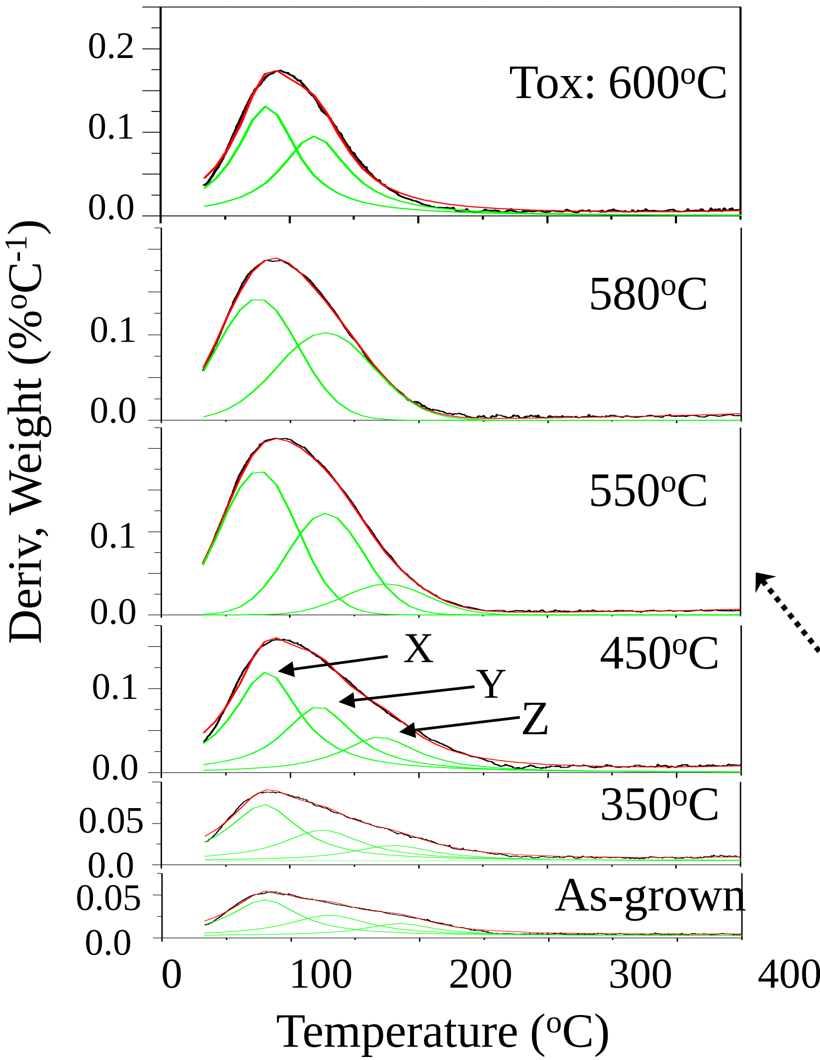


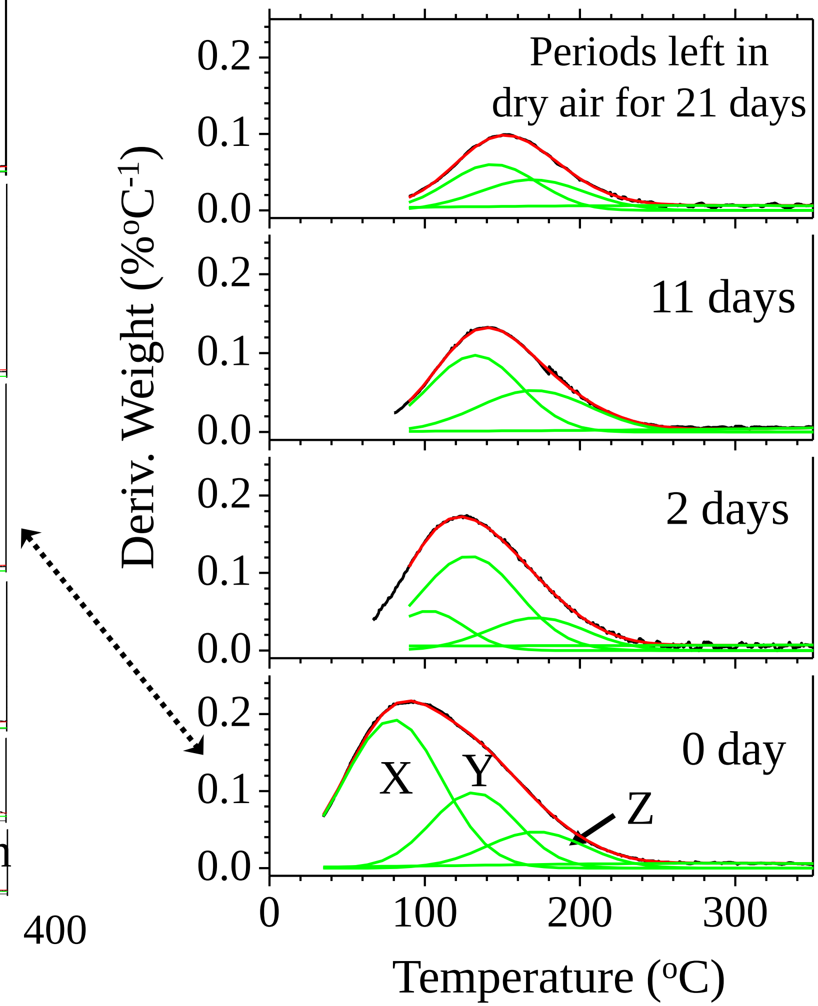


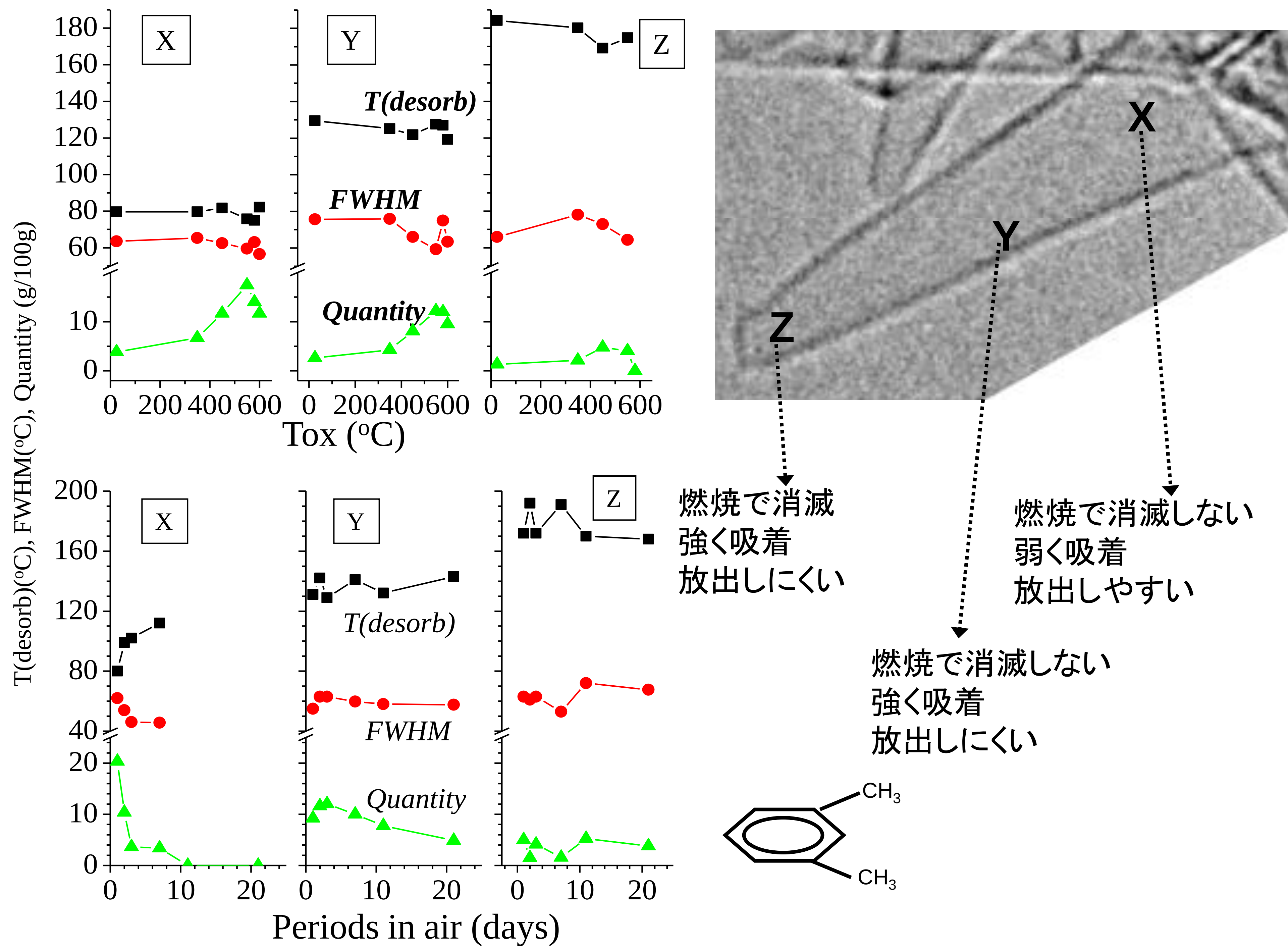


Xylene adsorption quantity depended on hole-opening temperatures. Adsorbed xylene was released slowly.

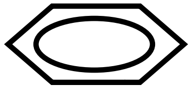


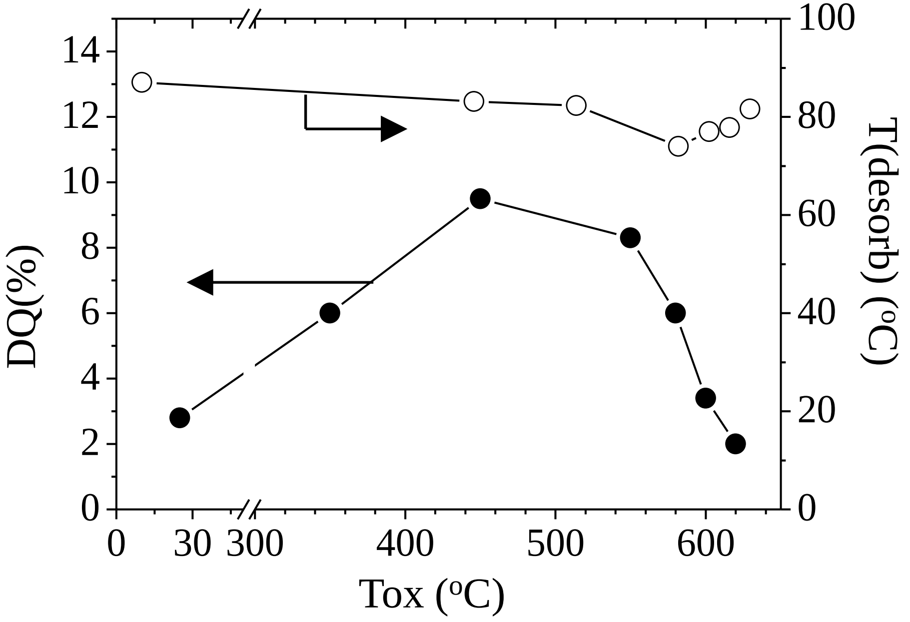


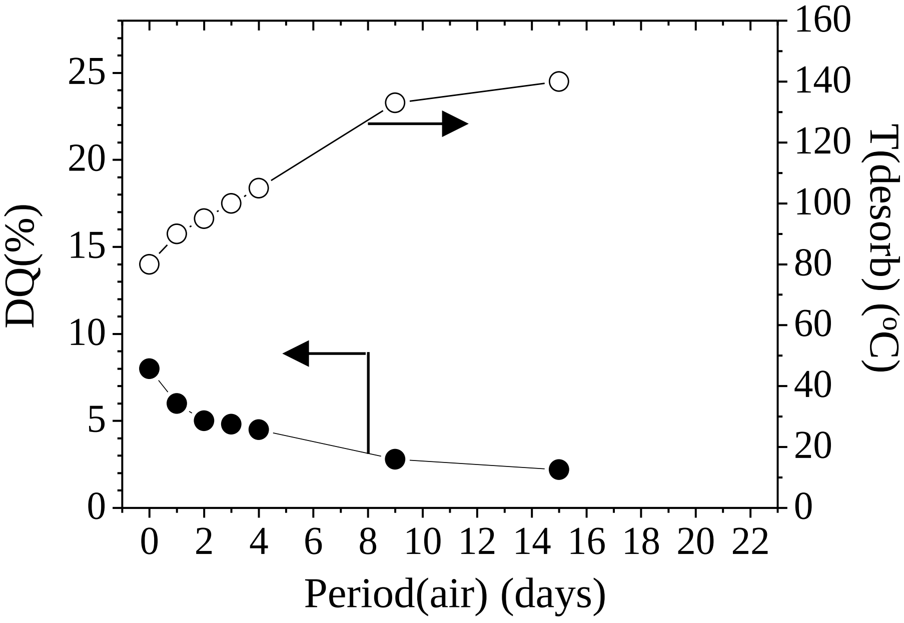



X
Y
Z
T(desorb)
FWHM
Quantity
T(desorb)(°C), FWHM(°C), Quantity (g/100g)
Tox (°C)
Periods in air (days)
燃焼で消滅
強く吸着
放出しにくい
燃焼で消滅しない
弱く吸着
放出しやすい
燃焼で消滅しない
強く吸着
放出しにくい
CH3
CH3

Benzene adsorption quantity depended on hole-opening temperatures.

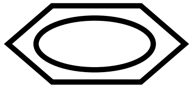


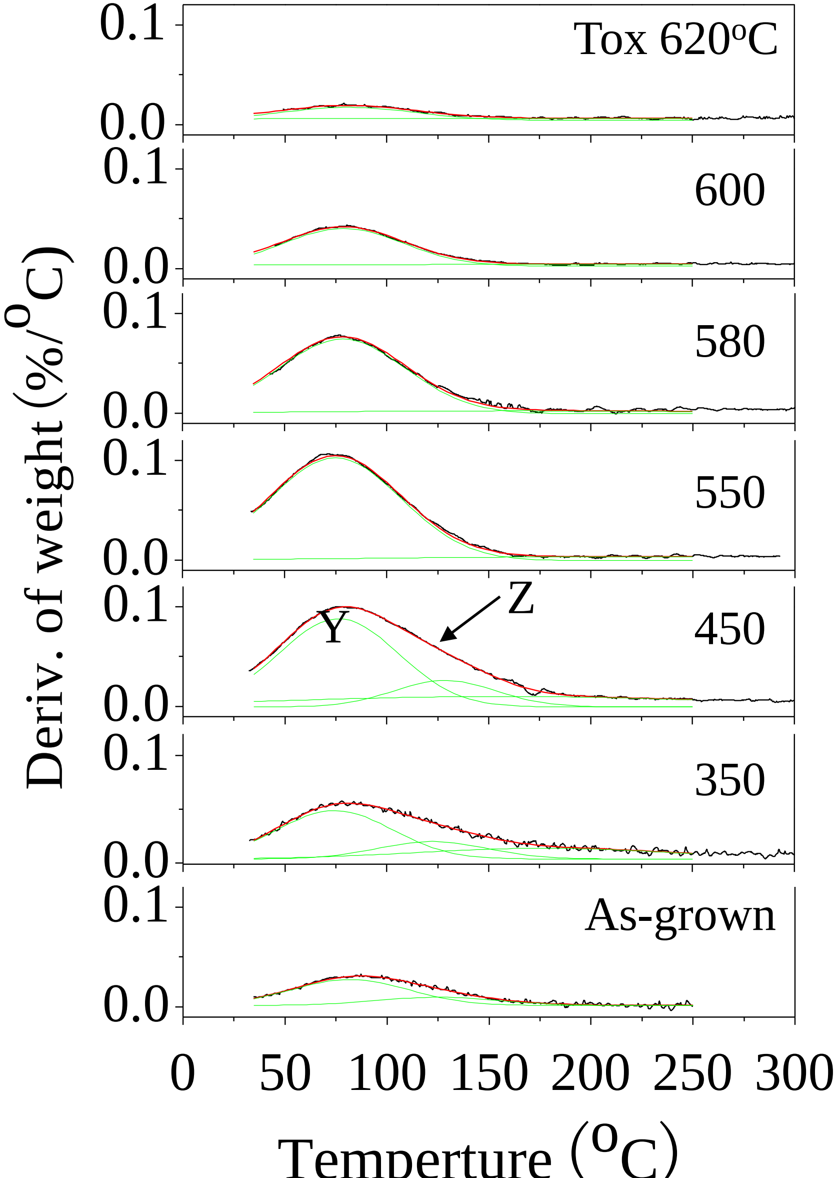


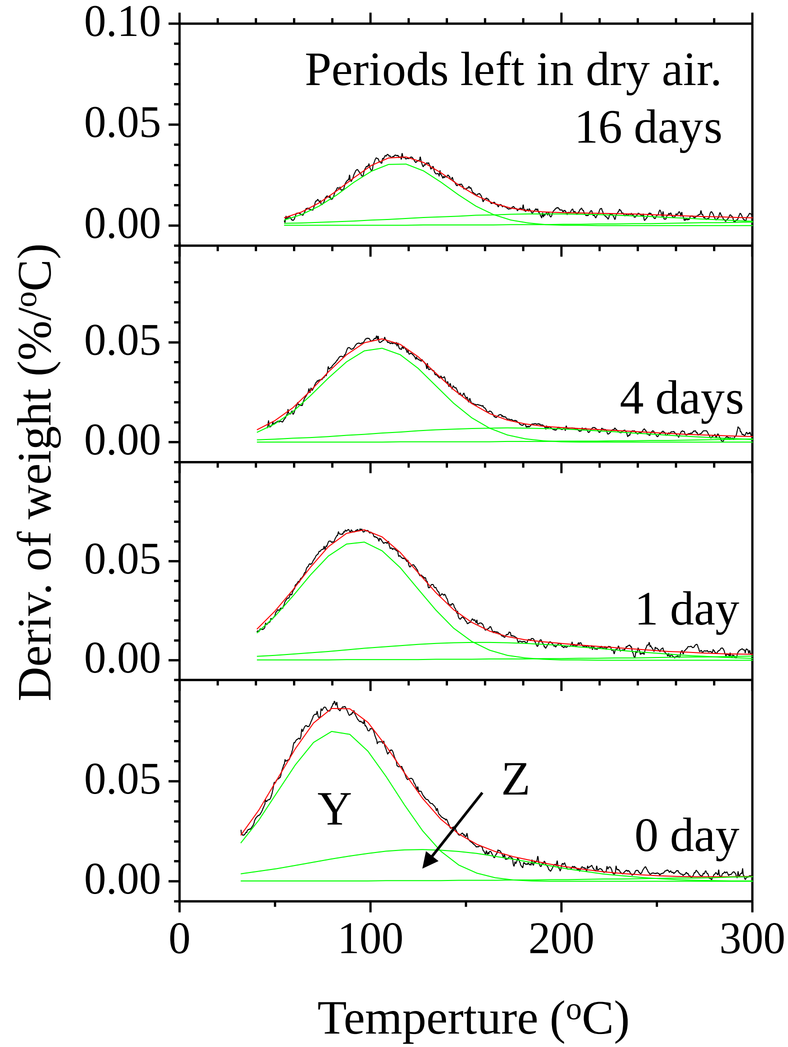


Yudasaka et al. JPCB 2005

Benzene adsorption quantity depended on hole-opening temperatures.

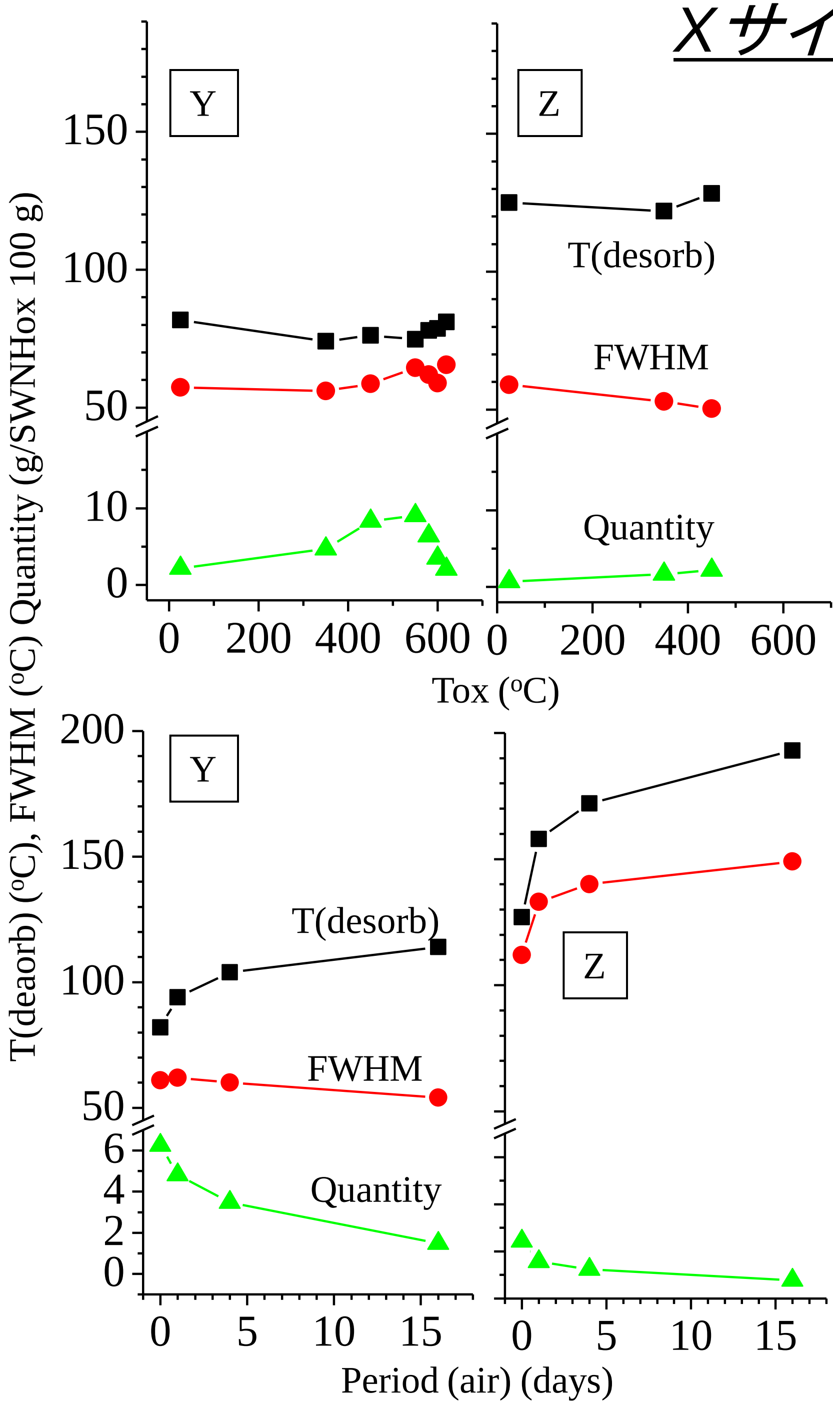


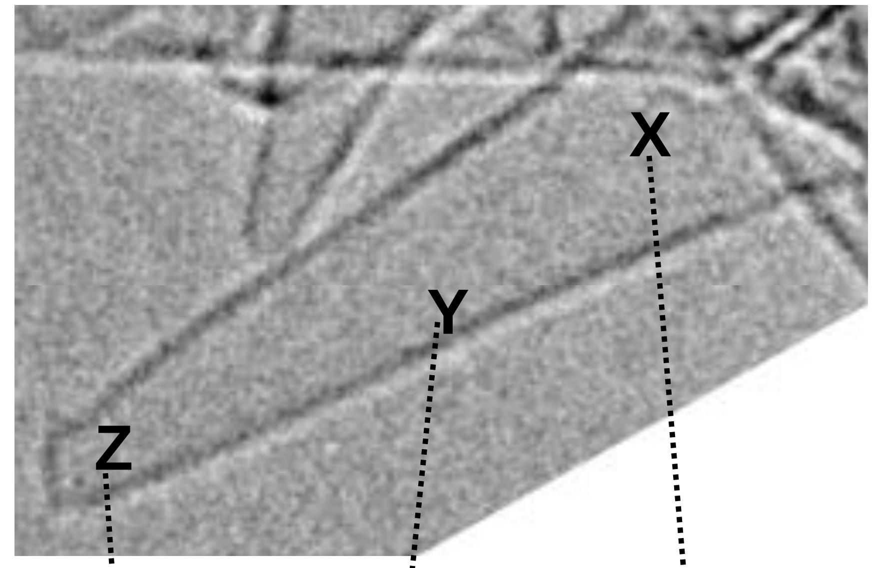




Yudasaka et al. JPCB 2005

Xサイトからの放出がない！



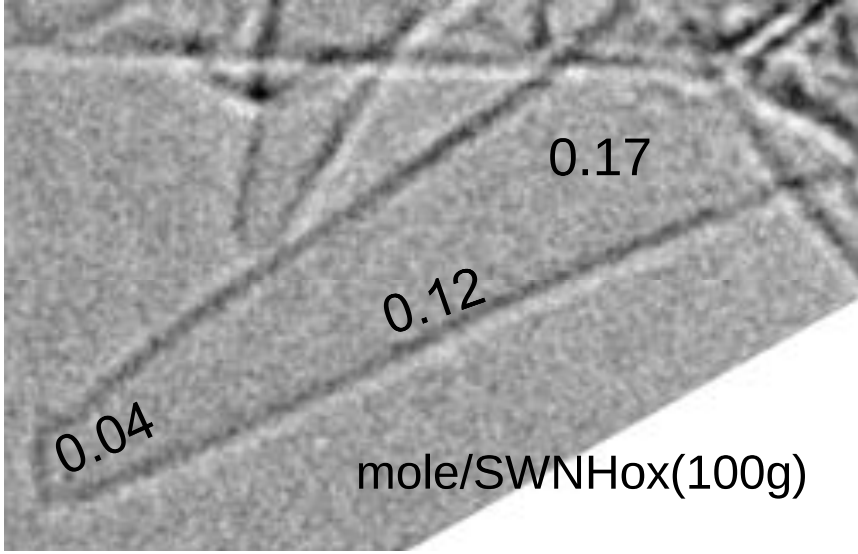


Z: 消滅しやすい
強く吸着
放出しにくい

Y: 消滅しない
強く吸着
放出しにくい

X: 消滅しない
弱く吸着
放出しやすい

Yudasaka et al. JPCB 2005

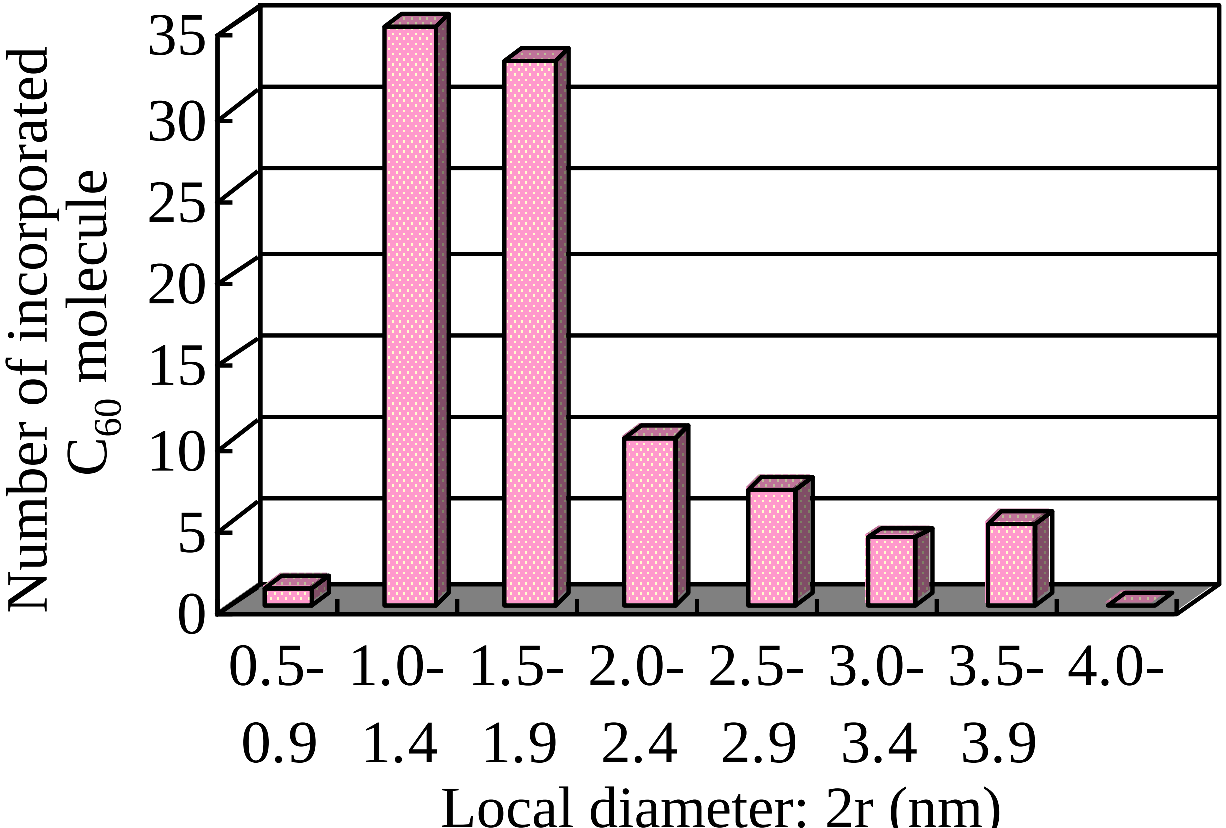


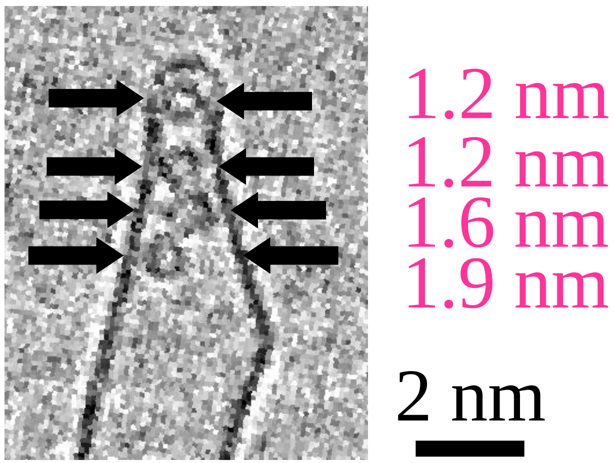
	sites	X	Y	Z
Xylene/SWNHox	Desorption quantity (mole/SWNHox(100g))	0.17	0.11	0.046
	Desorption temp (^oC)	75	120	170
	sites		Y	Z
Benzene/SWNHox	Desorption quantity (mole/SWNHox(100g))	Not detected	0.12	0.026
	Desorption temp (^oC)	Not detected	80-110	130-190

Yudasaka et al. JPCB 2005

Relation between number of C_{60} molecules and local diameters of NHox

C_{60} molecules (0.7 nm) were preferentially incorporated at sites of NHox with diameters of 1−2 nm.

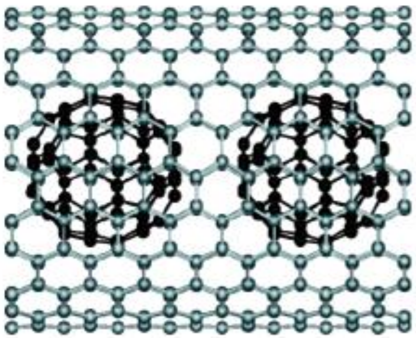




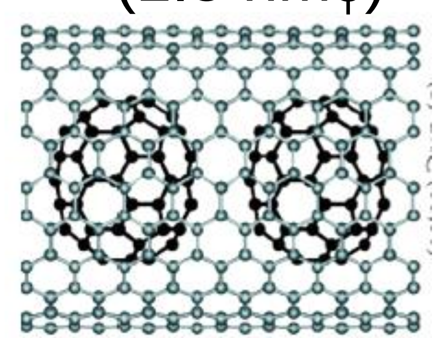
K. Ajima, et al. *Adv. Mater.* **2004**, *16*, 397–401.

Stability of peapod depends on diameter of SWNTs

C_{60} encapsulation in nanospaces by van der Waals force

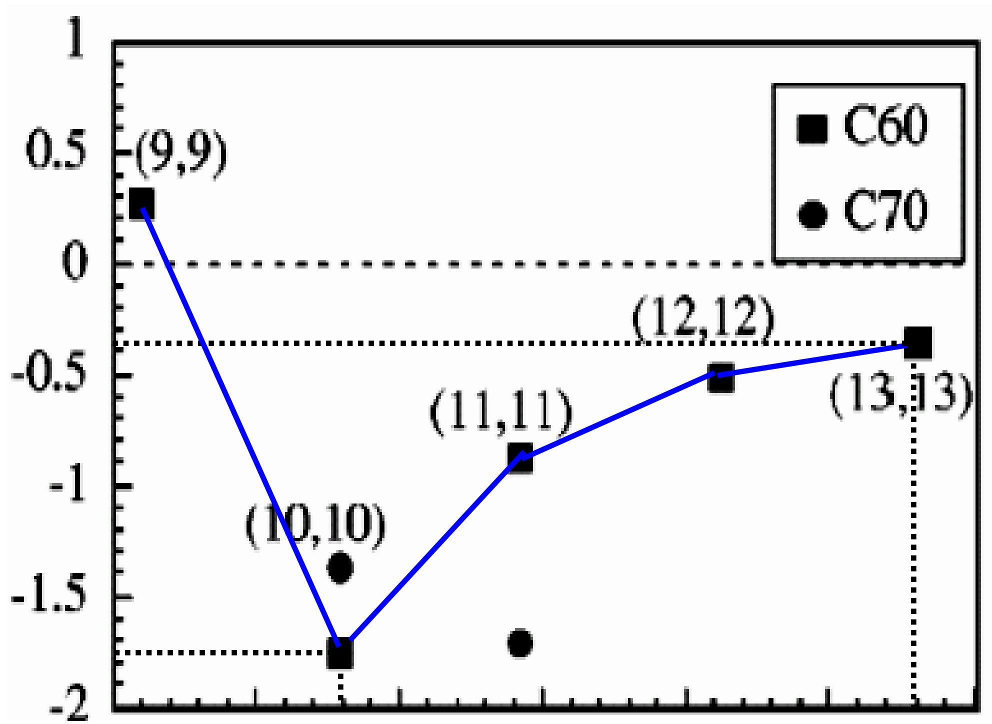


C_{60}@SWNTs (1.5 nmϕ)



C_{70}@SWNTs (1.5 nmϕ)

ΔE (eV/Fullerene)



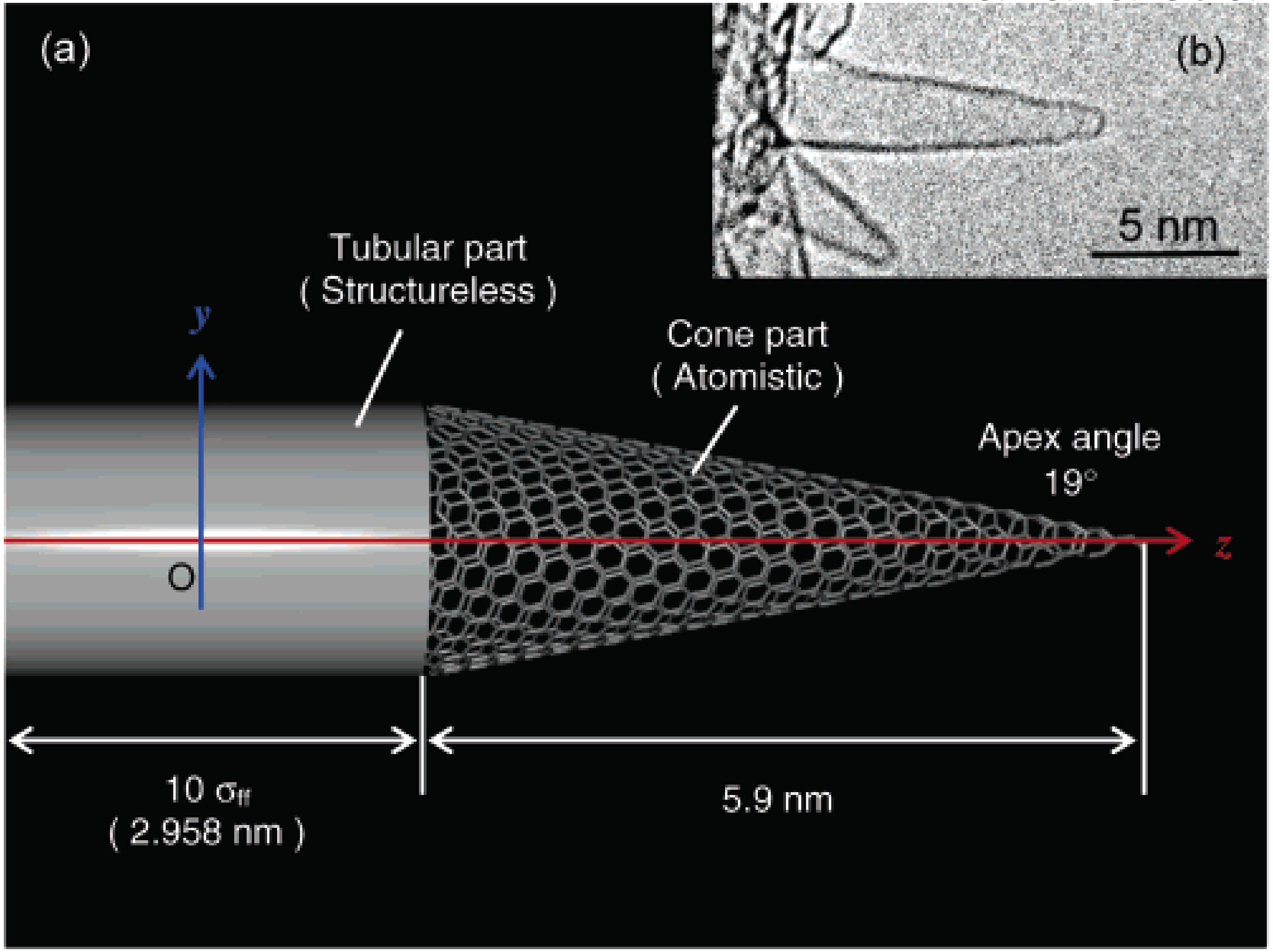
1.2 1.3 1.4 1.5 1.6 1.7 1.8

SWNT diameter (nm)

S. Okada et al., *Phys. Rev. B* **2003**, *67*, 205411–205415.

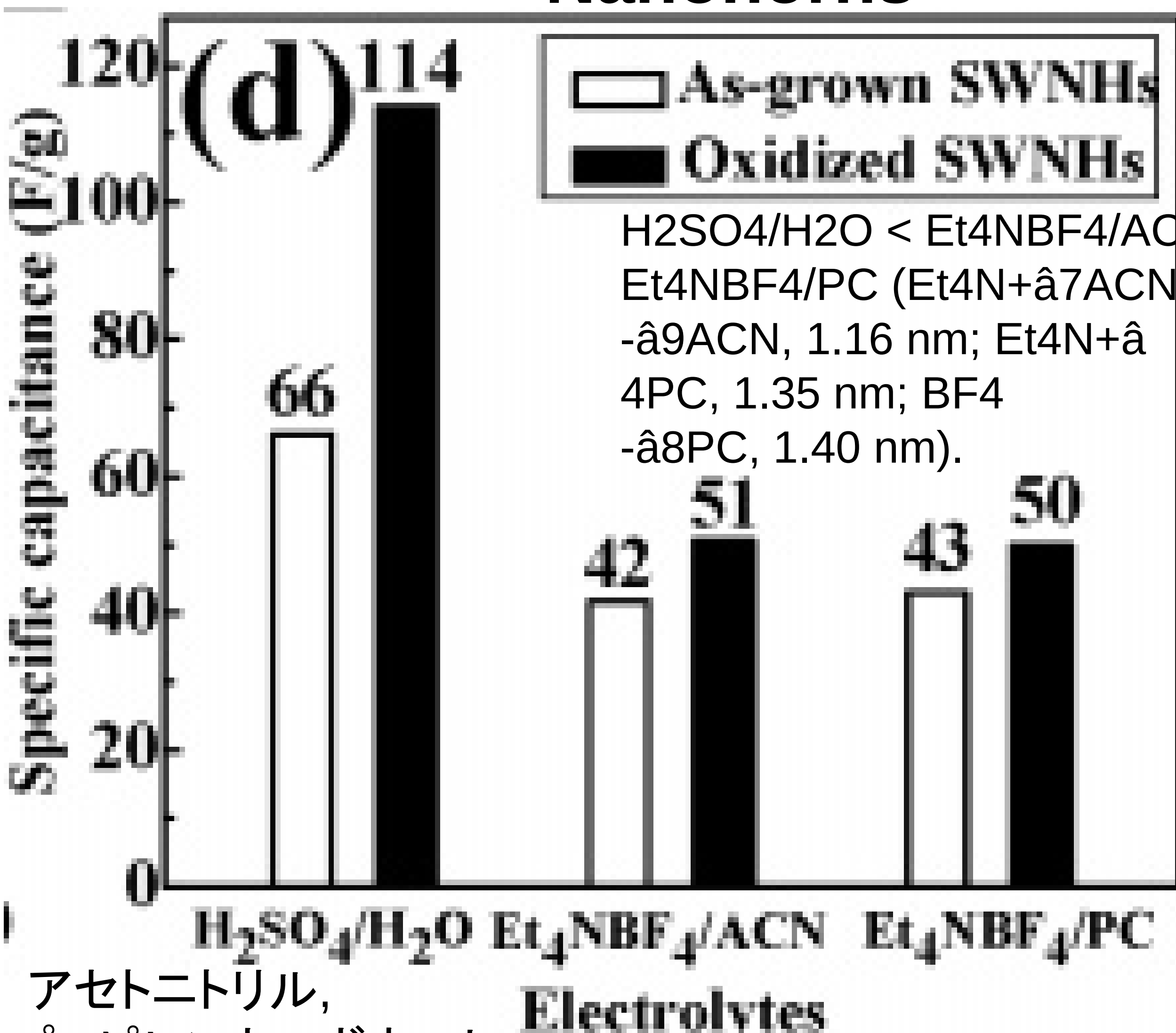
Quantum Effects on Hydrogen Isotope Adsorption on Single-Wall Carbon Nanohorns

Tanaka et al. JACS 2005



Quantum effects cause the density of adsorbed H_2 inside the SWNH to be 8-26% smaller than that of D_2

Nanowindow-Regulated Specific Capacitance of Supercapacitor Electrodes of Single-Wall Carbon Nanohorns



H2SO4/H2O < Et4NBF4/ACN < Et4NBF4/PC (Et4N+â7ACN, 1.30 nm; BF4 -â9ACN, 1.16 nm; Et4N+â 4PC, 1.35 nm; BF4 -â8PC, 1.40 nm).

CAN アセトニトリル,
PC　プロピレンカーボネート

Yang et al.
JACS 2006