2nd Workshop on Nanoscience: Carbon-Related Systems and Nanomaterials
July 3 - 7, 2012, NCKU, Tainan, Taiwan

Nanocarbon Materials: Synthesis and Structure Characterizations (I)

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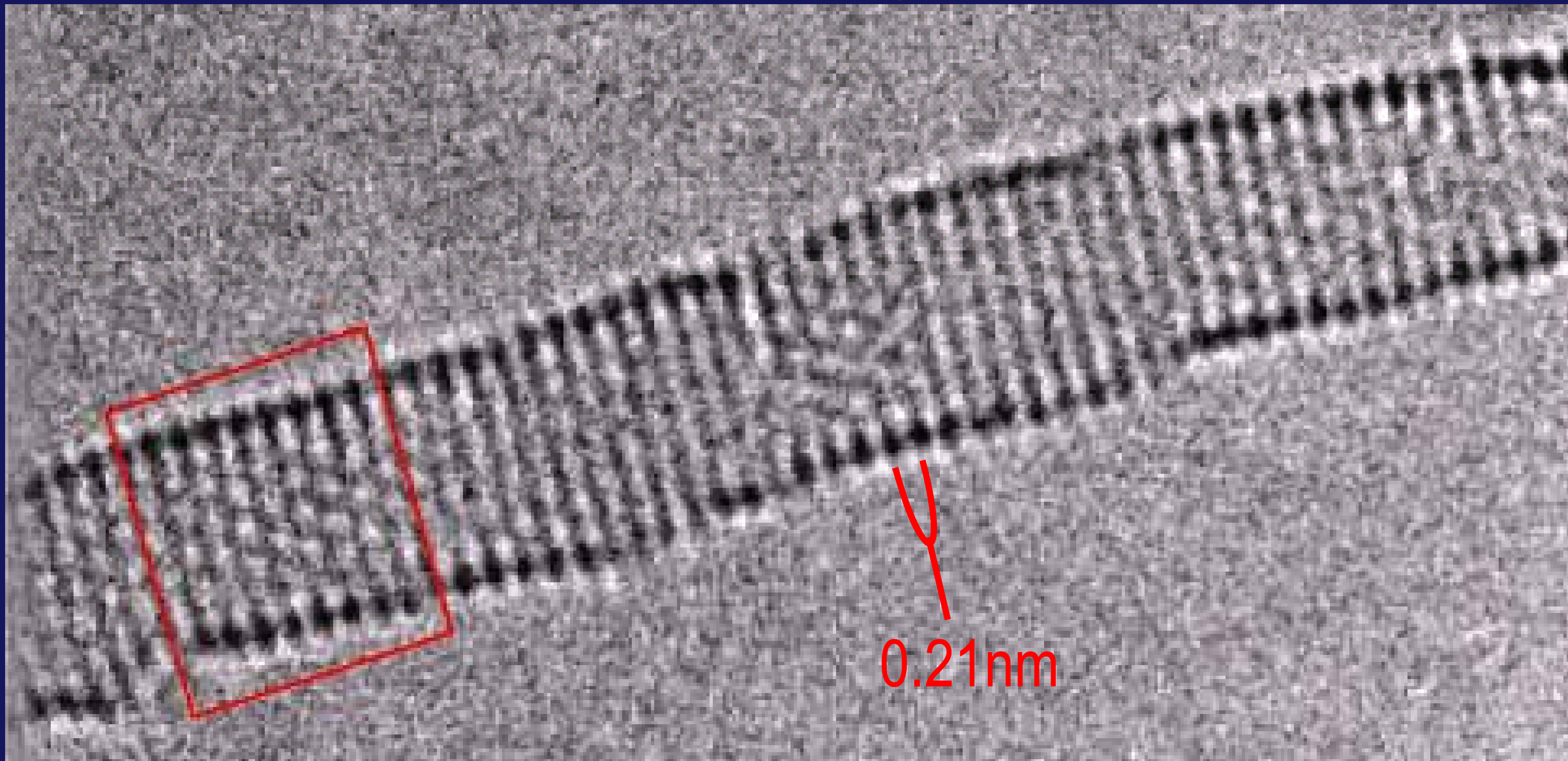
Meijo University
NEC

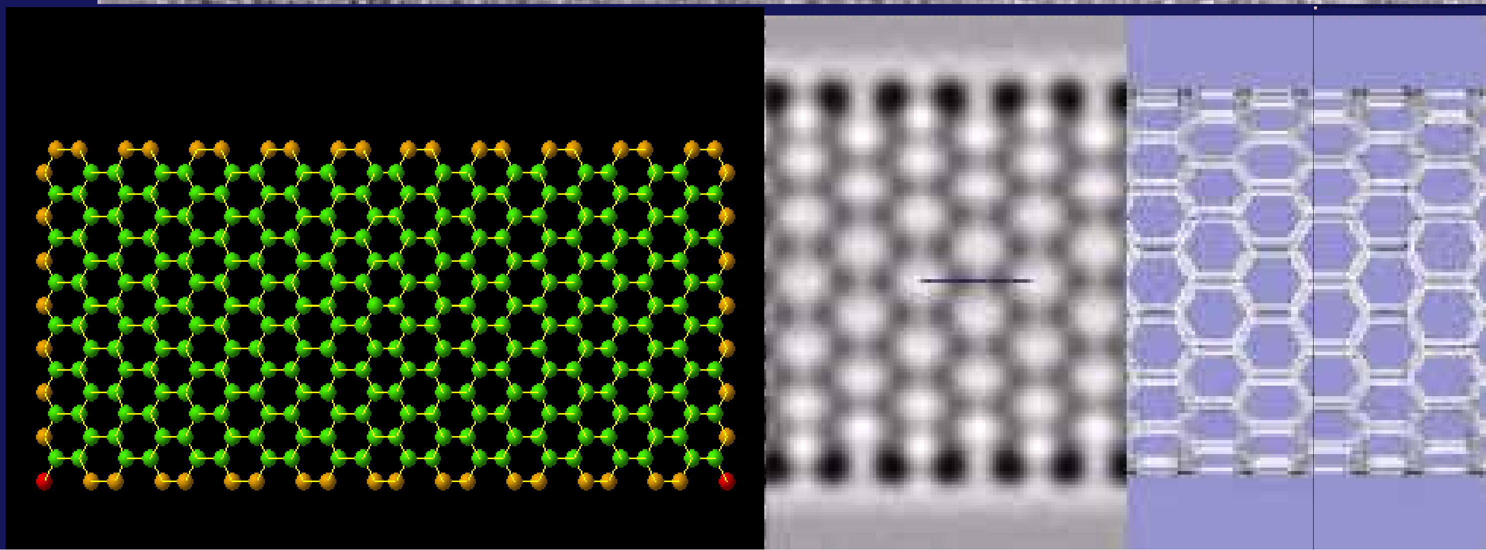
http://nanocarb.meijo-u.ac.jp/jst/iijima.html

Direct imaging of carbon atoms of CNT

Suenaga, et al. *Nature Nanotech.* 2007



by S. Maruyama



C-C bond (0.14nm) resolution

SWNT (18, 0)

What is so special for CNTs?

- Nanometer sizes: quasi-one-dimensional
- Tubular structure: a new concept of solid
- New properties: semiconducting or metallic
- The all atom co-ordinations are known!

  ab-initio calculation (all material properties can be predicted precisely !)
- Artificial structure: not in nature

Possible applications of CNT s

Carbon nanotubes

FE electron source
FED, X-ray tubes

Semiconducting (Metallic)
Flexible transistor

Flexible

Large surface area
Gas adsorbent
Super-capacitor
Black body
Biomedicine

Electric conductor
Conductive plastic films
LSI-via-wiring
Heater

Chemically stable

Nano-size needle
SPM probes

Tensile strength

Heat conductor
Radiator
Heavy ion charge stripper

Light weight
Composite materials (metal, polymer)
MEMS

Outline

- **Reorganization of sp^2 carbon, and the tubule growth**
- **Synthesis of nano-carbon materials**

  Carbon nano-tubes (CNTs)

  Carbon nano-horns (CNHs)

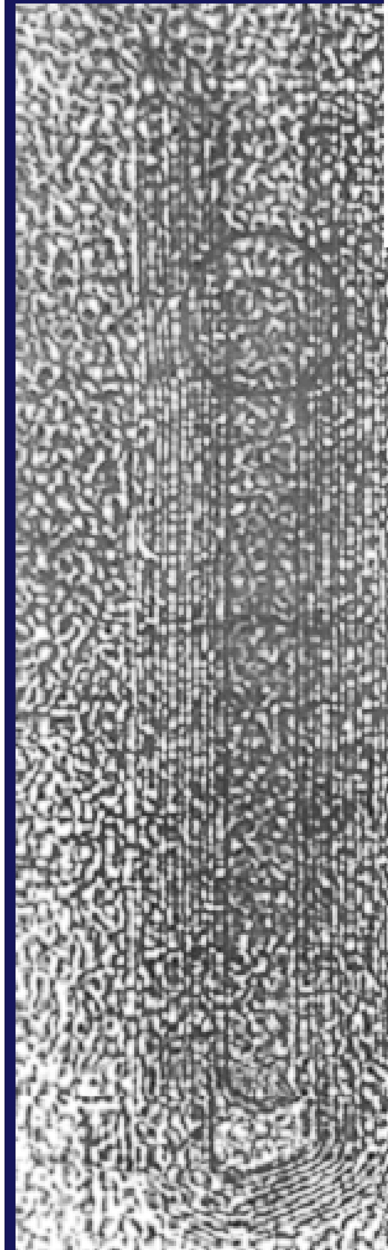
  Graphene sheets
- **HRTEM & EELS imaging of sp^2 carbon materials**

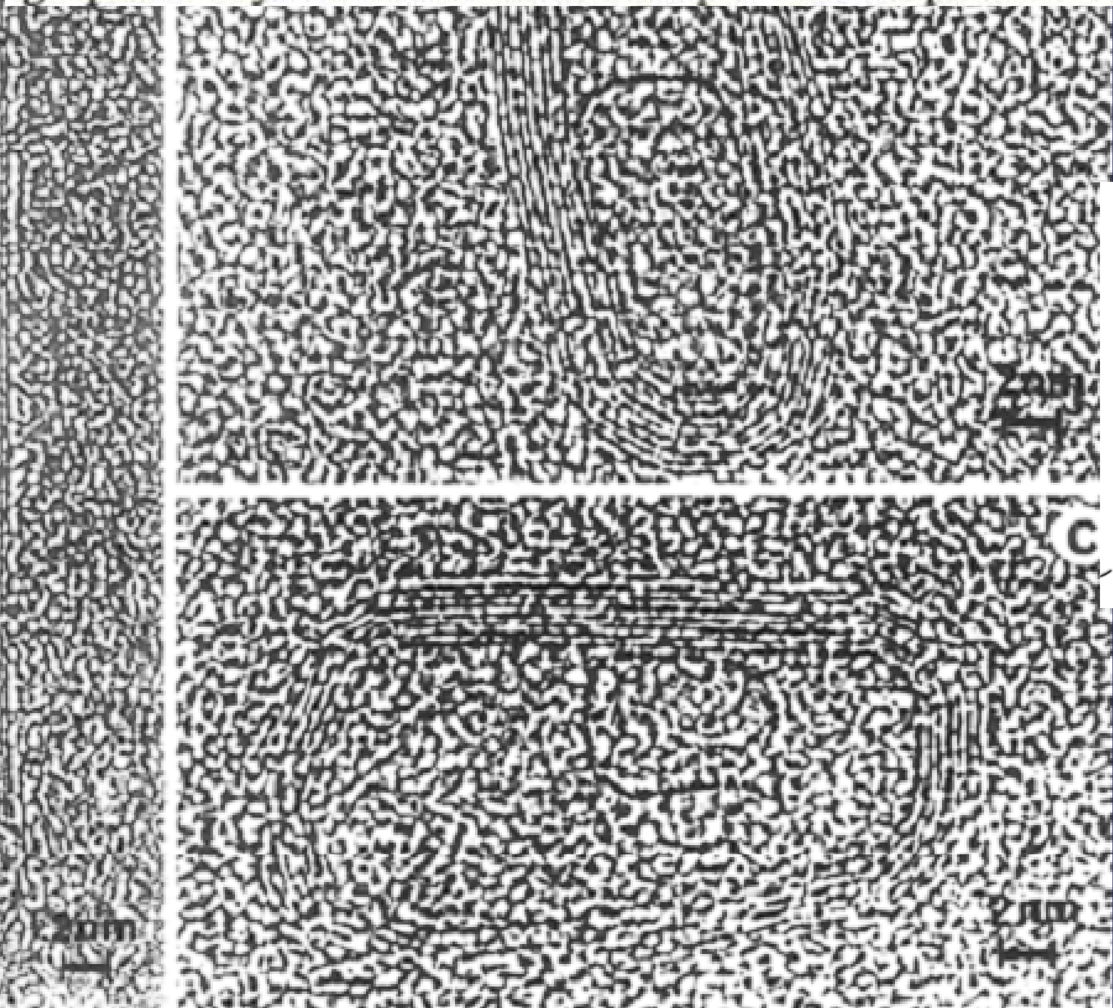
  on individual atom basis
- **Some applications of nanocarbon materials**

Multi-wall carbon nanotubes have been reported in 1980

Iijima, *J. Microscopy* 1980

An objective aperture was not used. Thus individual dark lines represent the regions where the population of carbon atoms is higher than elsewhere. The single sheets are seen as loops of dark lines, which are inside the tubular-shaped particles of graphitic carbon. Fringe images corresponding to the (0002) lattice plane of the graphite crystal form closed loops. These particles are presumably embedded in





Imaging of a single atom sheet

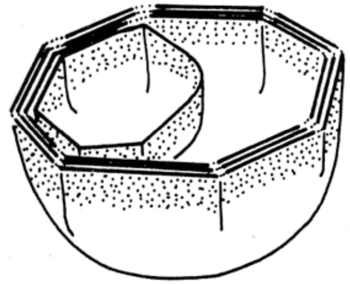
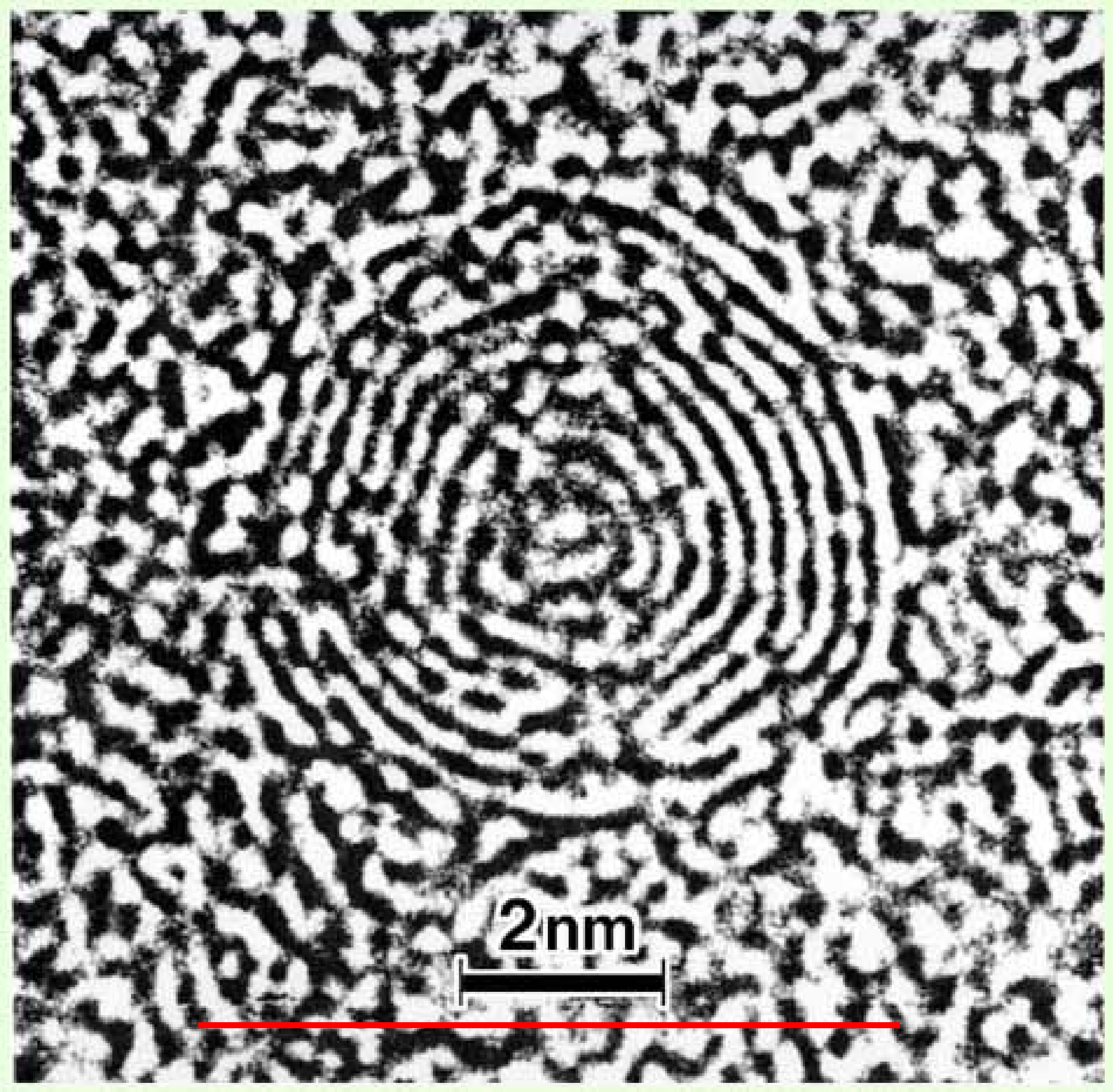
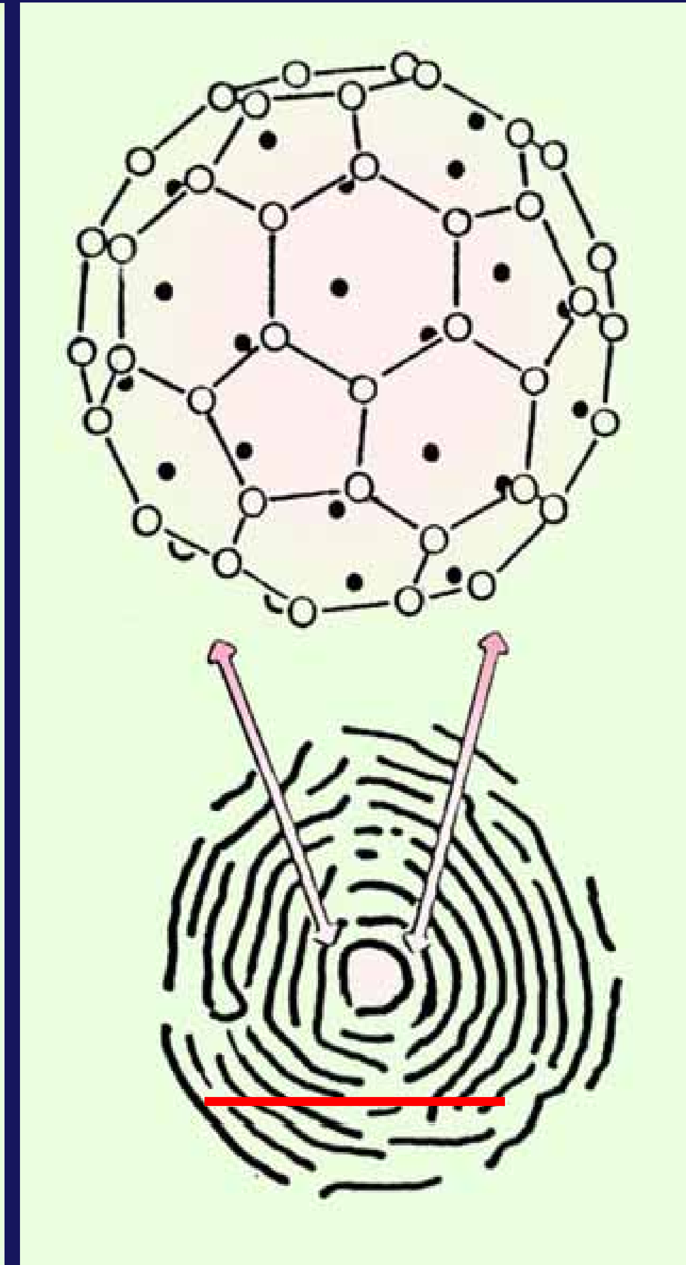


Fig. 3. A schematic three-dimensional drawing of the shell of the graphitized carbon particle shown in fig. 2a. Hatched portions of the shell where the layers are nearly parallel to the incident electron beam becomes visible in the micrographs.

A C_{60} has been observed in a graphite sphere (Onion)

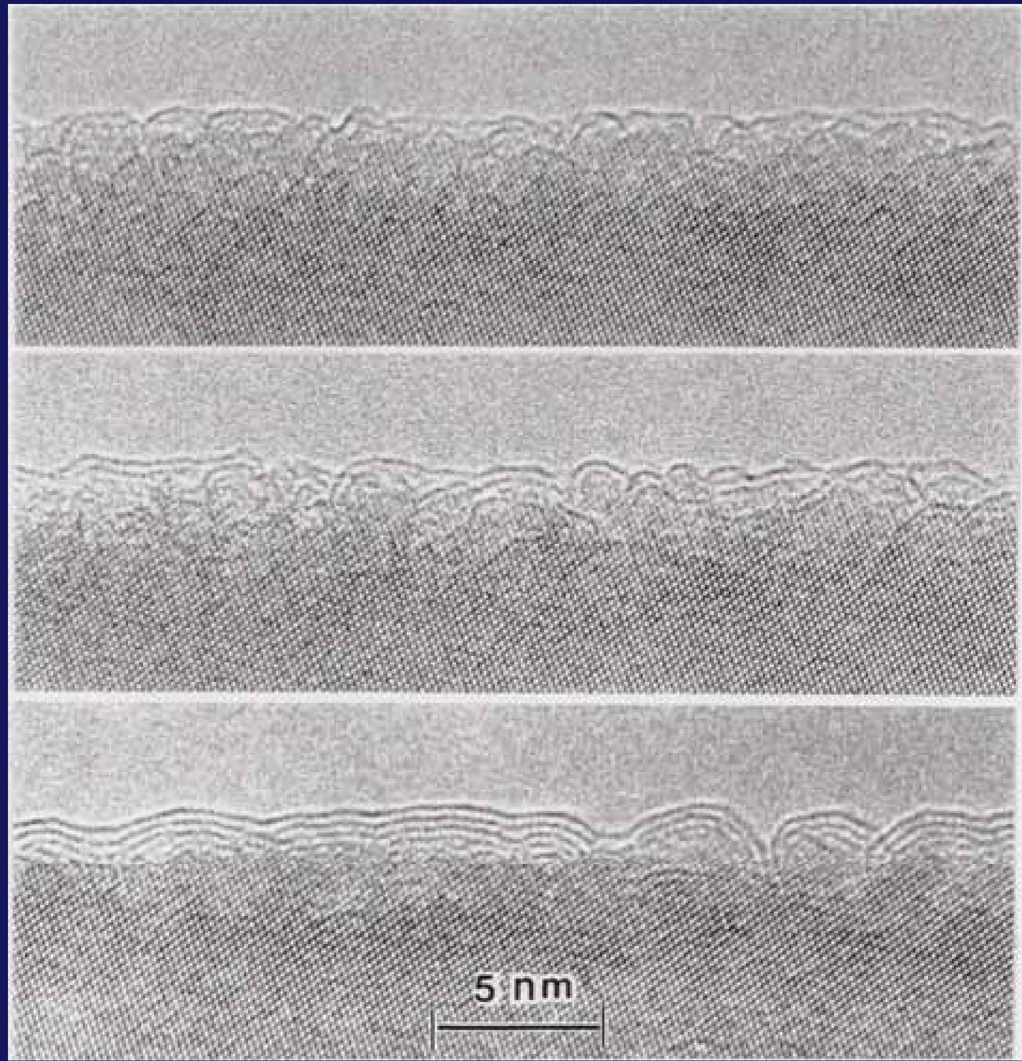
Iijima, *J.Cryst. Growth,* 1980, and *JPC*., 1987

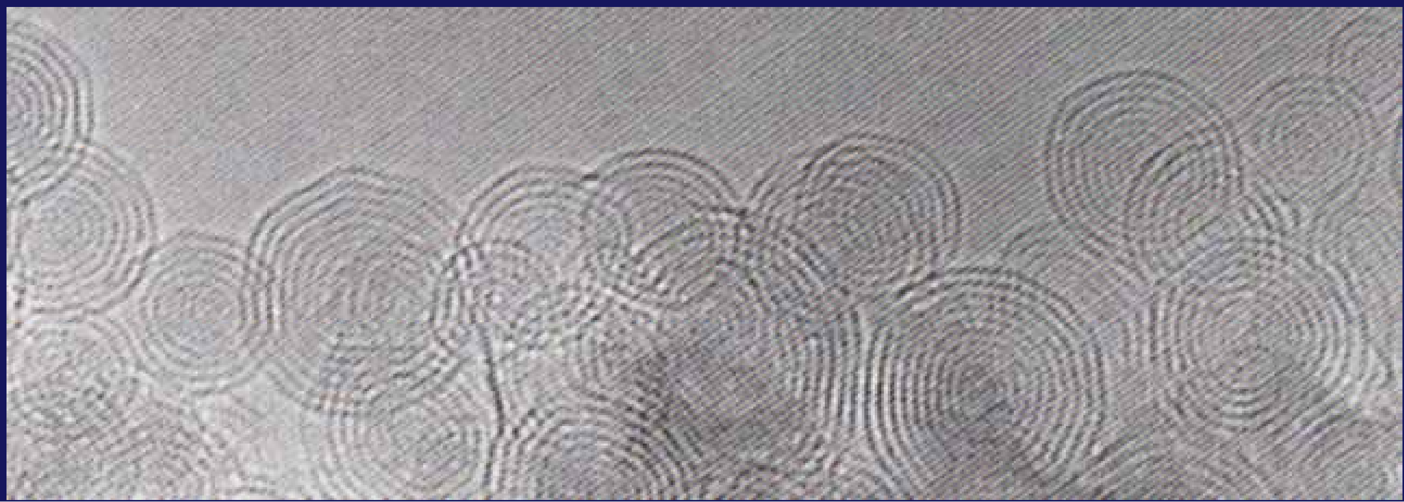




Conversion from diamond to graphite balls (onions) by electron beam irradiation

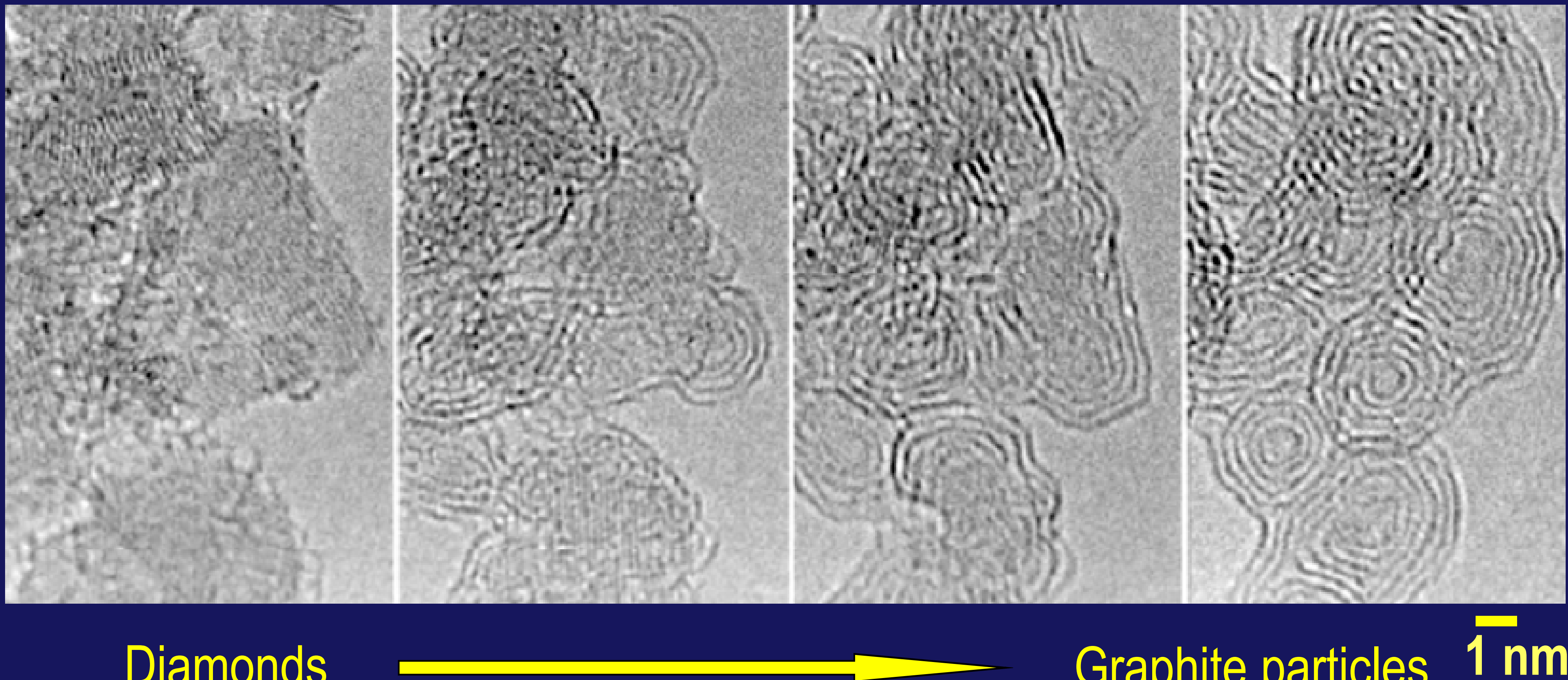
L-C. Qin and S. Iijima, *CPL*, 262,(1996)252



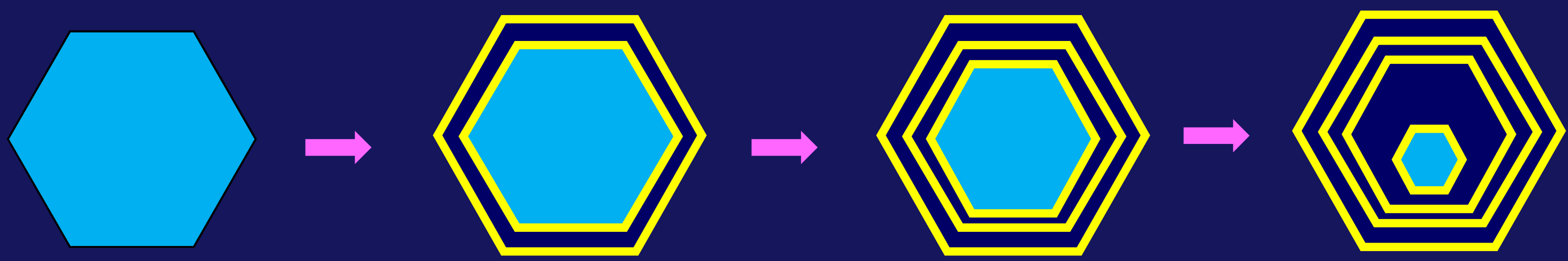


Transformation of nano-diamond clusters to graphite particles due to electron irradiation

Y-K Kwon, et al., *PRL*, 82,(1999)1470.



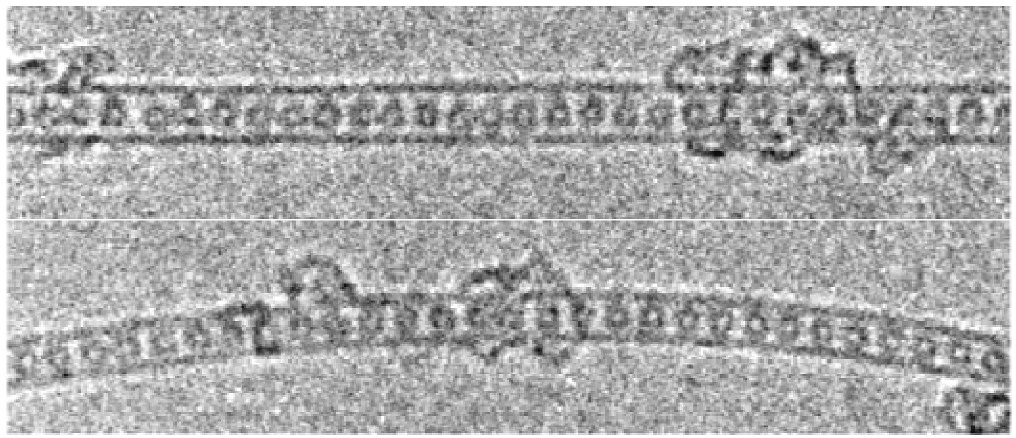
Diamonds → Graphite particles



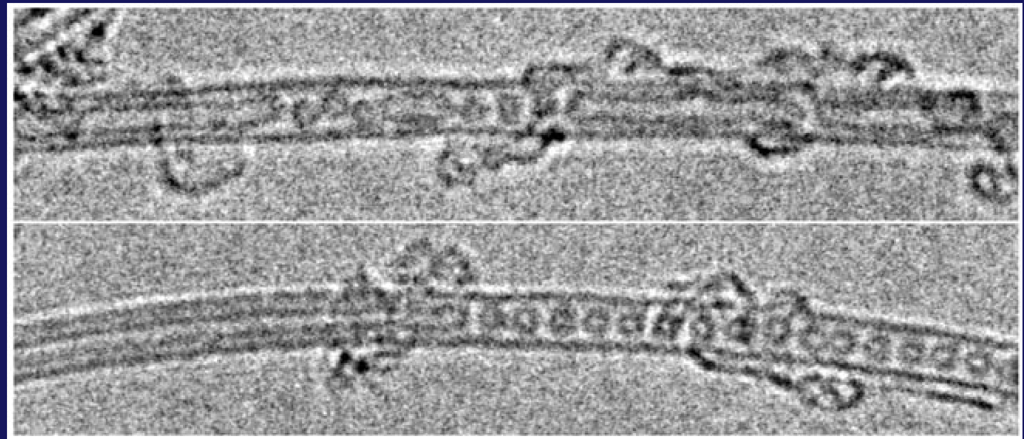
DWNT Formation by Heat Treatment of Peapods

Bandow, et al. *C.P.L.*,2001

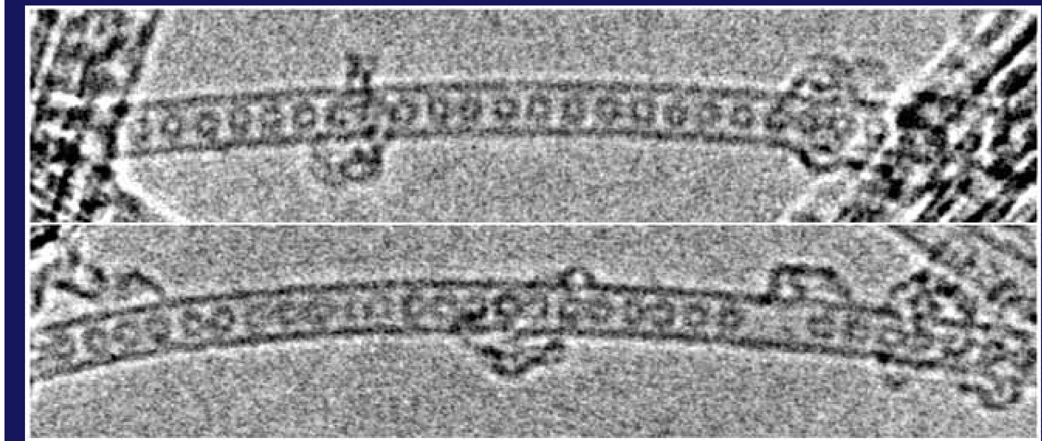
R. T.



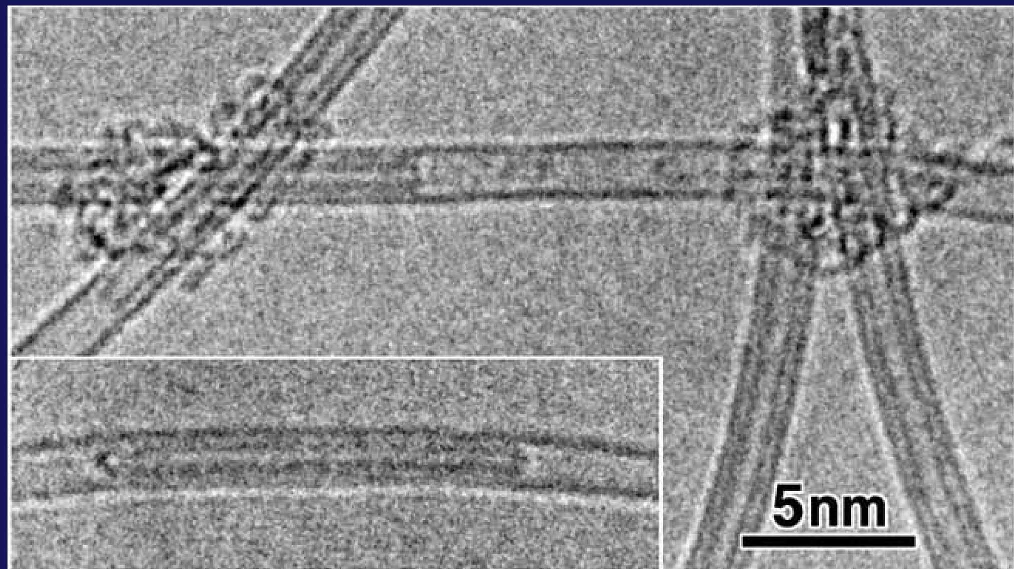
1000°C



800°C

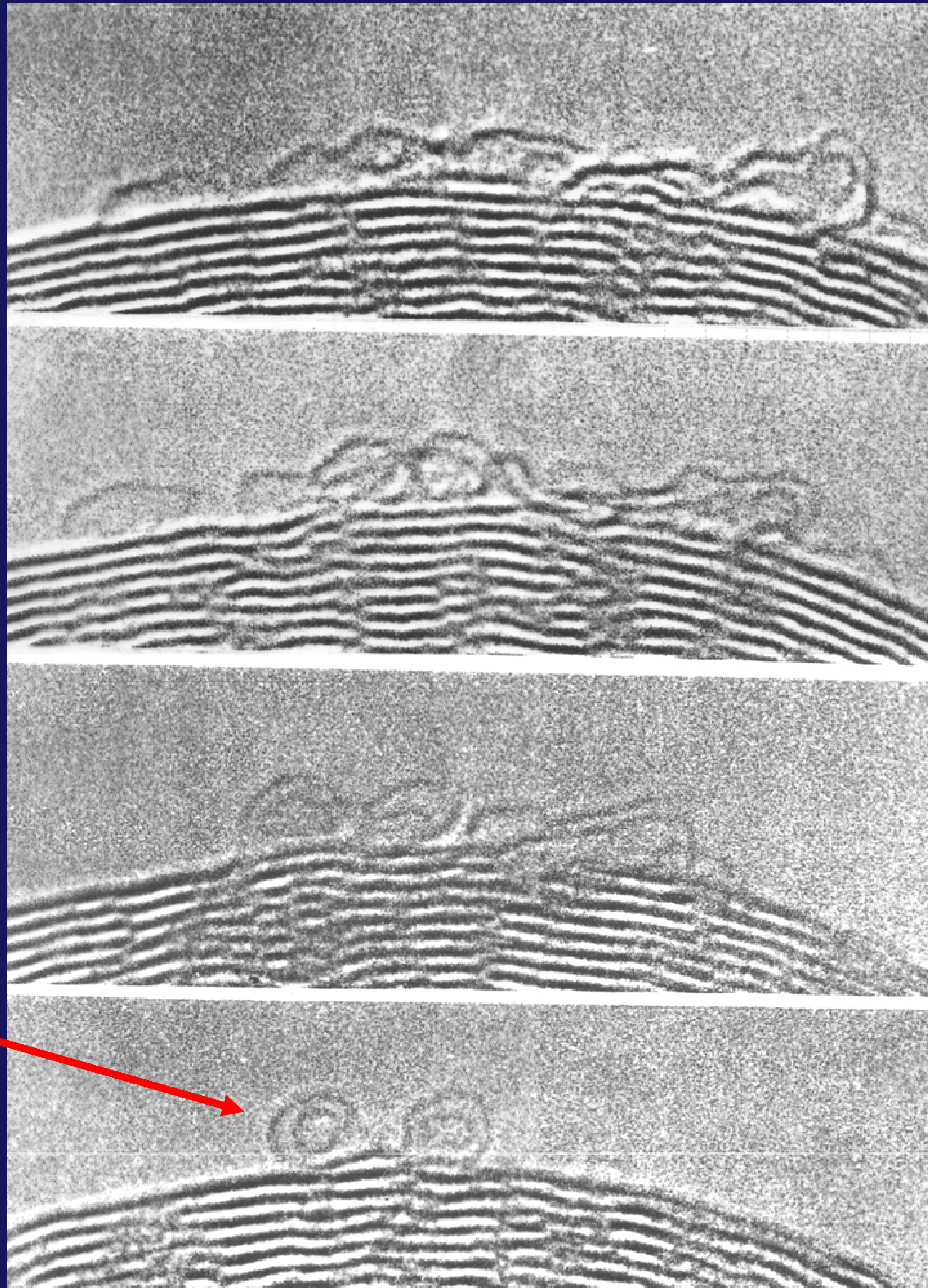


1200°C



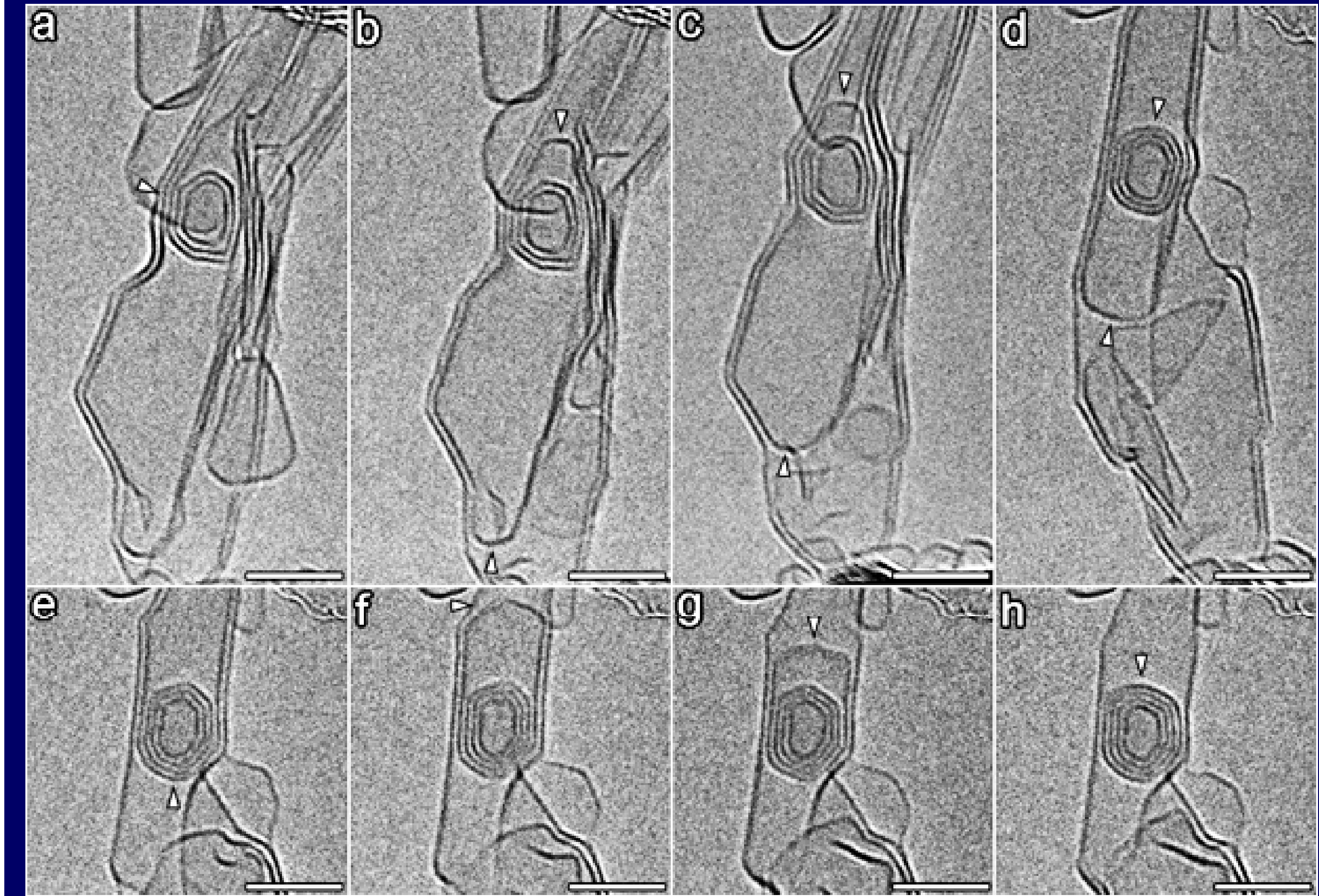
Fullerenes formation from defective graphene frakes due to electron beam irradiation

$C_{60}@C_{240}$

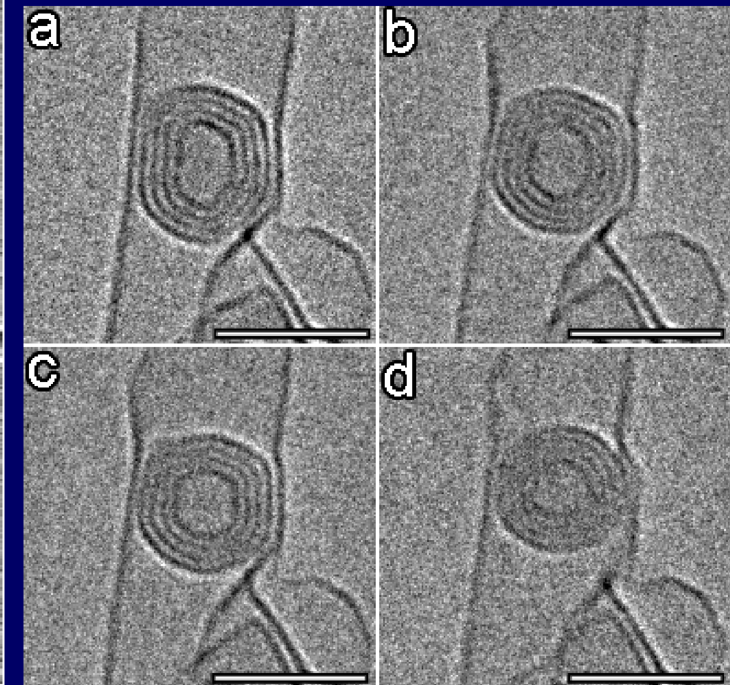


Qin & Iijima, 1996

Formation and structure tailoring of carbon onion at high temperatures



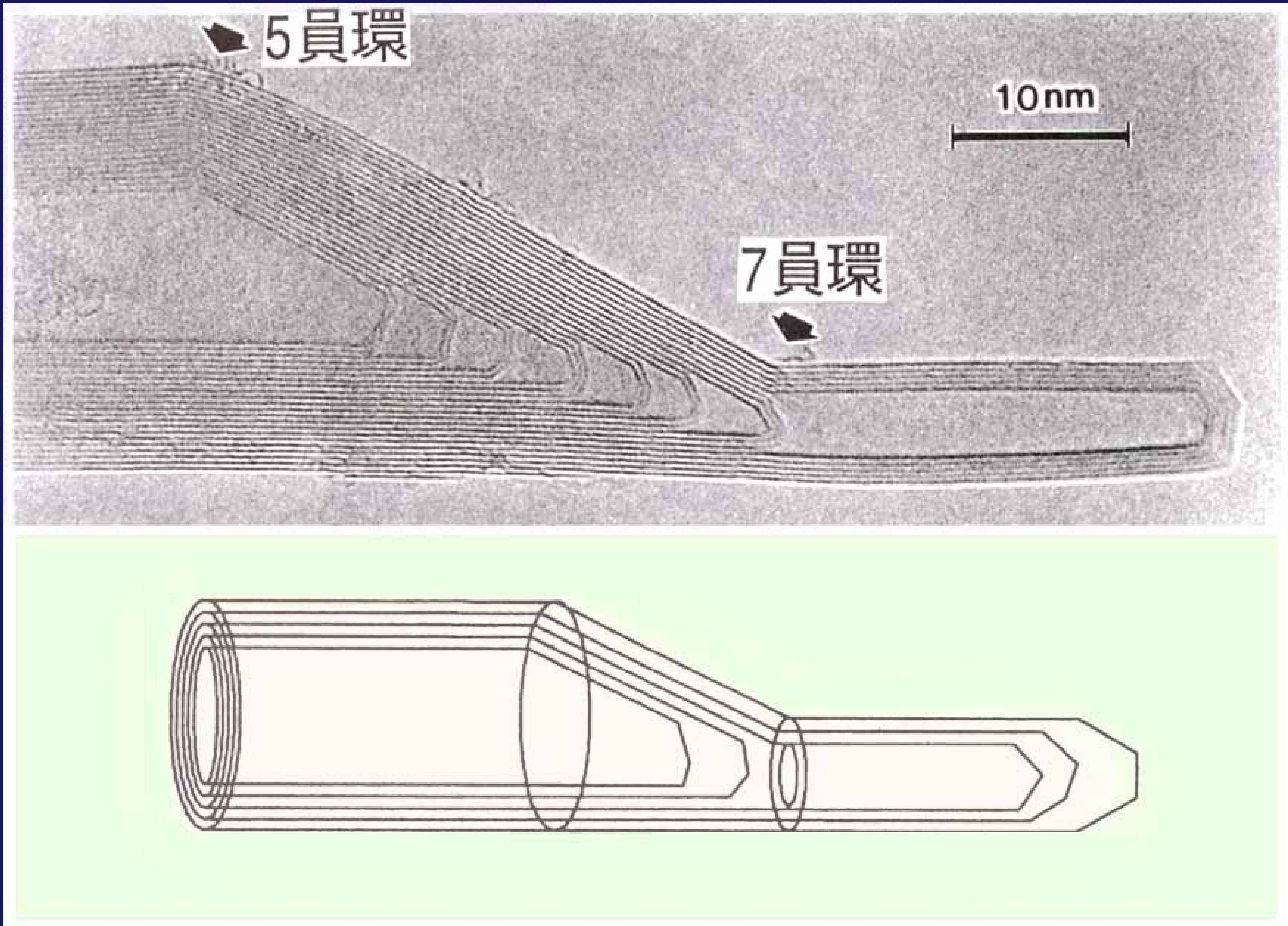
C. H. Jin et al., 2009



We report here an *in situ* structure tailoring of the shell-by-shell formation of carbon onions by means of high-resolution transmission electron microscopy. An inner-most fullerene seed first forms and acts as the central nucleation core to produce a multi-shell carbon polygon. The as-formed carbon polygon was controllably transformed to the carbon onions through the so-called “hot shrinkage” process, which is similar to that of buckminsterfullerene as proposed by S. Irle et al.

Pentagon and Heptagon in Graphene

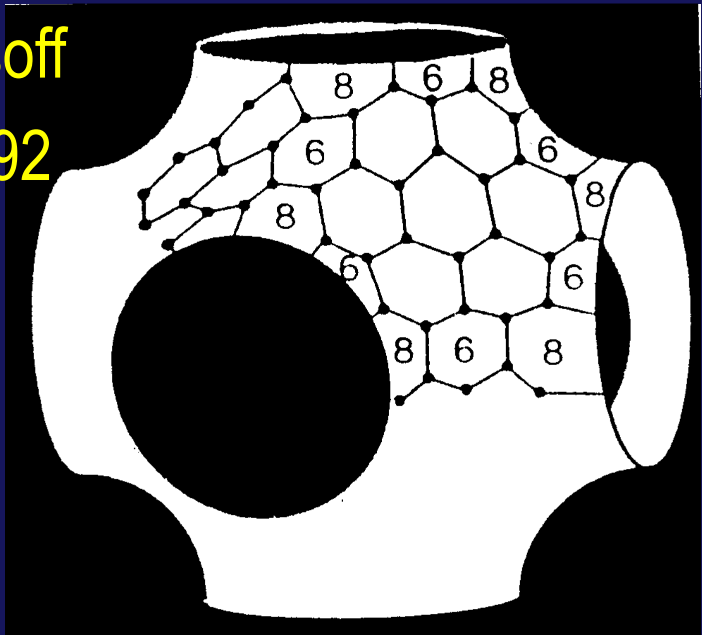
Iijima, et al., *Nature*, 356, 776(1992)



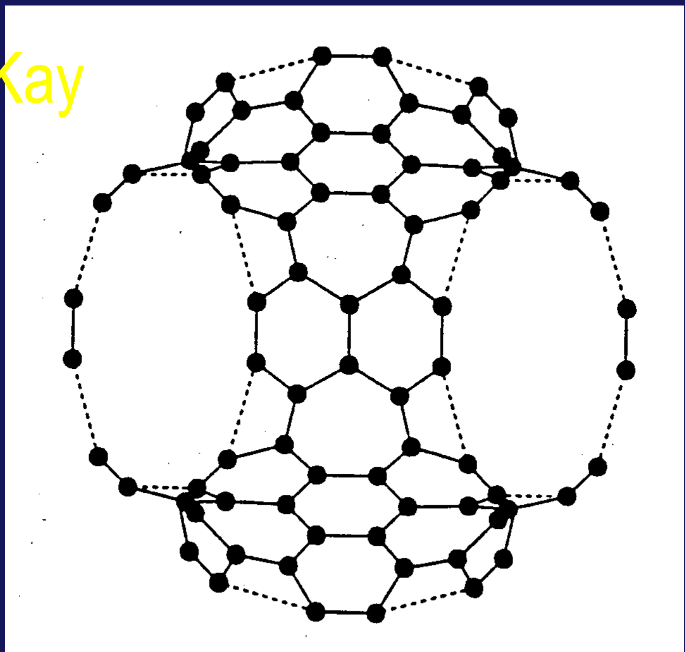
Disclinations due to 5-, 7-, and 8-membered rings

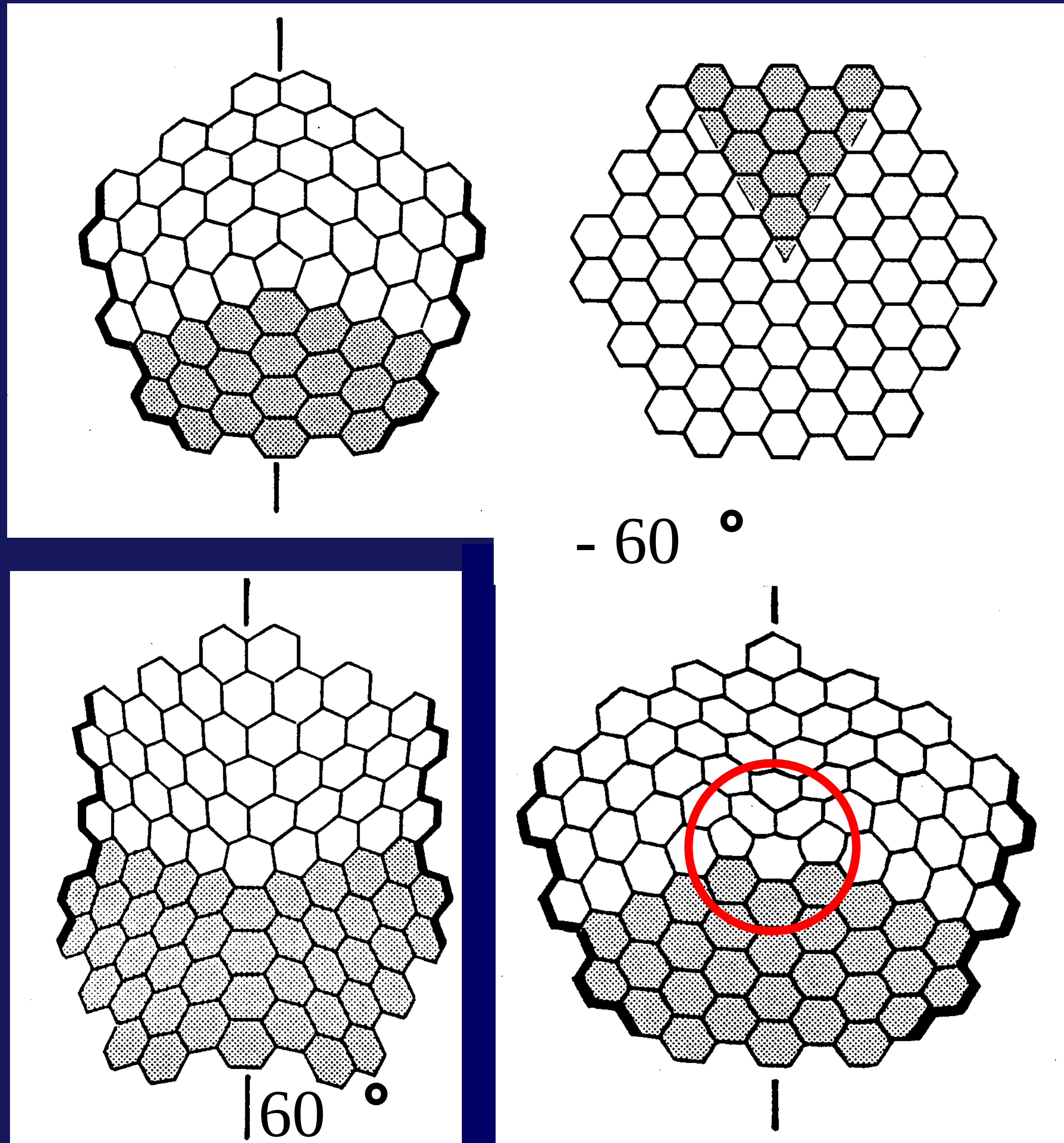
Iijima, et al., *Nature*, 1992

Tersoff 1992



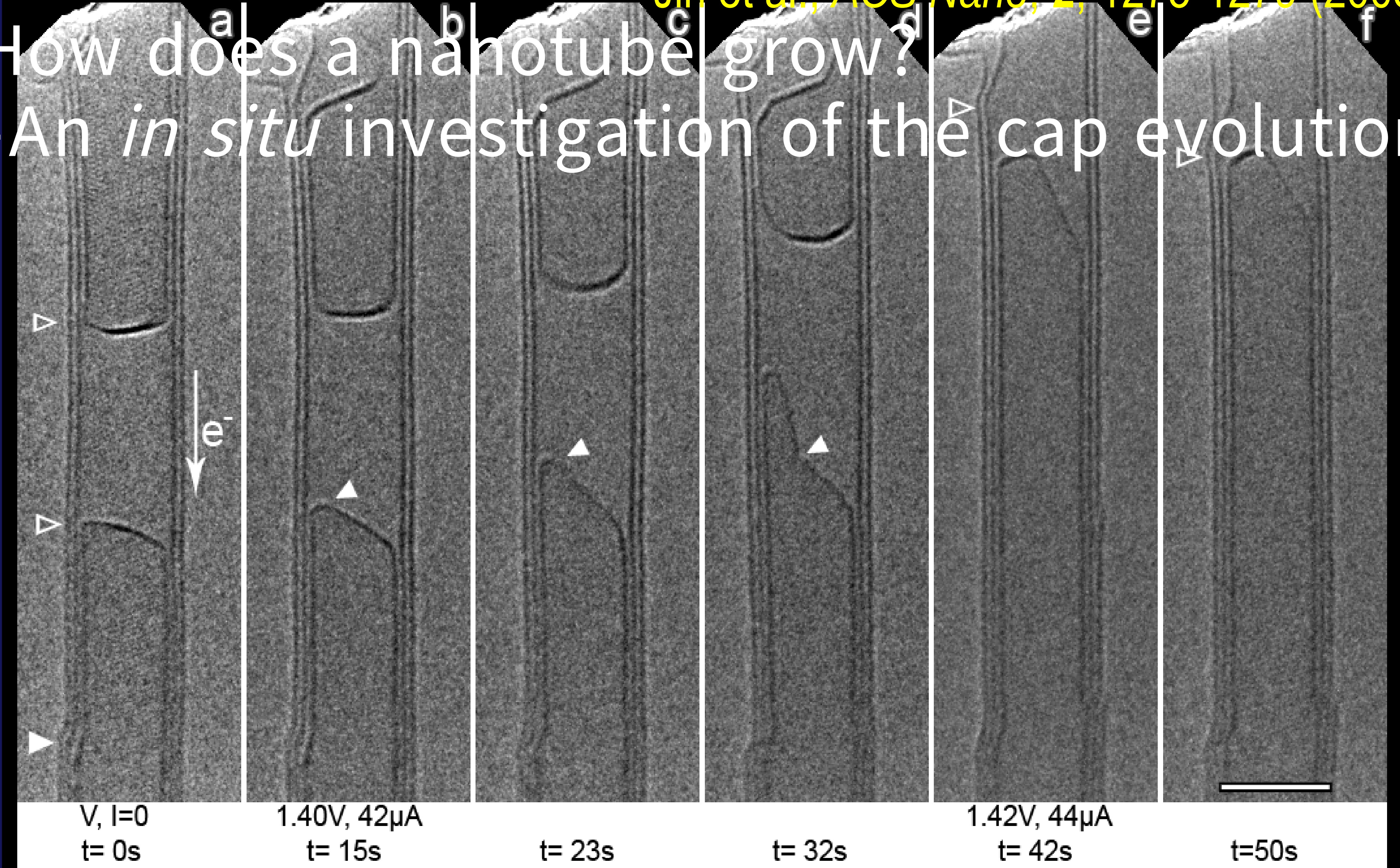
McKay

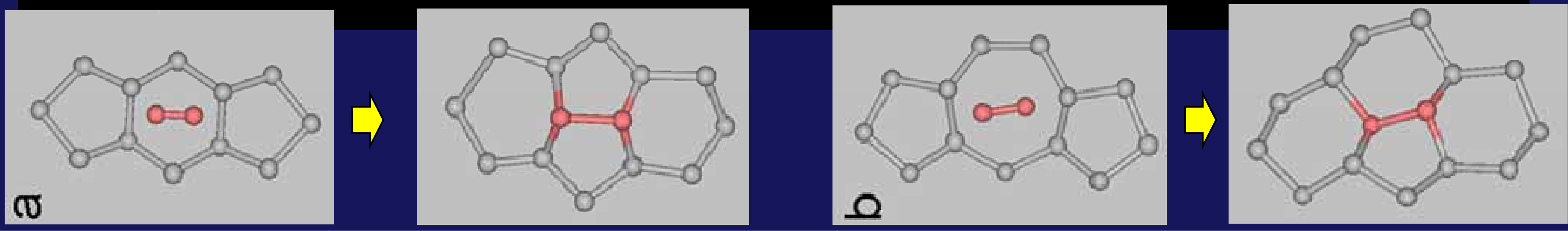




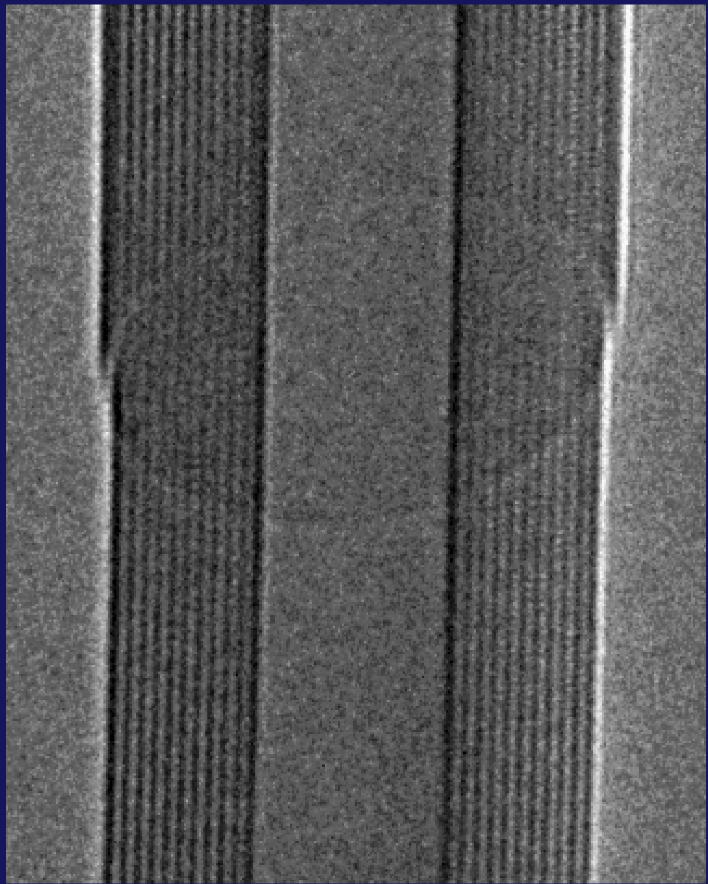
How does a nanotube grow?
-An *in situ* investigation of the cap evolution-

Jin et al., *ACS Nano*, **2**, 1275-1279 (2008)

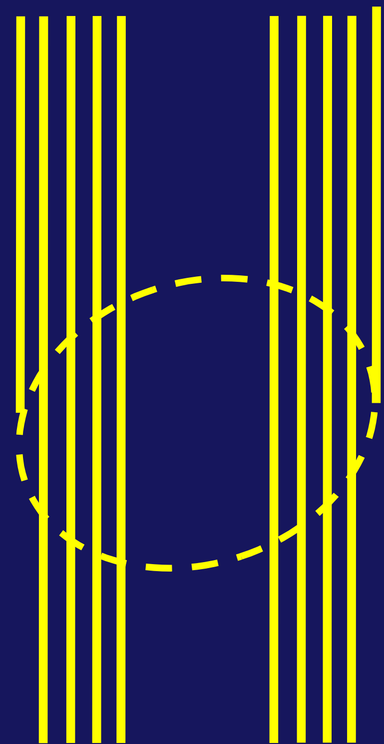


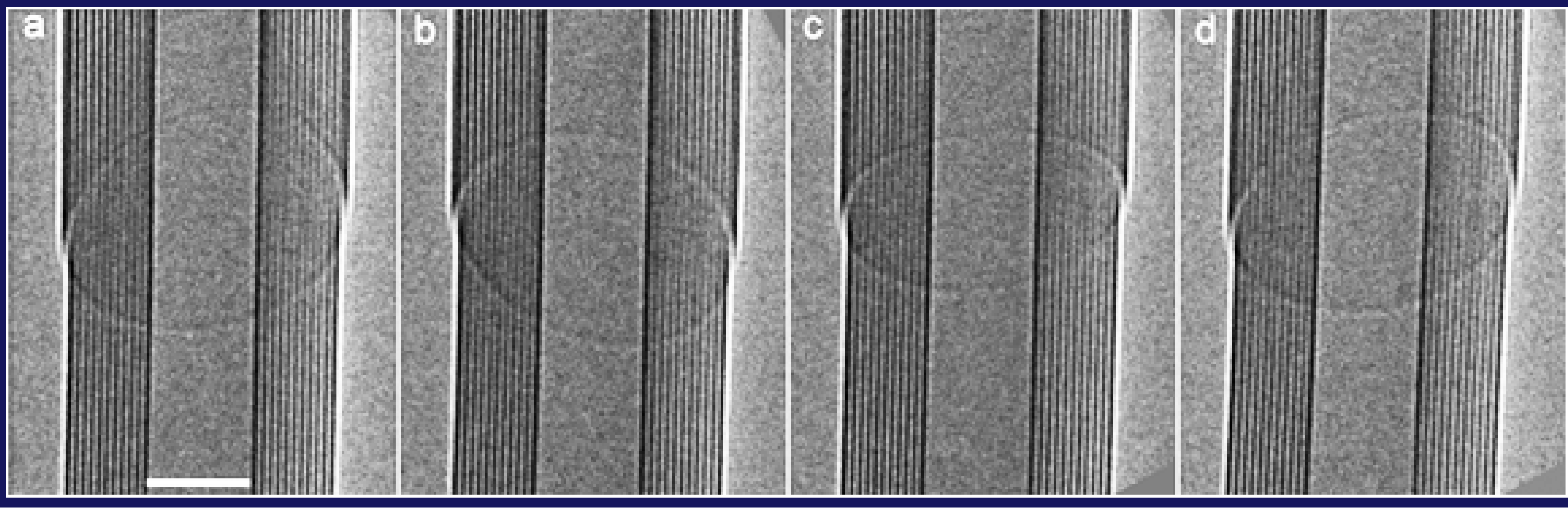


Instability of an open edge



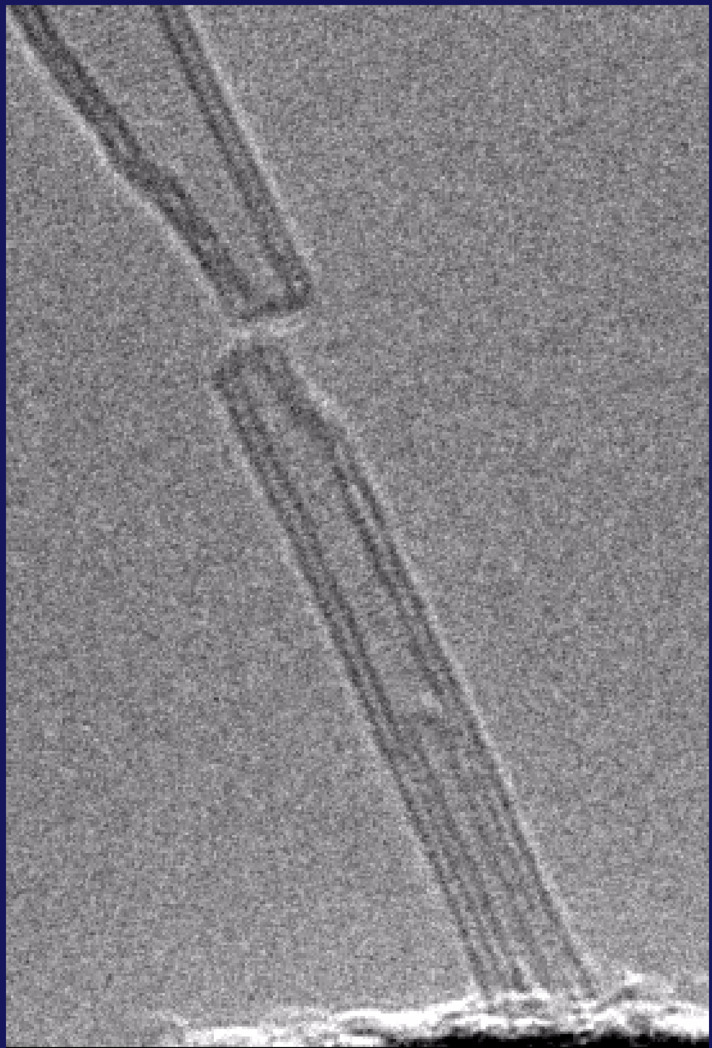
Chaunhong Jin, et al., *Nano Res.*, **1**, 434 (2008)

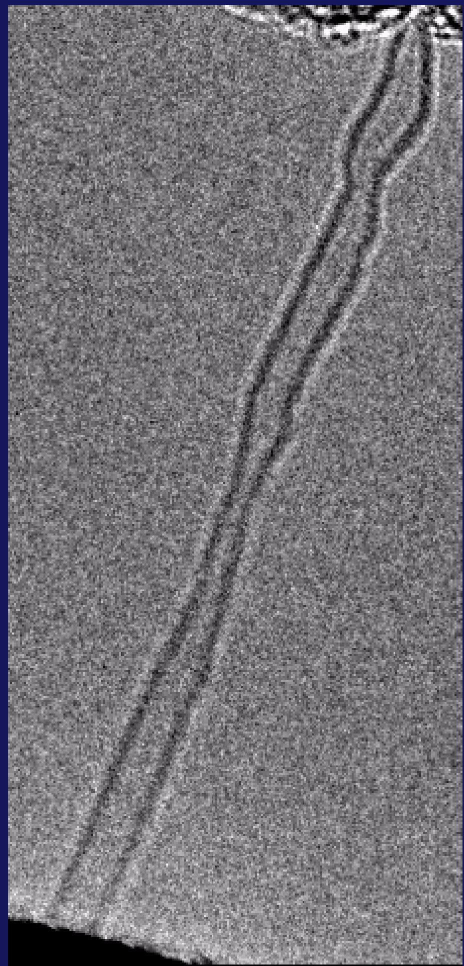


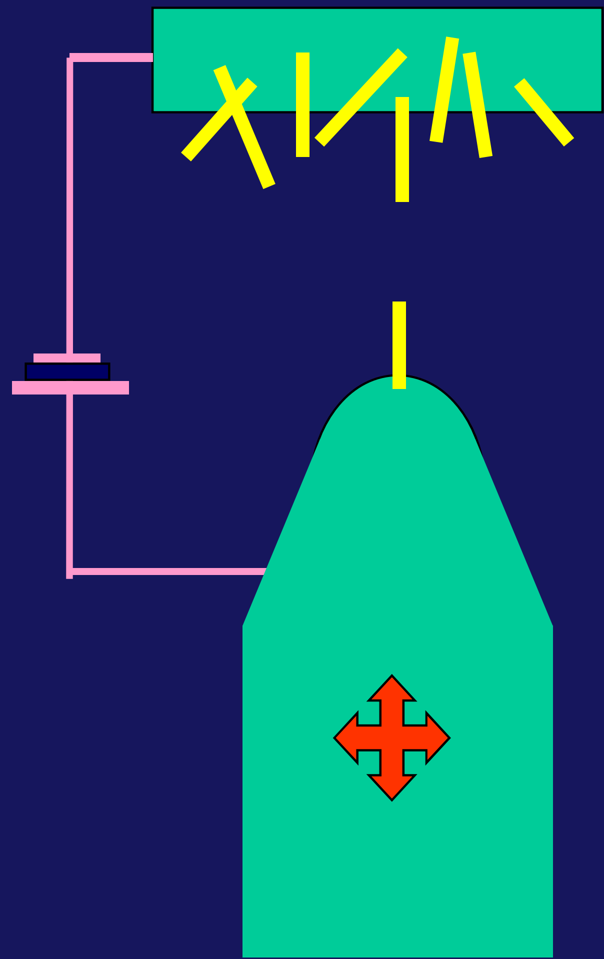


“Plumbing” of SWCNTs

C. Jin. et al., *Nature Nanotech*.,2007

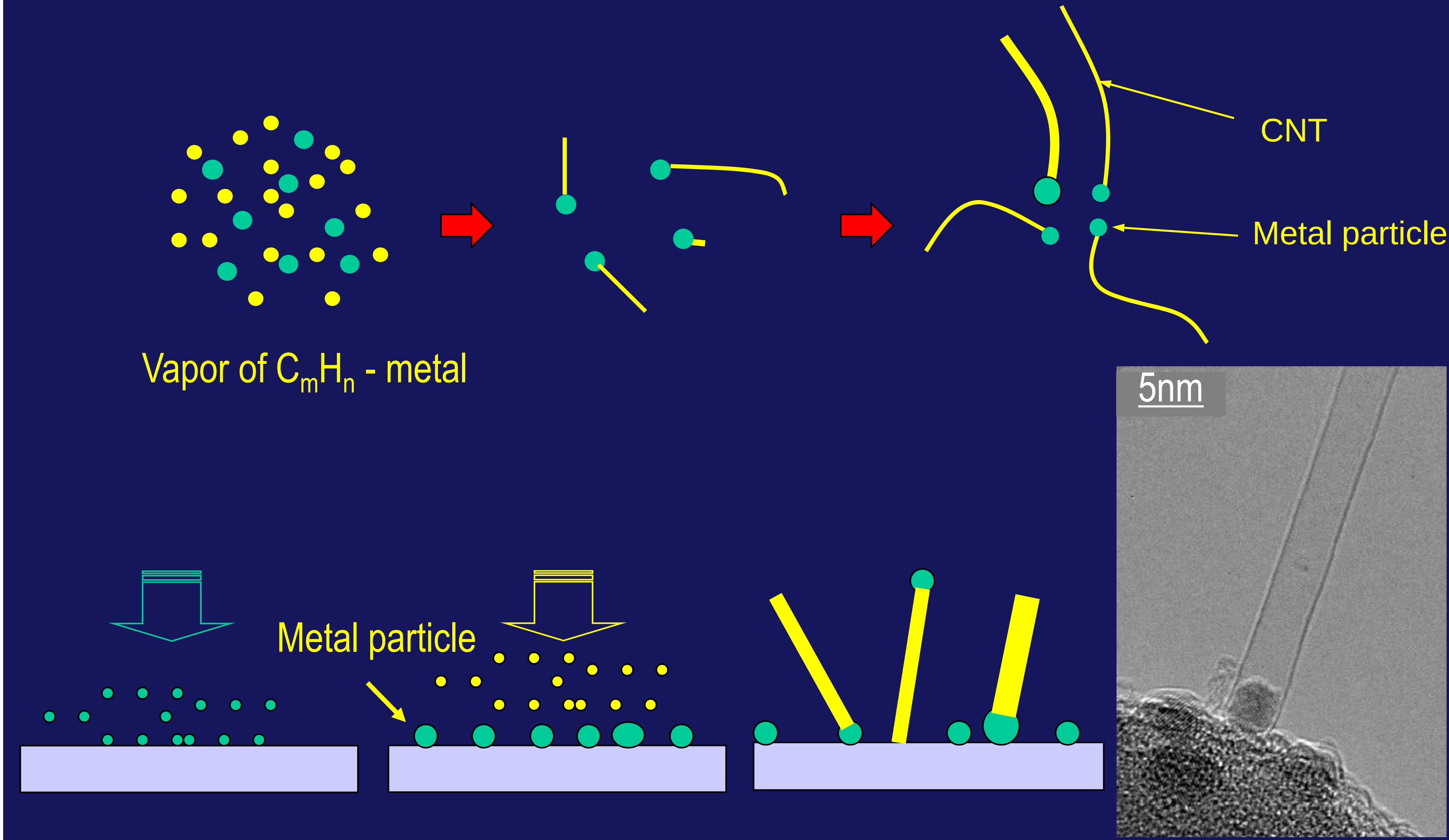






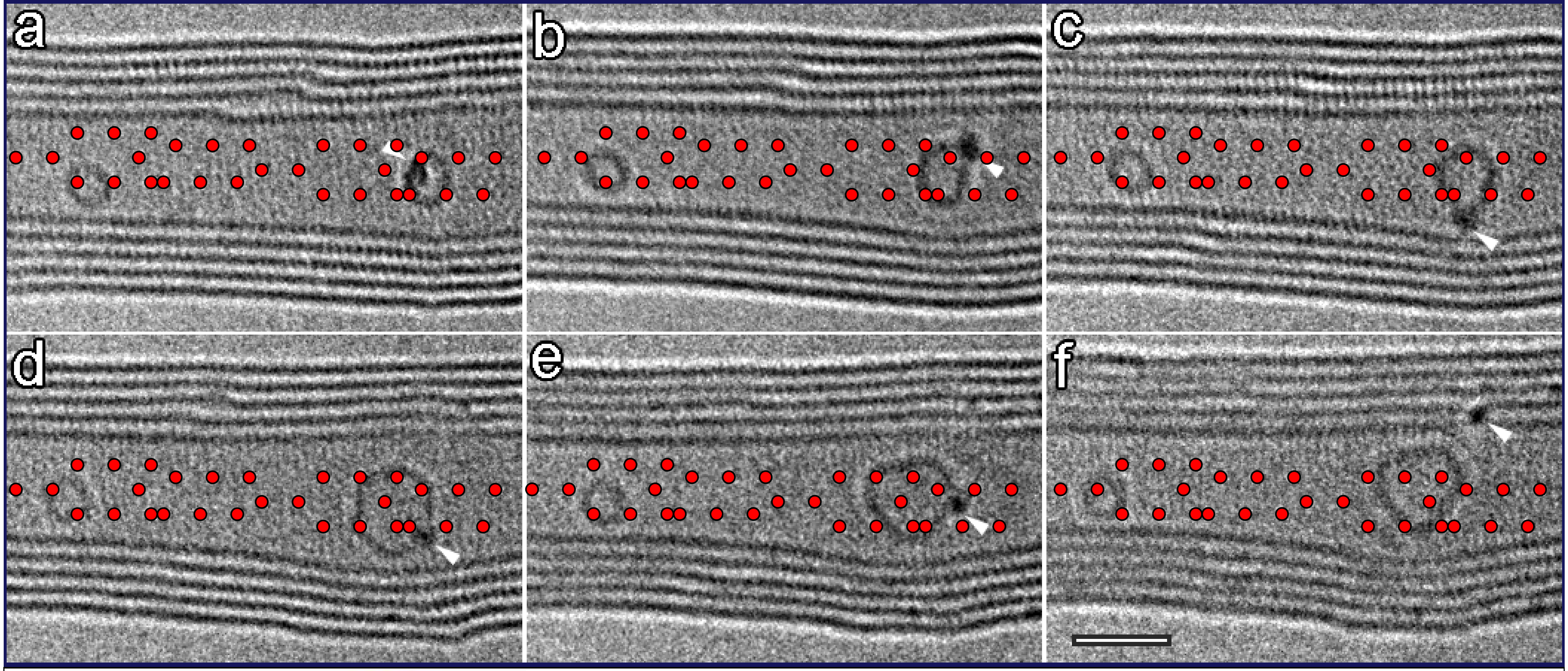
A role of metal catalysts

Catalyst-CVD growth of CNT

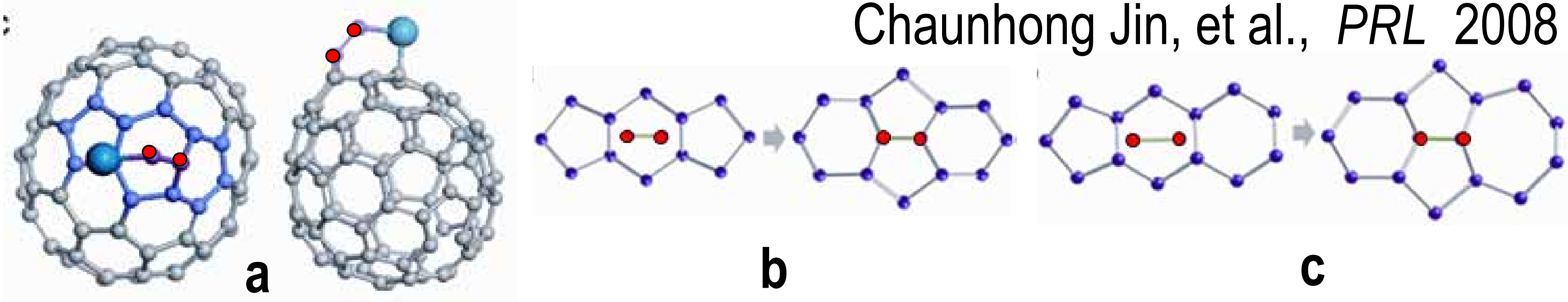


Hongwei et al. *Small*, 2005

Direct evidence of metal catalyst for fullerene growth



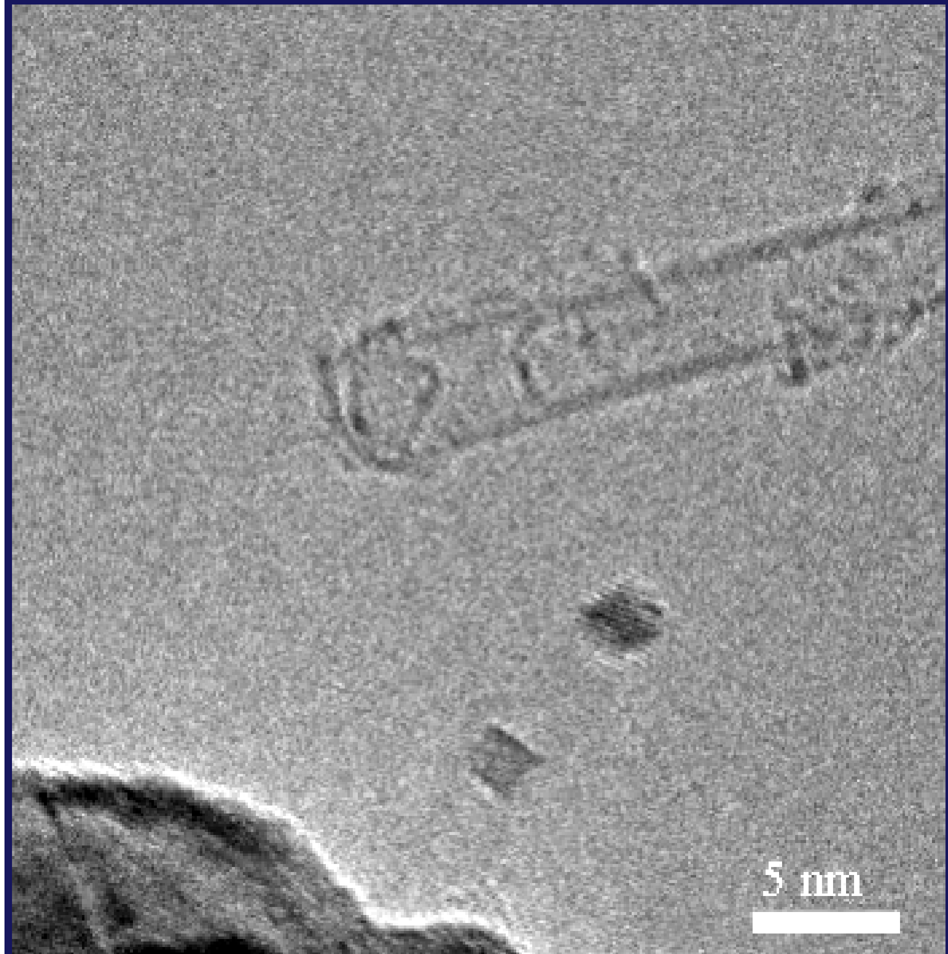
Chaunhong Jin, et al., *PRL* 2008

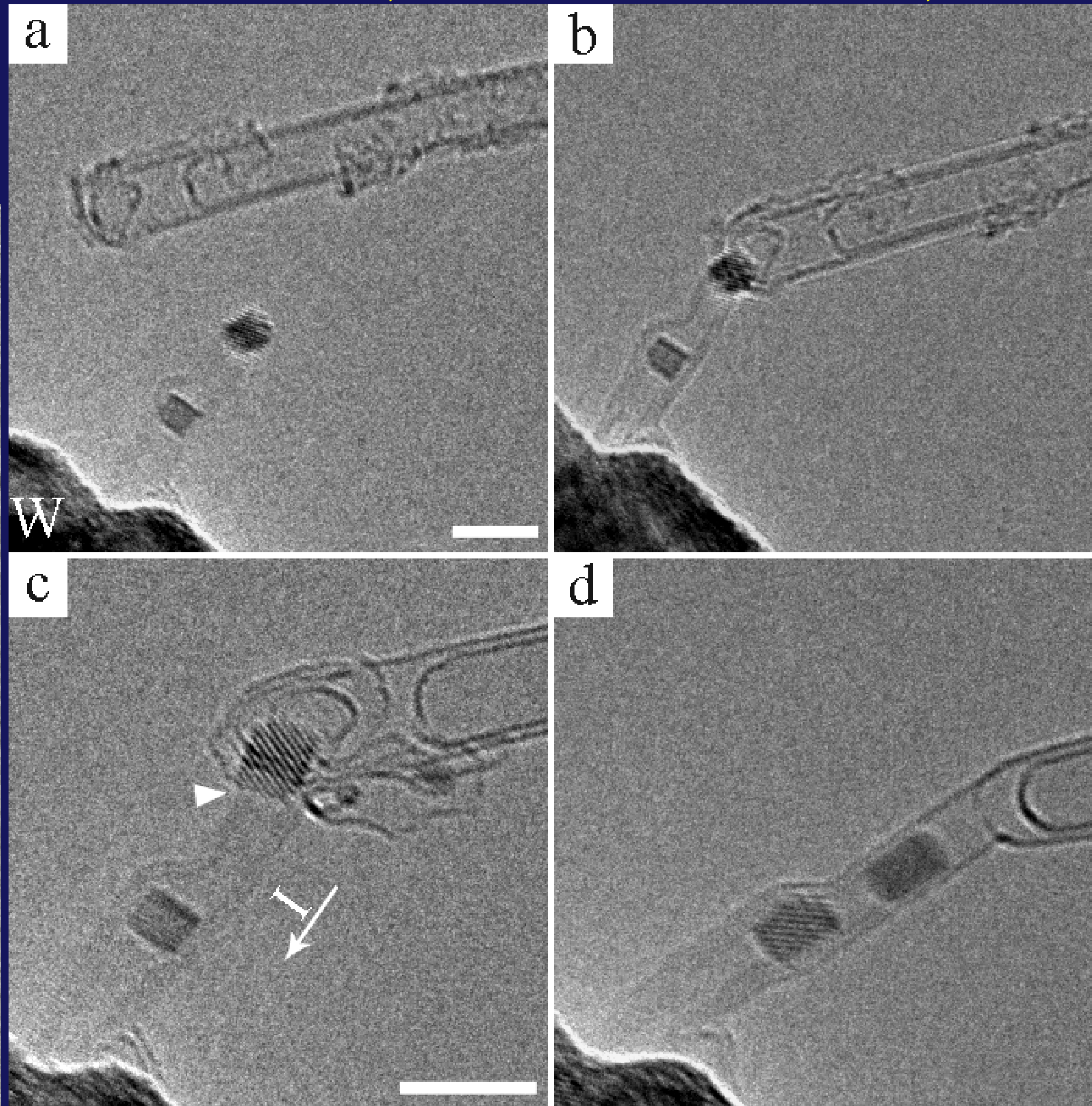


“Plumbing” of CNTs

C. Jin. et al., *Nature Nanotech*.,2007

A role of metal catalyst





With the assist of tungsten, two CNTs with completely different diameters and chiralities can also be seamlessly joined.

Outline

- **Reorganization of sp^2 carbon, and the tubule growth**
- **Synthesis of nano-carbon materials**

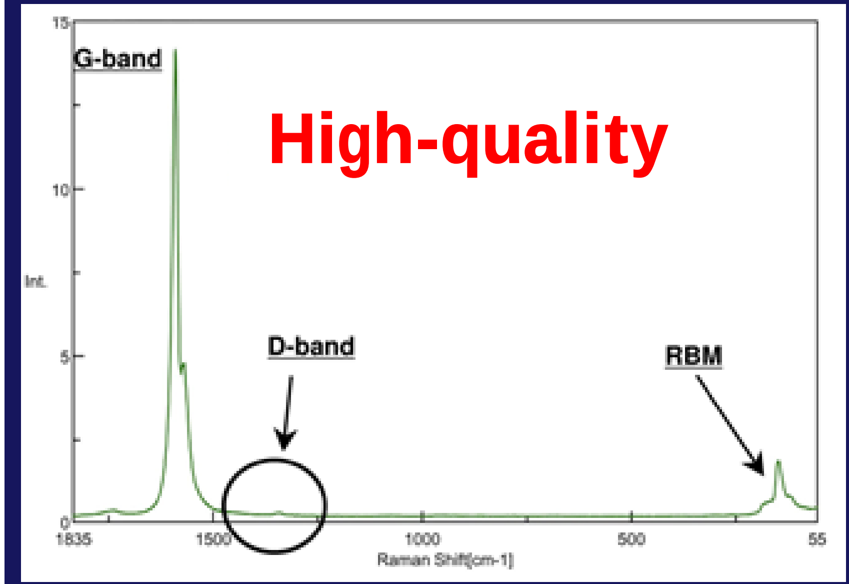
    Carbon nano-tubes (CNTs)

    Carbon nano-horns (CNHs)

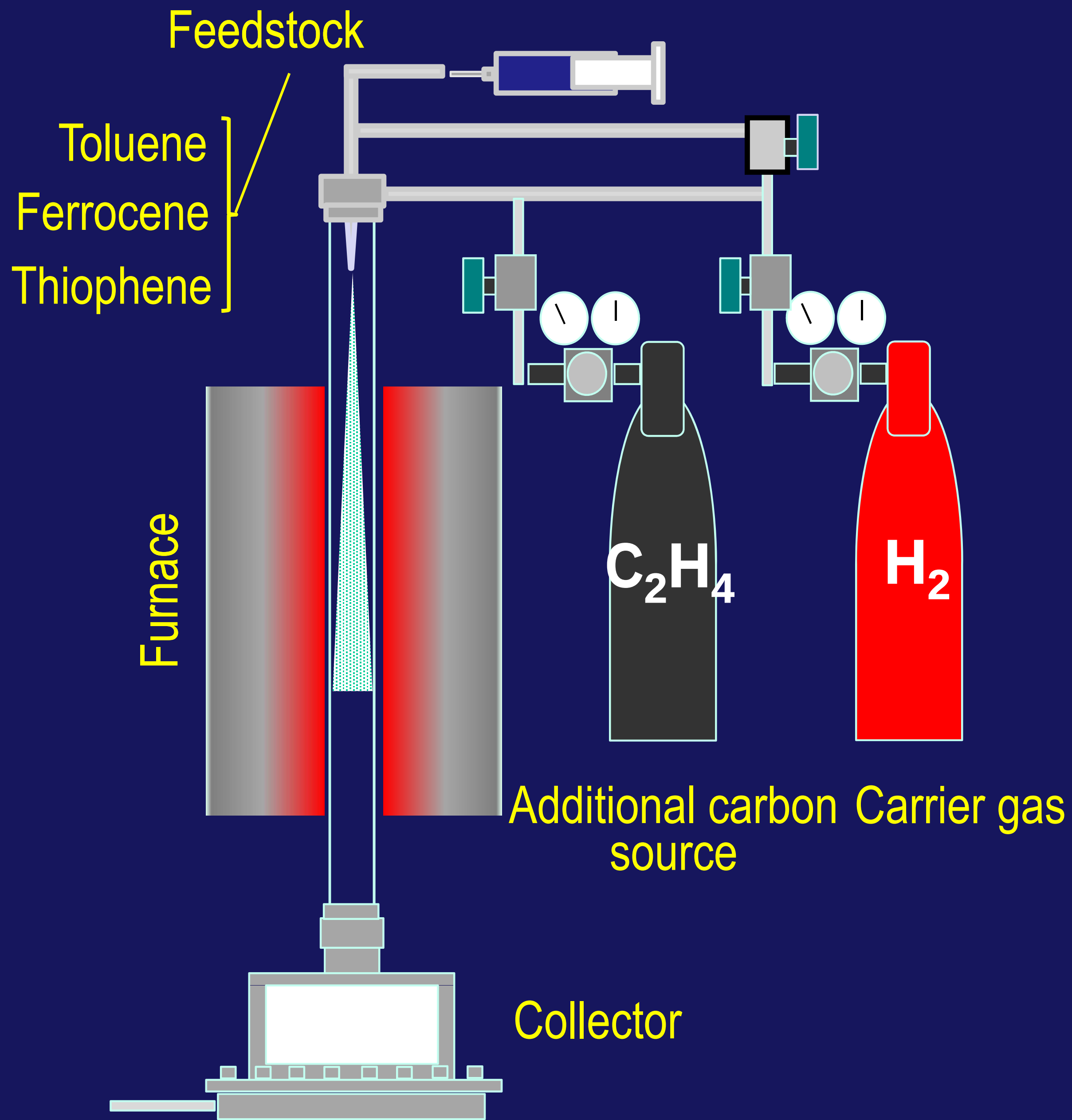
    Graphene sheets
- **HRTEM & EELS imaging of sp^2 carbon materials on individual atom basis**
- **Some applications of nanocarbon materials**

Enhanced Direct injection pyrolytic synthesis (eDIPS) method

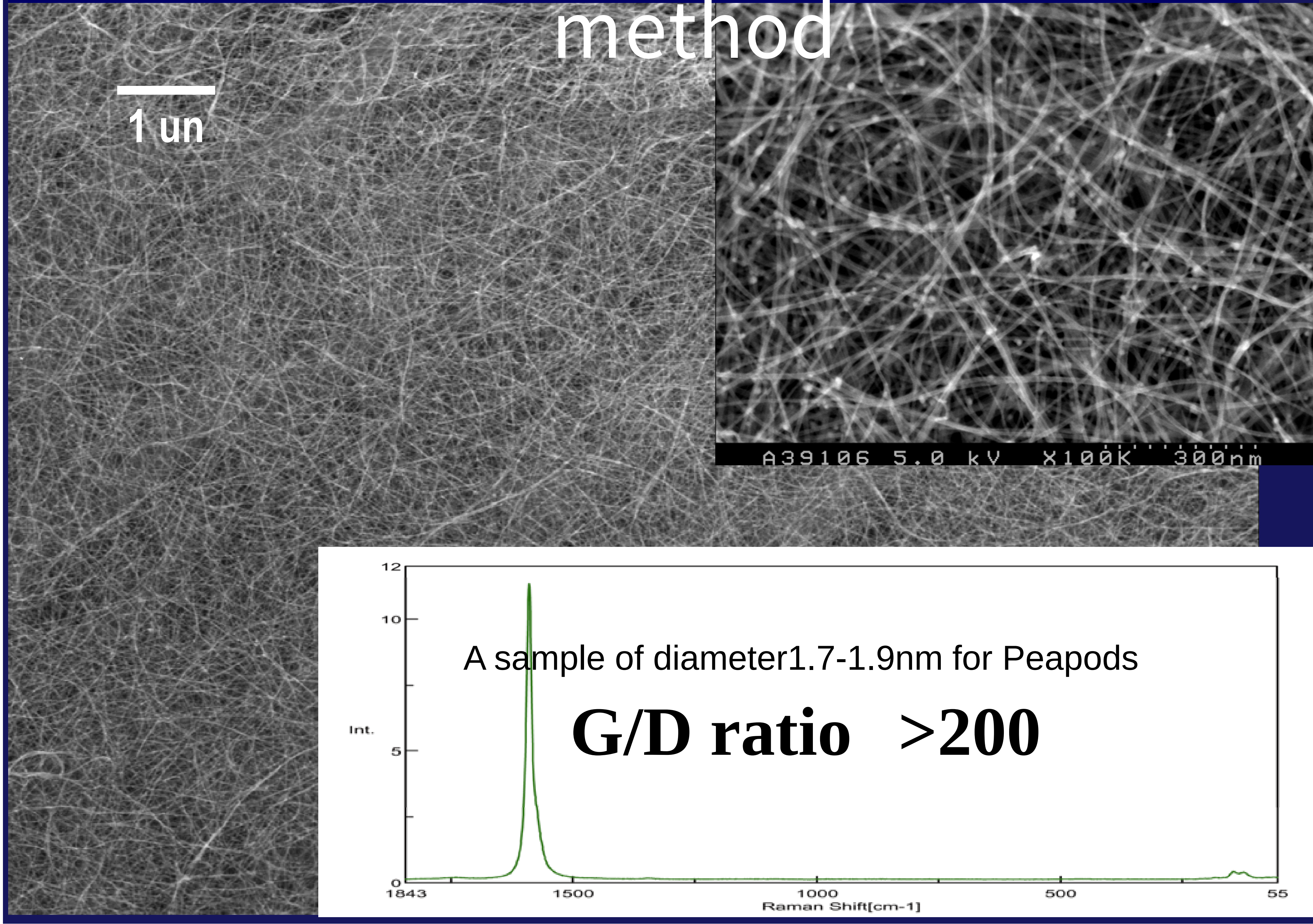
T. Saito et al., *Nihon Butsuri Gakkai-shi*, **62**, 591 (2007).



Scaling up for industry



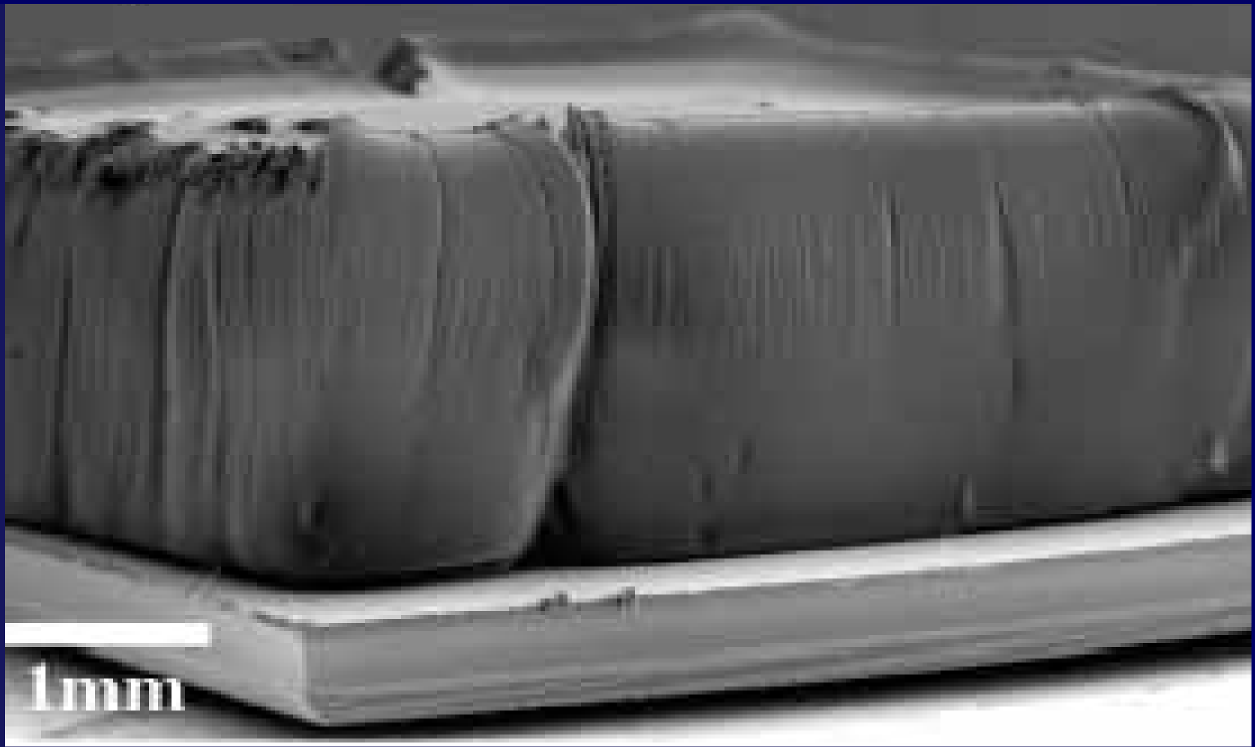
High purity SWCNTs by DIPS method



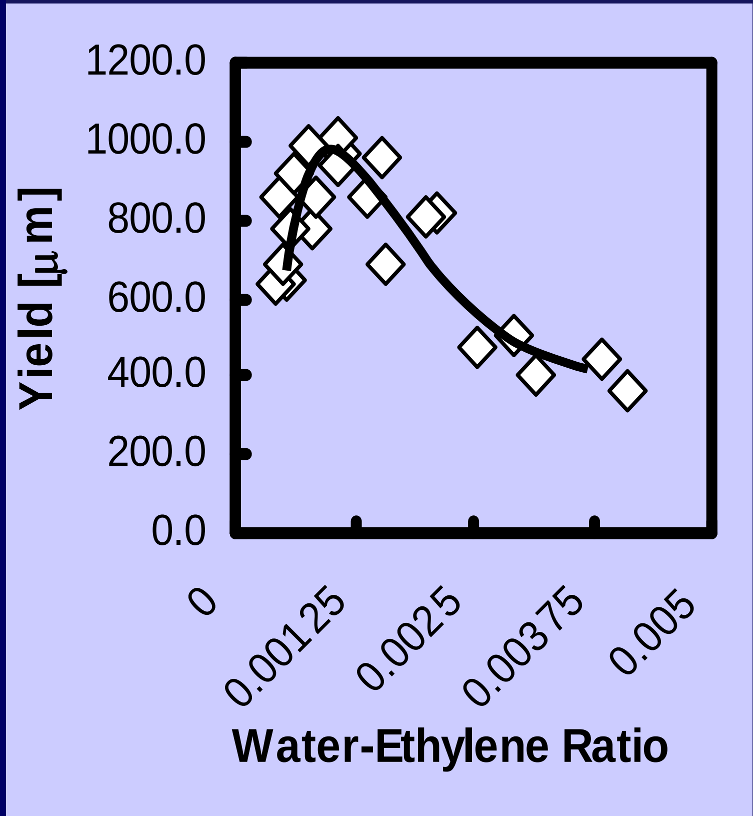
T. Saito, et al.,J.Phys.Chem. 2005

Super-Growth SWCNT technology

Hata et al. *Science* 2004



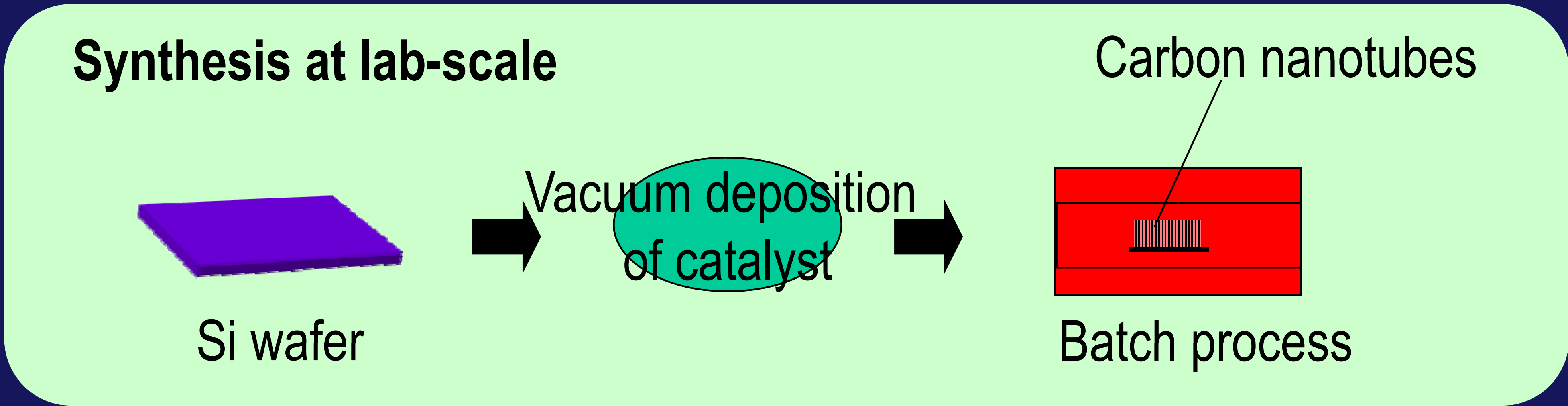
Futaba et al., *PRL* 2005

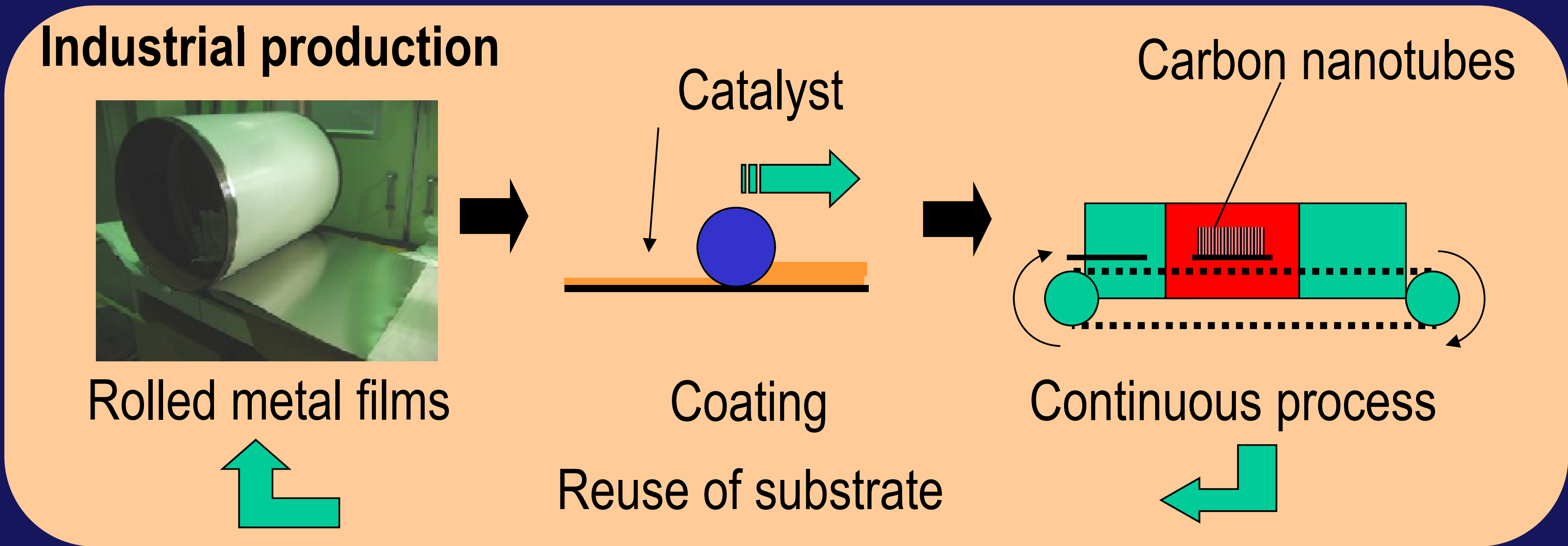


Substantial cost down and efficiency!

- Size: 2 x 2cm → $50\ X\ 50cm^2$
- Substrate: Si → Stainless steel foil
- Carrier gas: He + H_2 → N_2 + H_2

Large-scale production of SWCNTs





Large-scale CVD synthesis of SWCNT

2011

Sample will be supplied by AIST+ Nippon Zeon

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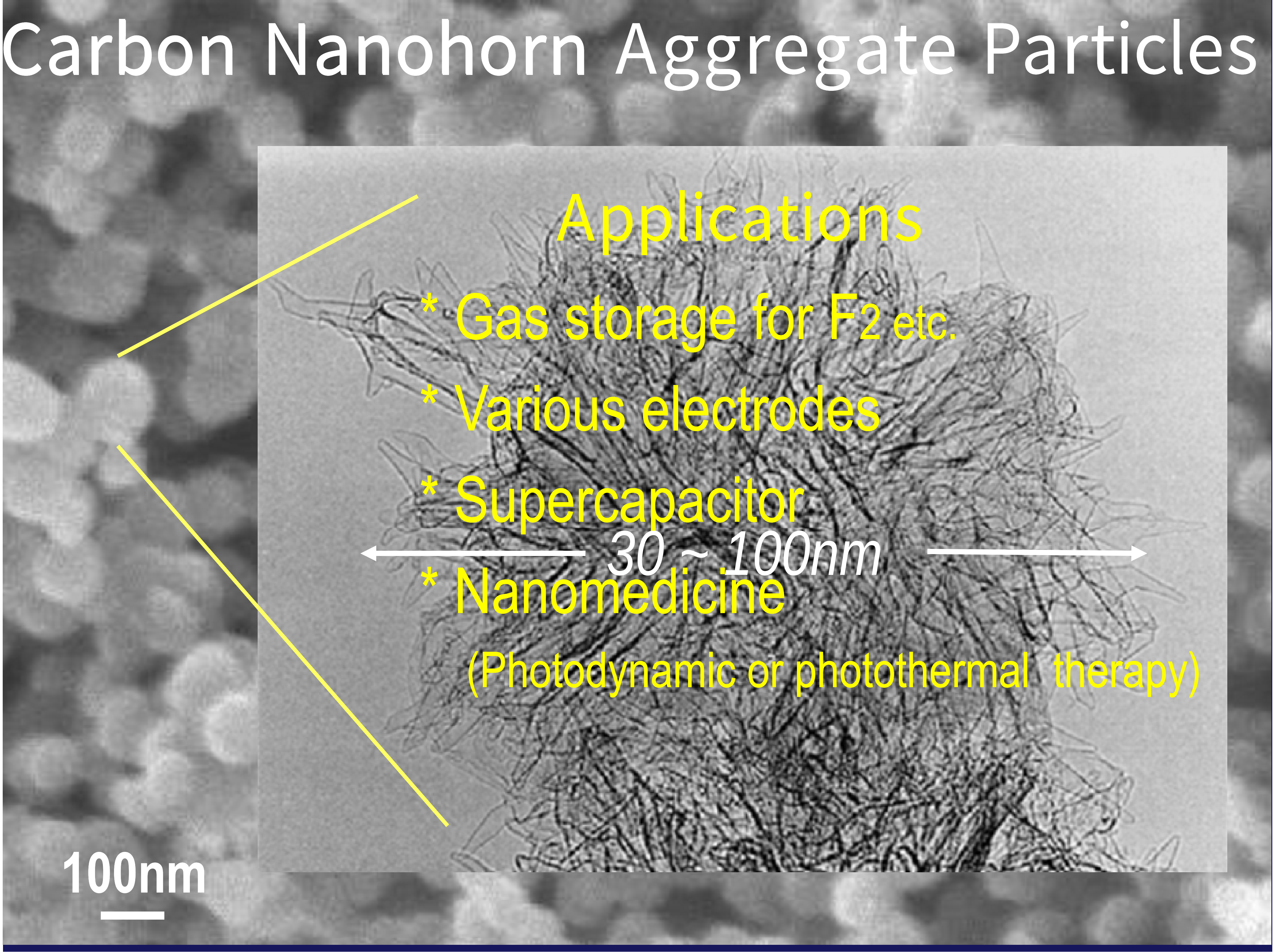
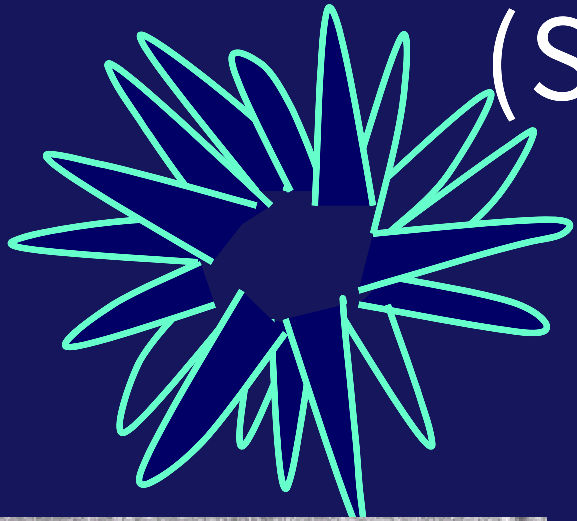
- **Synthesis of nano-carbon materials**
  - *Carbon nano-tubes (CNTs)*
  - *Carbon nano-horns (CNHs)*
  - *Graphene sheets*
- **HRTEM & EELS imaging of sp^2 carbon materials on individual atom basis**
- **Some applications of nanocarbon materials**


Carbon Nanohorn Aggregate Particles
Applications
* Gas storage for F2 etc.
* Various electrodes
* Supercapacitor
30 ~ 100nm
* Nanomedicine
(Photodynamic or photothermal therapy)
100nm

Single-Wall Carbon Nanohorn (SWCNH)

SWCNH

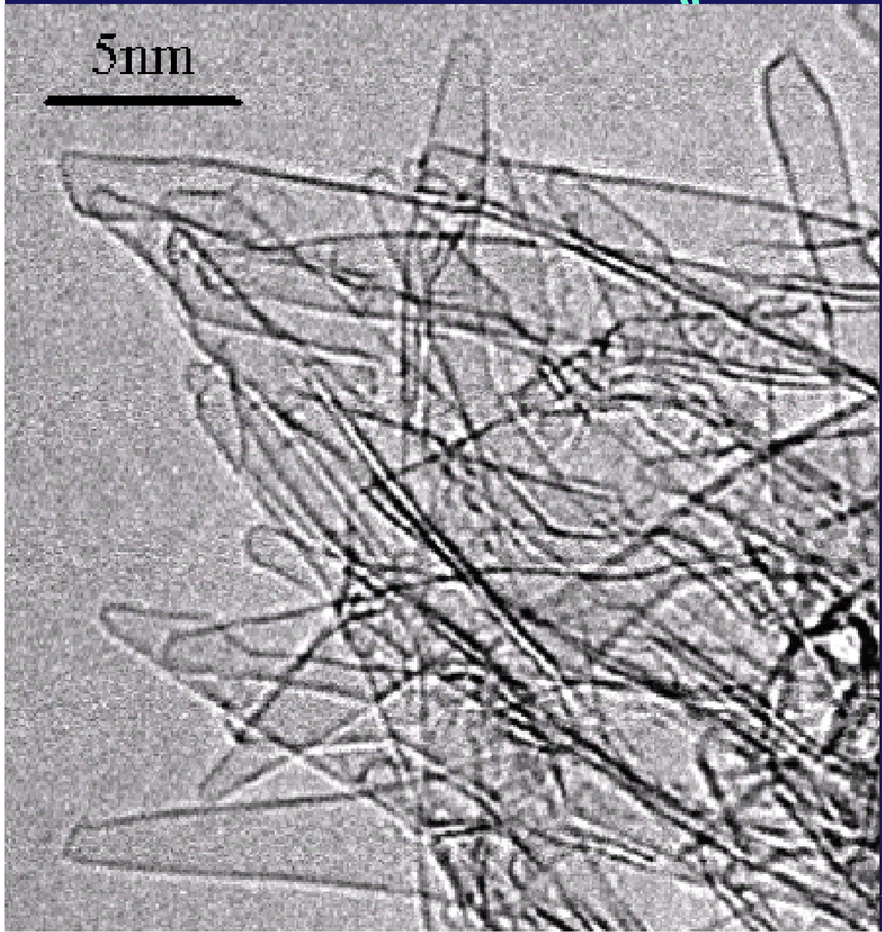


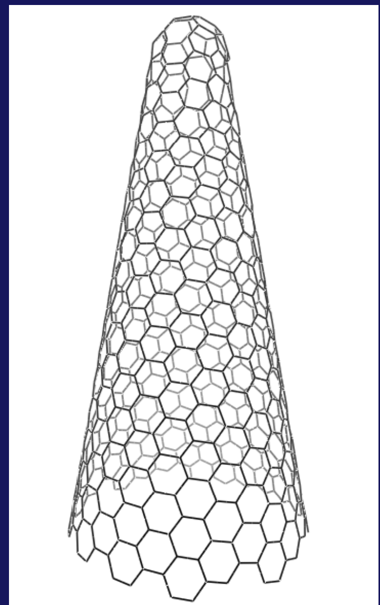
Nontoxicity!

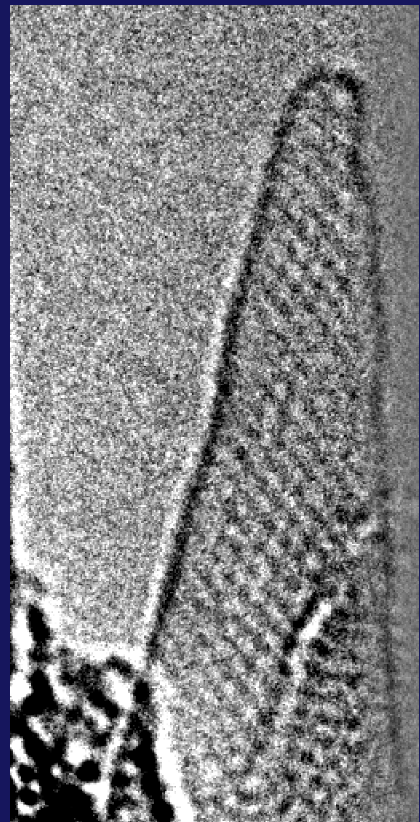
SWCNT

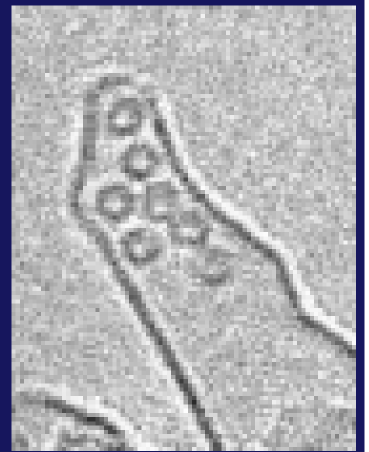
Toxicity :   < 0.03mg/m3

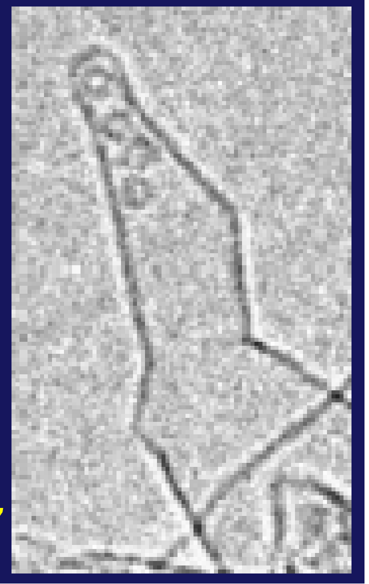
http://www.aist-riss.jp/main/modules/product/nano_rad.html









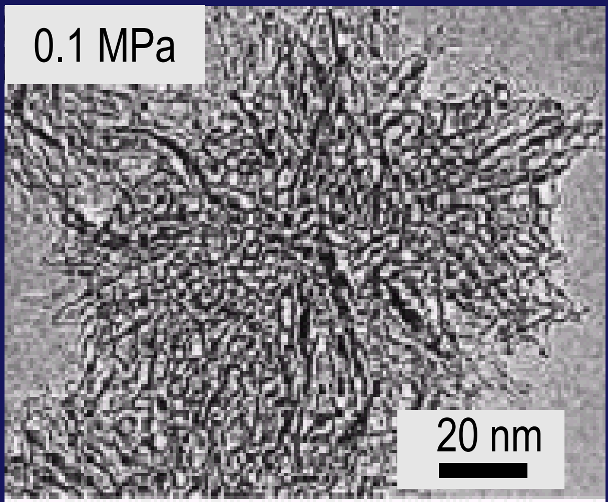


Ajima et al. Adv. Materials, 16 (2004) 397

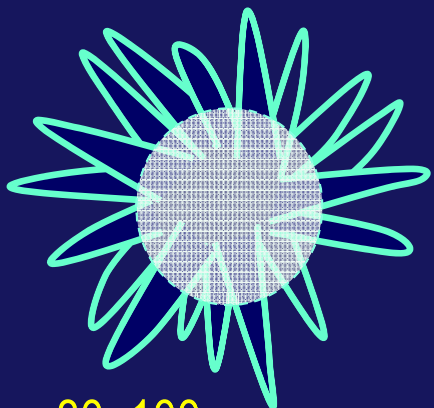
Nano-carbon Growth by CO_2 Laser Vaporization of graphite under Different Ar Gas Pressure Conditions

S. Iijima et al. CPL 309, 165 (1999), F. Kokai et al. Appl. Phys. A 77, 69 (2003)

Single-wall carbon nanohorn particles

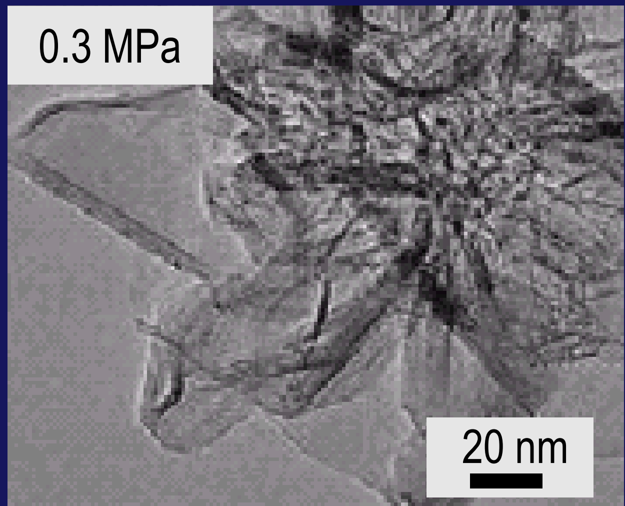


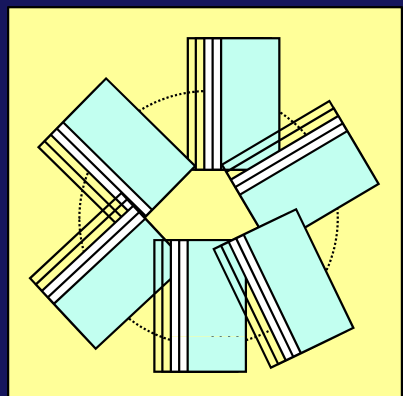
>90 % yield (100 g/h at NEC)



80–100 nm

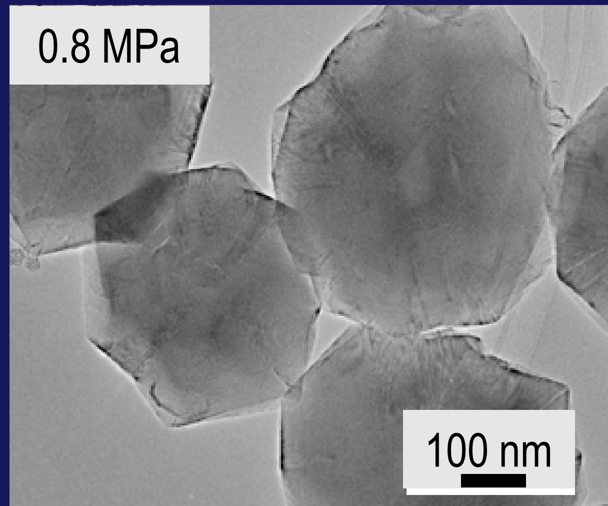
Platelet graphite particles



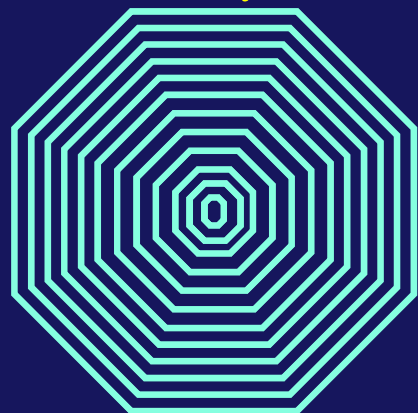


190–350 nm

Polyhedral graphite (PG) particles



>90 % yield



100–500 nm (Mean: 300 nm)

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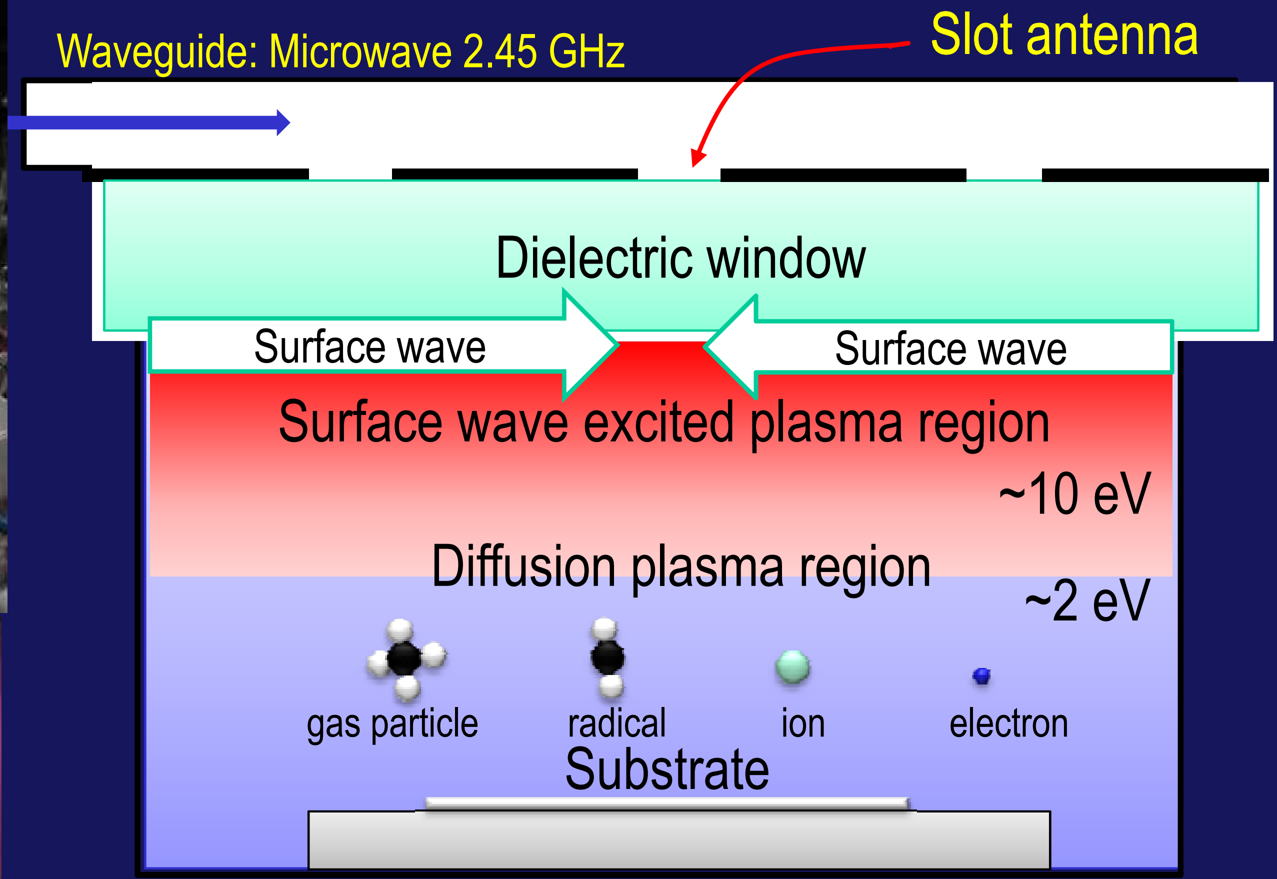
Large-area low-temperature SWP-CVD for graphene film synthesis

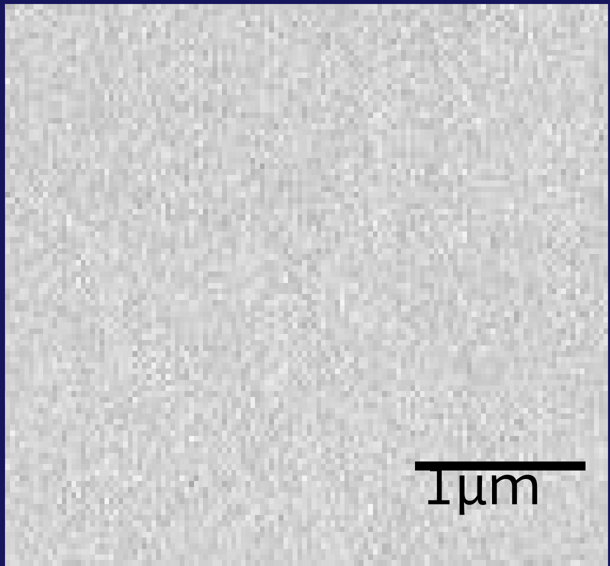
CVD area: 60 cm × 40 cm



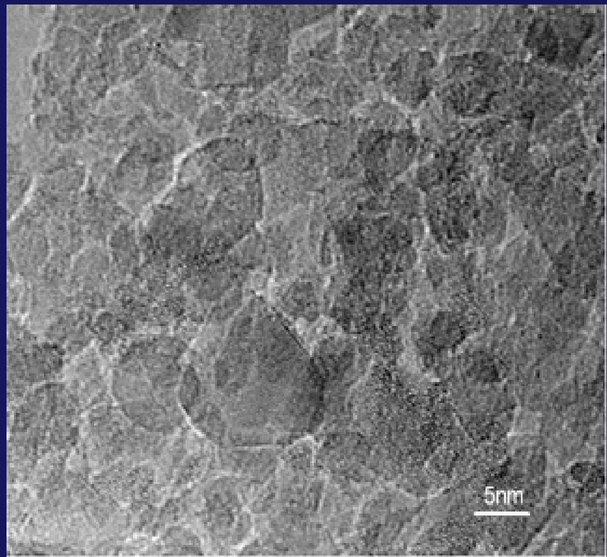
- MW power: 3-5 kW per a MW generator
- Gas: H_2/CH_4 /Ar
- Substrate: Cu (t30 μm) and Al (t12 μm) foils
- Gas pressure: 3-5 Pa
- Substrate temperature: below 400 ℃
- Deposition time: 30-180 s

Nano-crystalline diamond films with extremely smooth surface

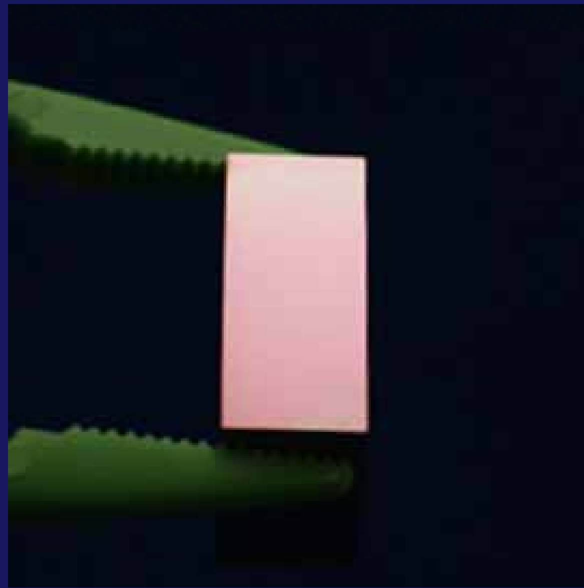
Hasegawa et al., *PRB*, 2010



SEM image



TEM image (Grain size: ～5nm)

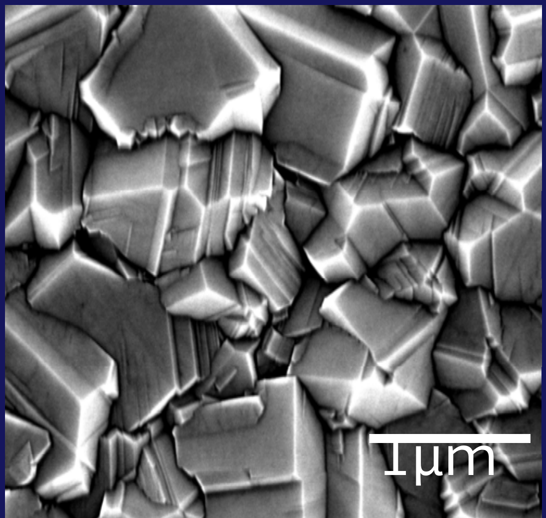


Metal (370℃)

Stainless steel, Cu, Fe

Al, Ti, Mo, WC(Co)

Si



A conventional diamond film

Glass (400℃)

Borosilicate glass

Soda-lime glass

Quartz

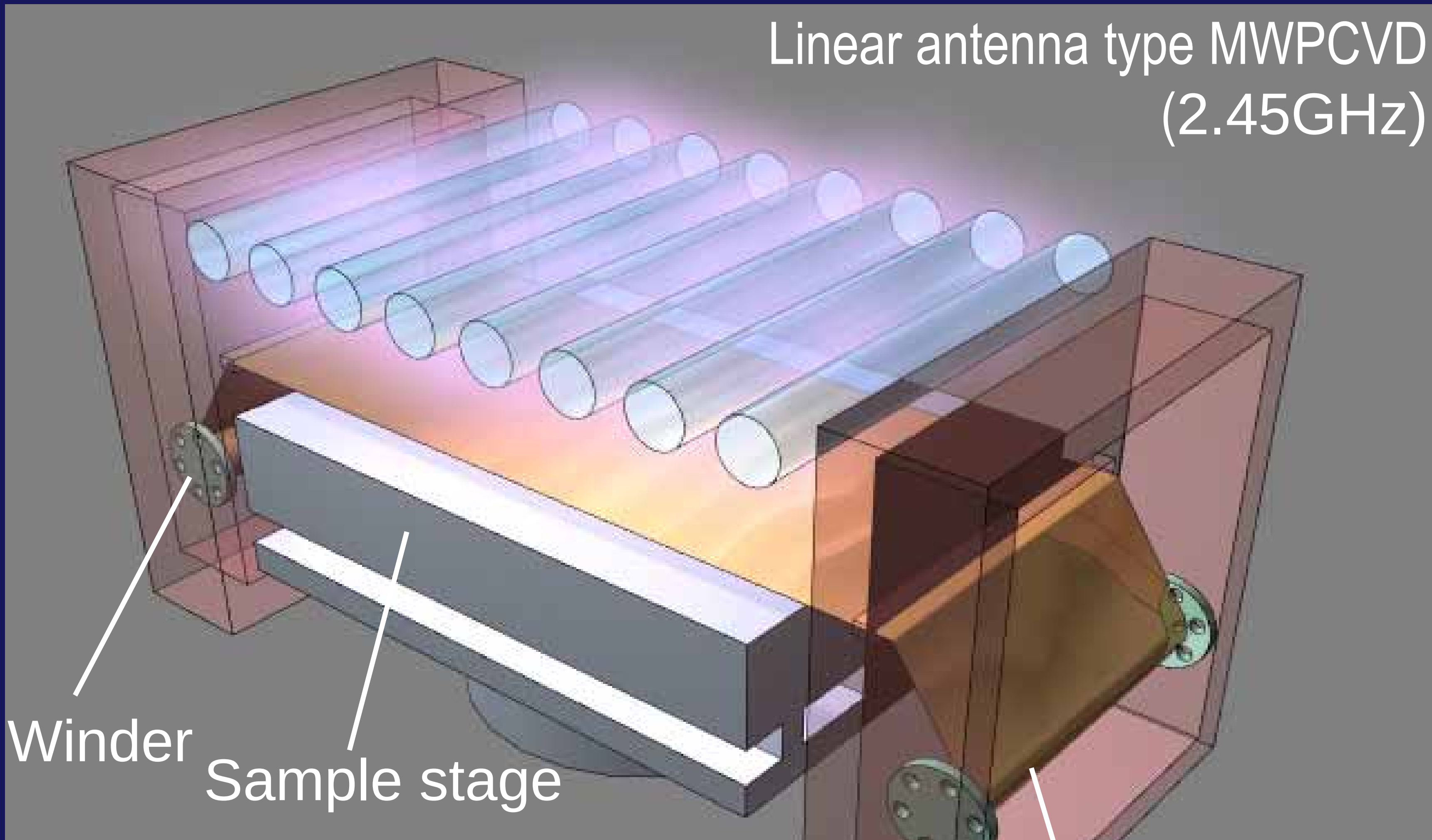
Sapphire

Plastic (100℃)

PPS

Polycarbonate

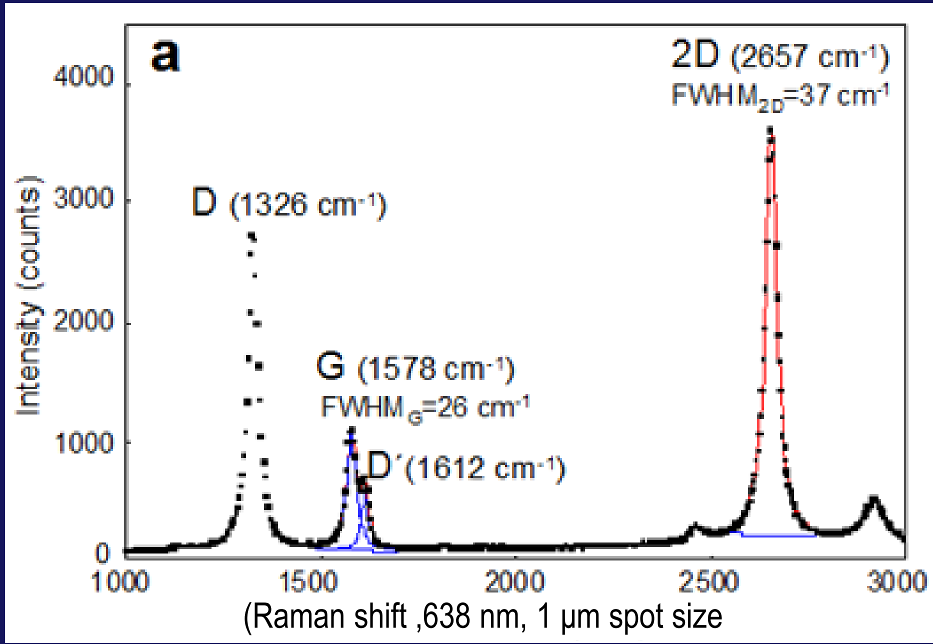
Graphene R2R System in SWP-CVD



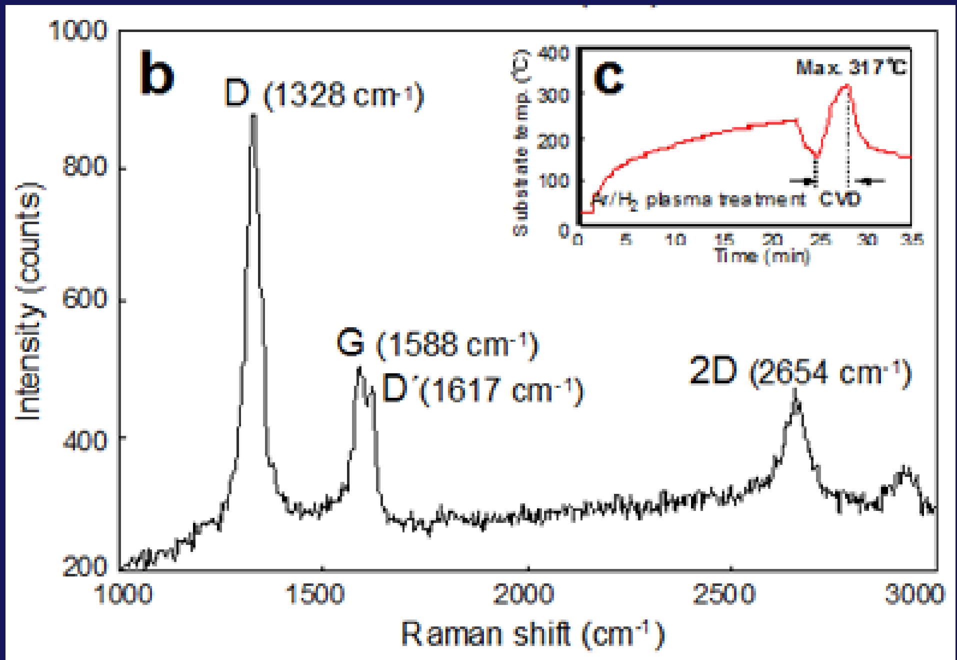
$CH_4/(CH_4+H_2)$ [%]	10~70
Pressure [Pa]	30~500
Temperature [ºC]	350~380
Flow speed [mm/s]	2~10

Characteristics of graphene-based films as transparent electrodes

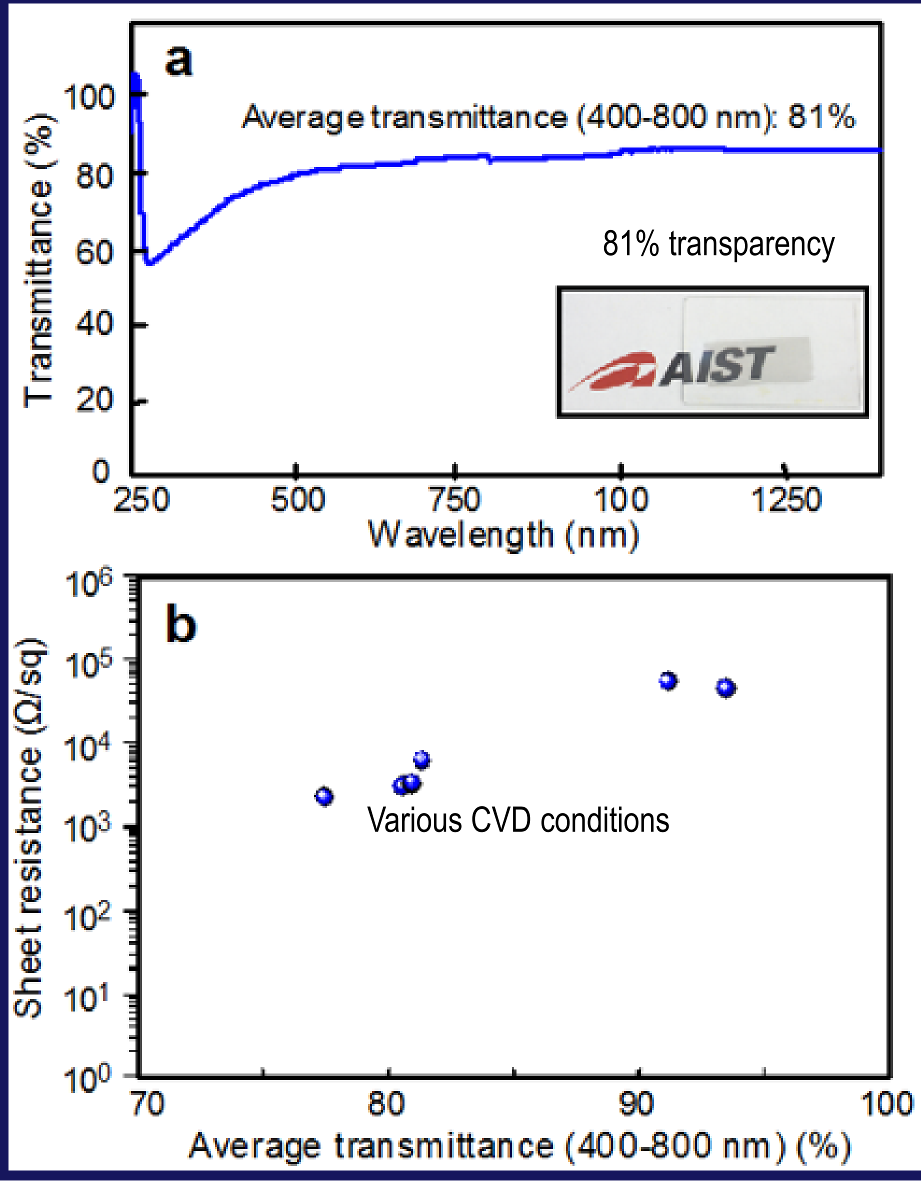
Hasegawa et al., JAP, 2010



(a) Cu foil (CVD conditions: 5 Pa, $CH_4/Ar/H_2$=30/20/10 sccm, 3 kW per a MW generator, 30 s) substrate temperatures below 400 ˚C



(b) Al foil (CVD conditions: 3 Pa, $CH_4/Ar/H_2$=30/20/10 sccm, 4 kW, 180 s).
(c) Substrate temperature profile.



Formation of various sp^2 carbon

Methods \ Types	SWCNT	MWCNT	Nano-horn	Fullerene	Amorphous	Graphene
Arc	×	○	○	○	○	×
Arc (Cat.)	○	○	×	○	○	×
Laser	×	×	○	○	○	×
Laser (Cat.)	○	○	×	○	○	×
CVD (Pyrol.)	×	×	×	×	○	×
CVD (Cat.)	○	○	×	×	○	○
CVD (Plas.+Cat.)	○	○	×	-	○	○

Summary

- **Reorganization of sp^2 carbon, and the tubule growth**
- **Synthesis of nano-carbon materials**

  Carbon nano-tubes (CNTs)

  Carbon nano-horns (CNHs)

  Graphene sheets
- **HRTEM & EELS imaging of sp^2 carbon materials on individual atom basis**
- **Some applications of nanocarbon materials**