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

# Nanocarbon Materials: Synthesis and Structure Characterizations (II)

Sumio Iijima

AIST / Nanotube Research Center
Meijo University
NEC

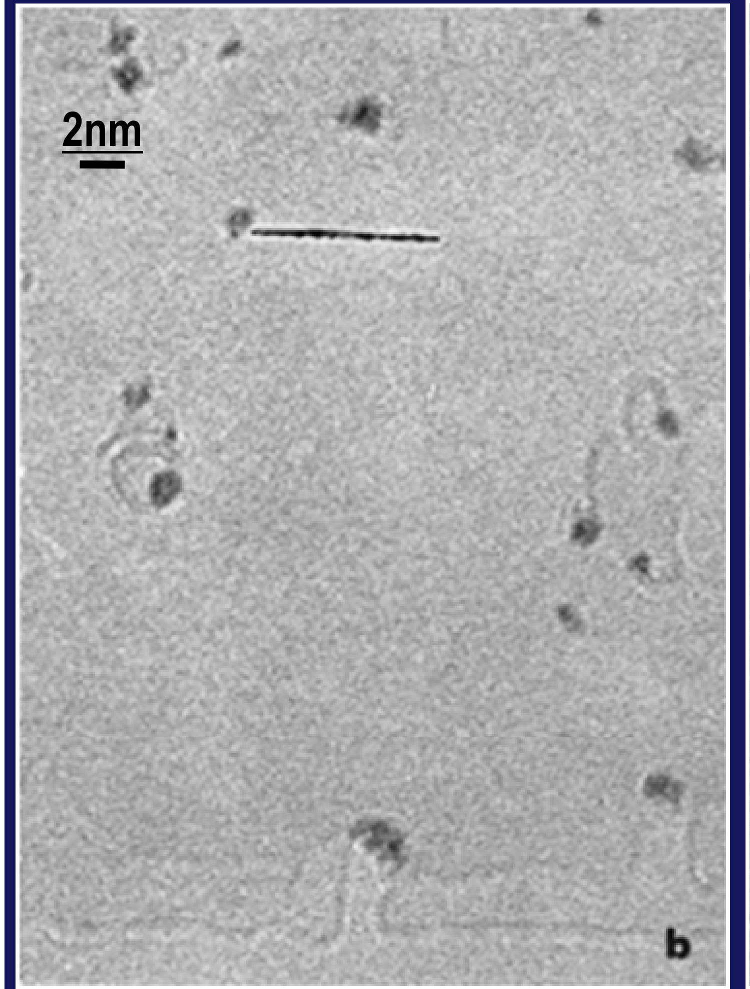
http://nanocarb.meijo-u.ac.jp/jst/iijima.html

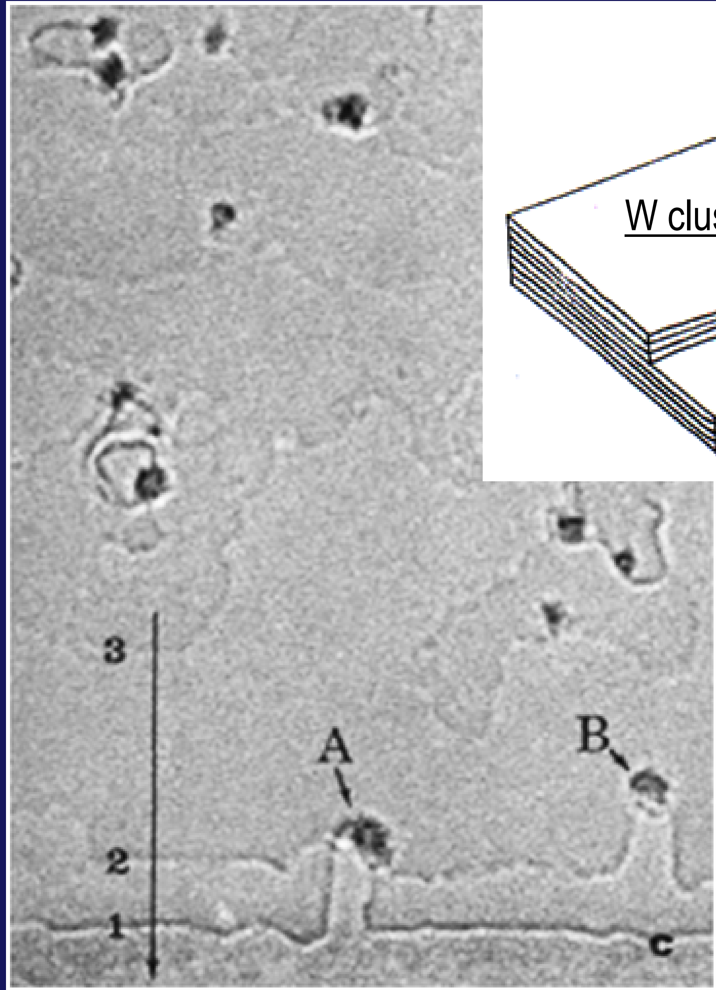
# Outline

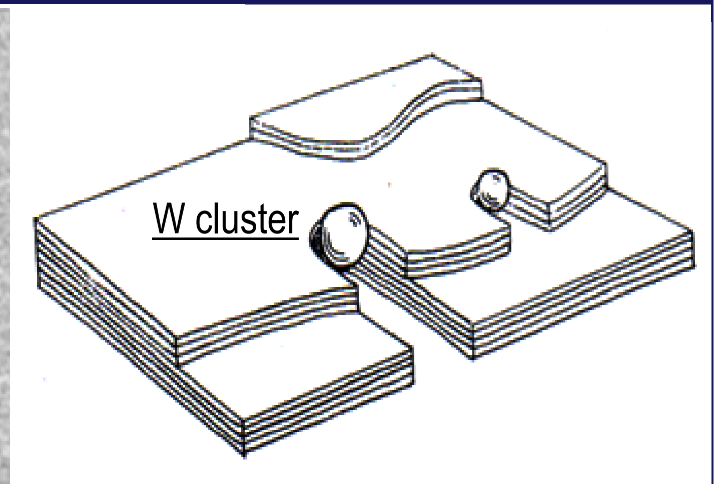
- Reorganization of $sp^2$ carbon, and the tubule growth
- Synthesis of nano-carbon materials
  - *Carbon nano-tubes (CNTs)*
  - *Carbon nano-horns (CNHs)*
  - *Graphene sheets*
- **HRTEM & EELS imaging of $sp^2$ carbon materials on individual atom basis**
- Some applications of nanocarbon materials

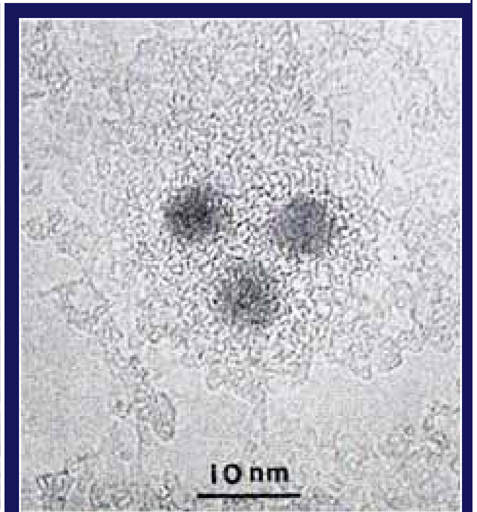
# Thin graphite film (graphene) for supporting HRTEM specimens

Iijima, *Micron*, **8**, 41-46 (1978)



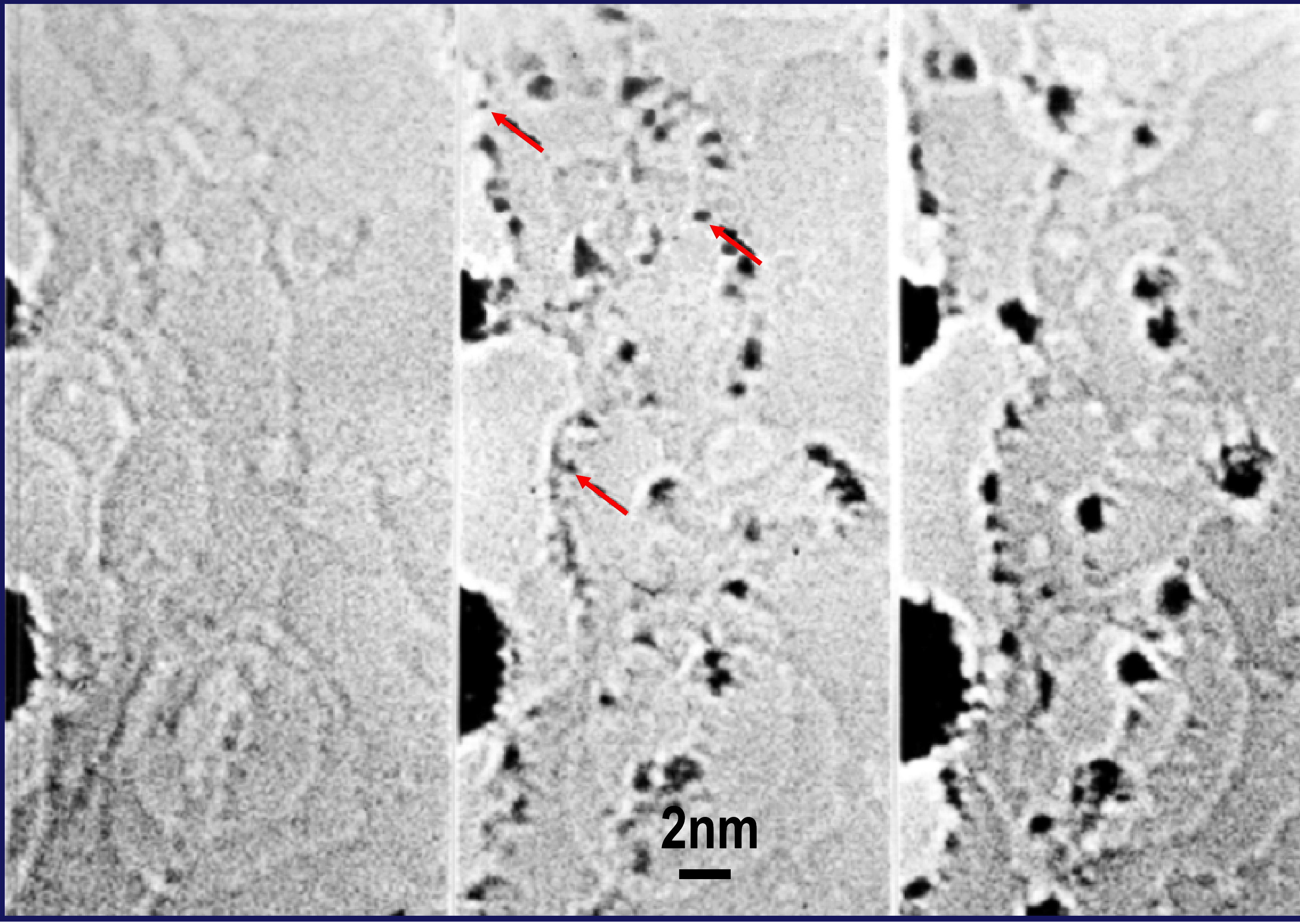




Apoferritin molecules

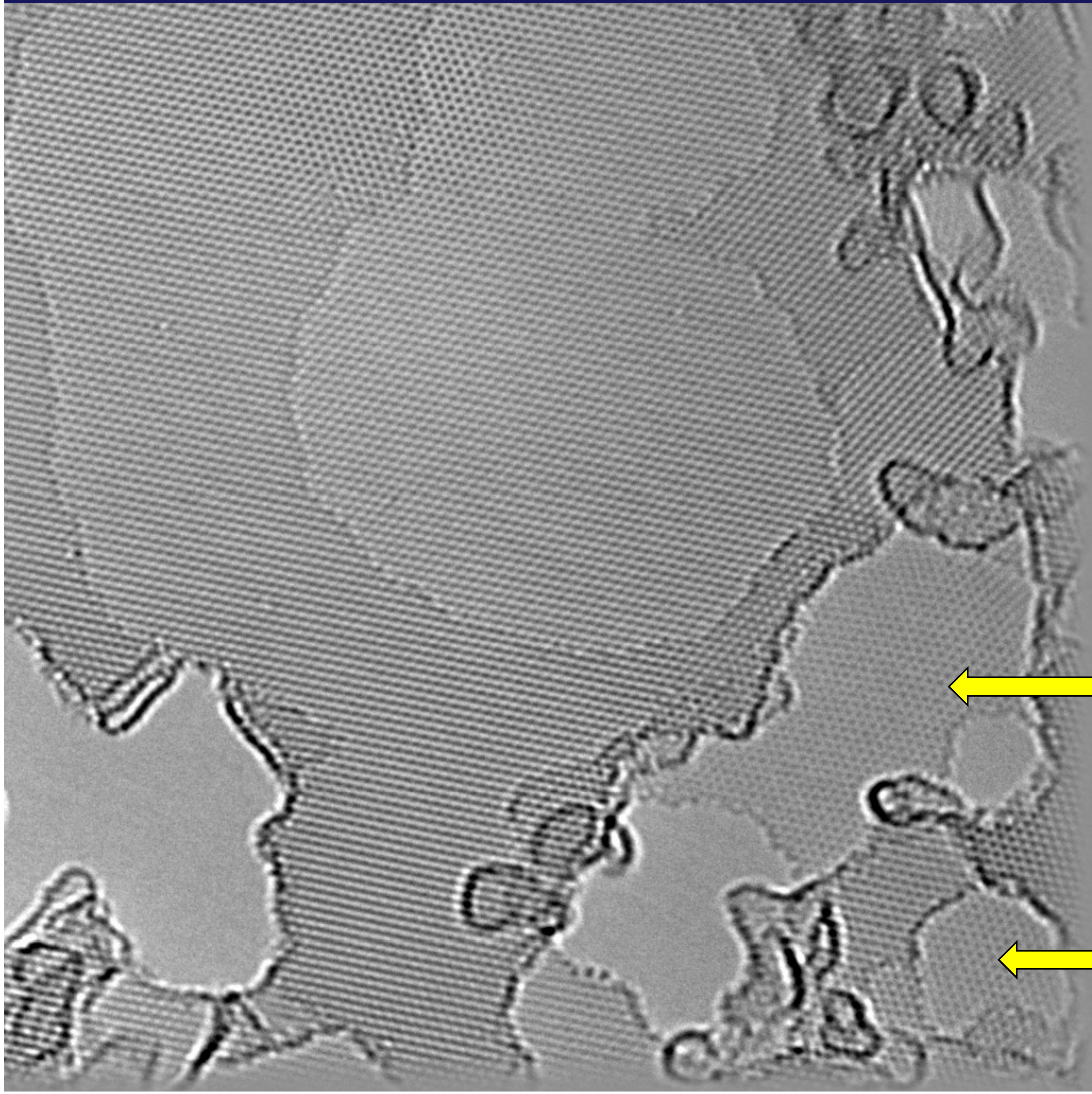
$WO_3 + C \longrightarrow W\ (\text{or } WC) + CO_2$

# Imaging of single atoms on a graphite film

Iijima, *Optik*, 1977



# A typical TEM image of the as-formed graphene



Chaunhong Jin , et al.,
*PRL* 2009

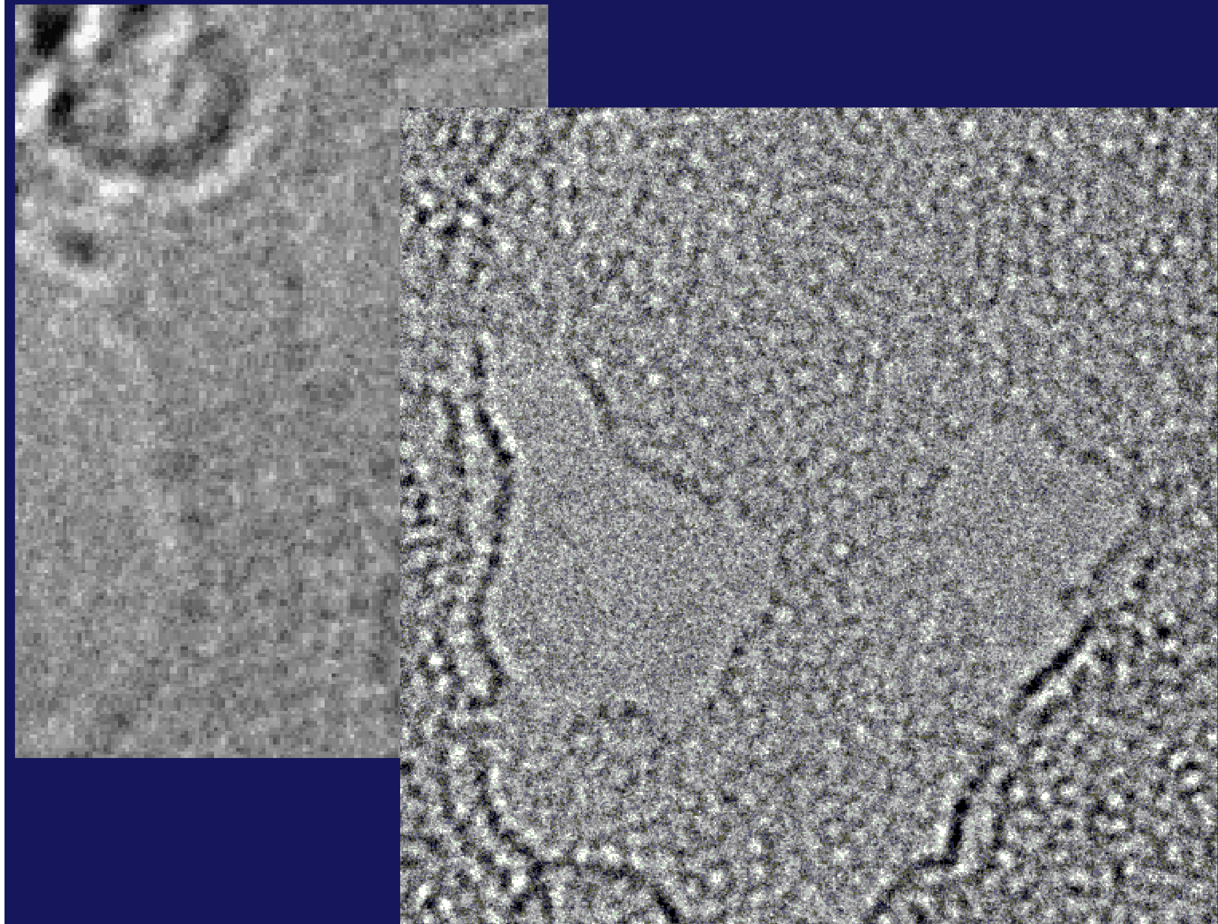
S. Iijima, *Optik*, 1977
Hashimoto et al., *Nature* 2004
C. Jin et al., *Nano Lett* 2008
C. Jin. et al., *ACS Nano* 2008

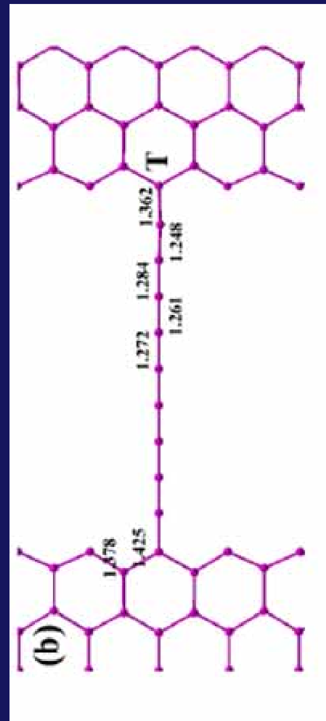
single layer

single layer

# Free-standing carbon monatomic chain

Chaunhong Jin , et al., *PRL* 2009






**Cumulene**

· · =C=C=C=C=· ·

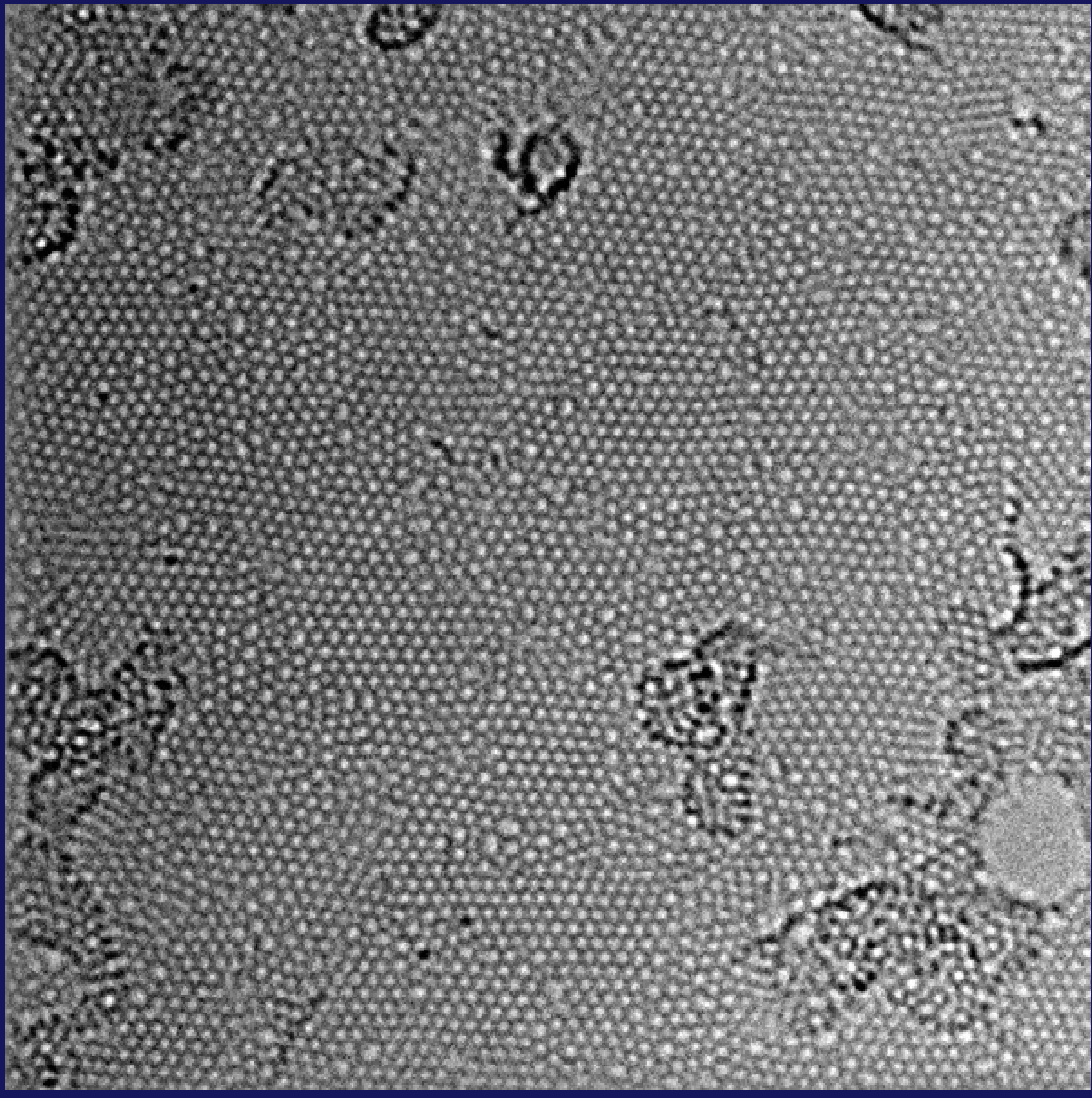
**Polyyne**

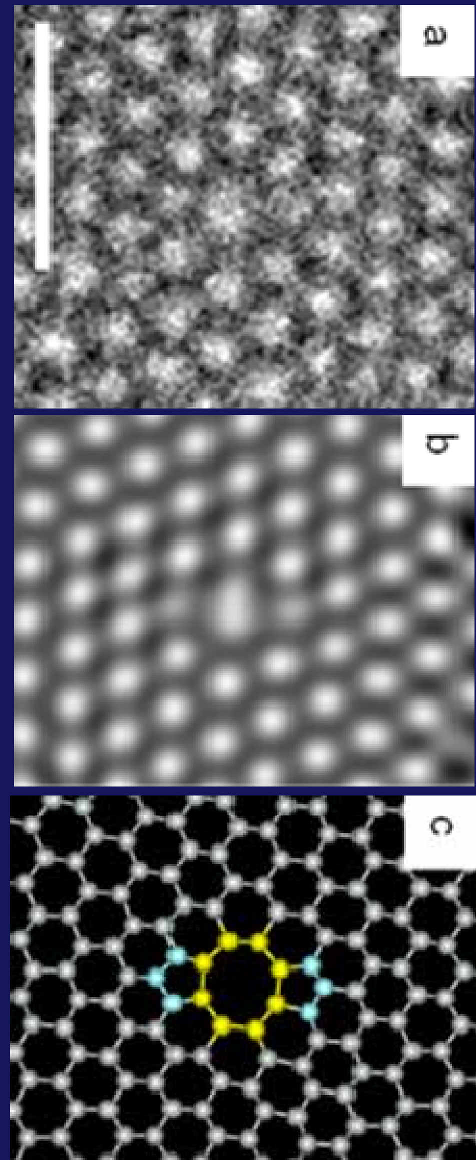
H− C≡C − · · · · · · −C≡C −H

The method similar to that for the metal quantum wires;   A lower beam intensity. 120 kV and 80 kV .

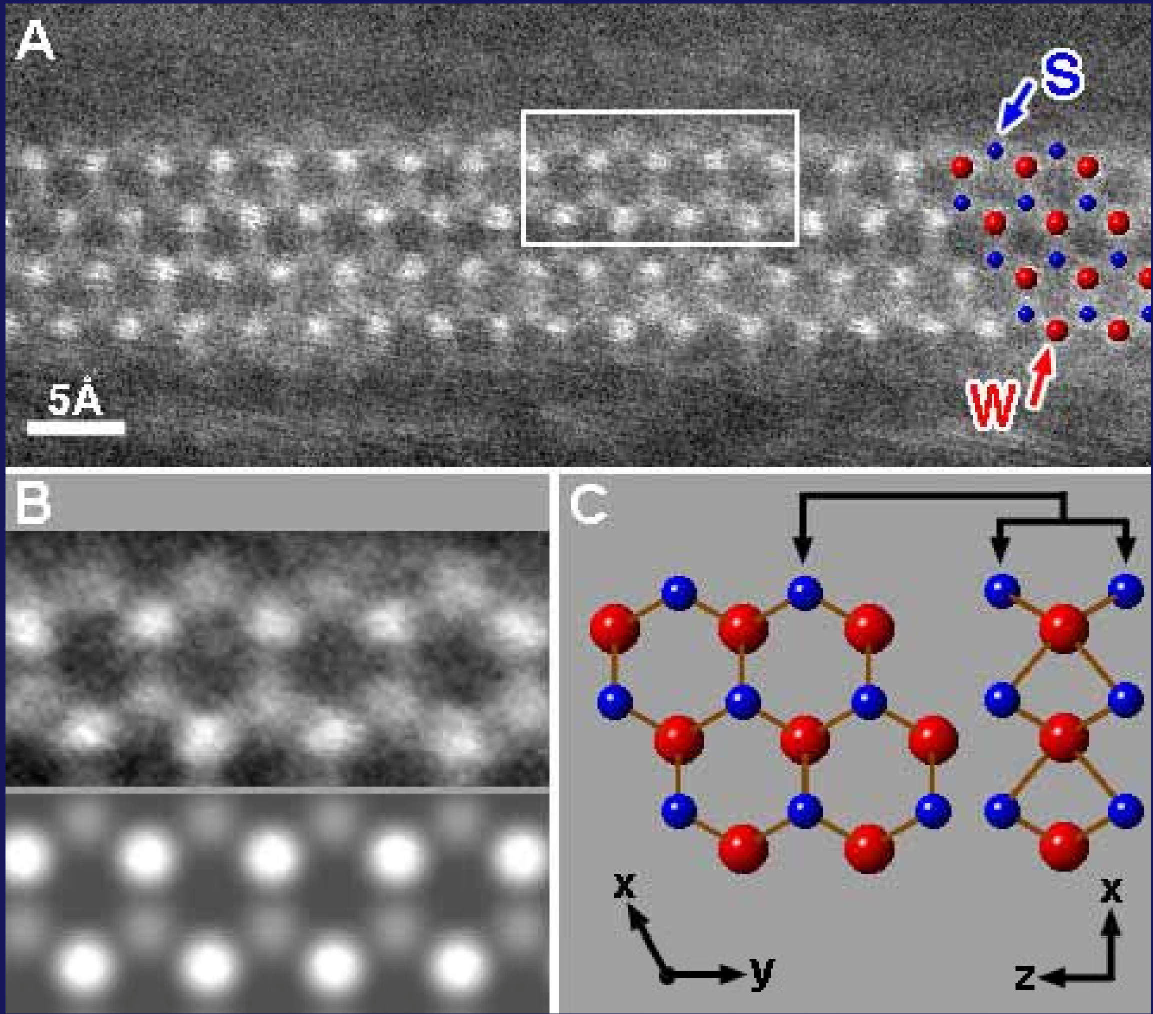
# Poly-crystalline graphene sheet with grain-boundaries and atomic defects

C.-C. Lu, et al. *Langmuire* **27** pp.13748-13753 (2011).





# ADF imaging of $WS_2$ nanoribbons (II)

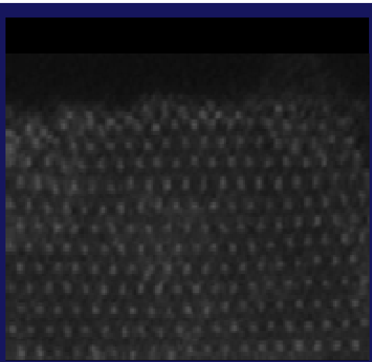



Z. Liu, et al.,
*Nature Comm*. 2011

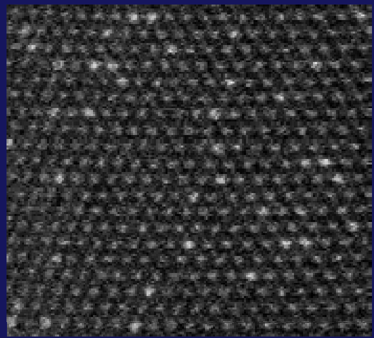
W atoms appear brighter than the S atoms. The edges of this monolayered $WS_2$ nanoribbon are S-terminated on one side (upper side) and W-terminated on the other side (lower side) and this structure does not change with width of monolayered $WS_2$ nanoribbon.
It is very interesting that only the zigzag edges were observed in this study.

(A) STEM ADF image of monolayered $WS_2$ nanoribbon encapsulated inside SWNT with [001] direction illustrated the trigonal symmetry, confirming the monolayered structure.
(B) (B) An enlarged view of the rectangle region in A and the corresponding simulated image (lower part).
(C) (C) Model of monolayered $WS_2$ structure looking through [001] and [010] directions.

# $Mo_{1-x}W_xS_2$ single layers

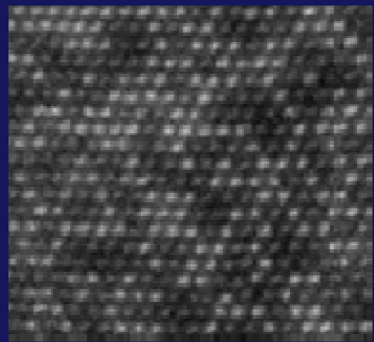


#1000



#0802

X=0



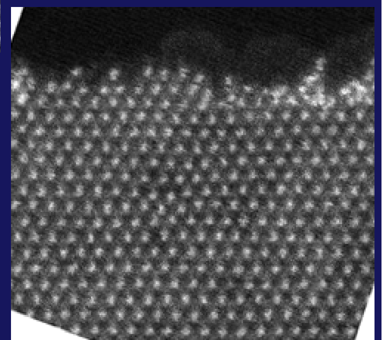
#0505

W content

#0208

We can see how two kinds of atoms are mixed in a solid solution!

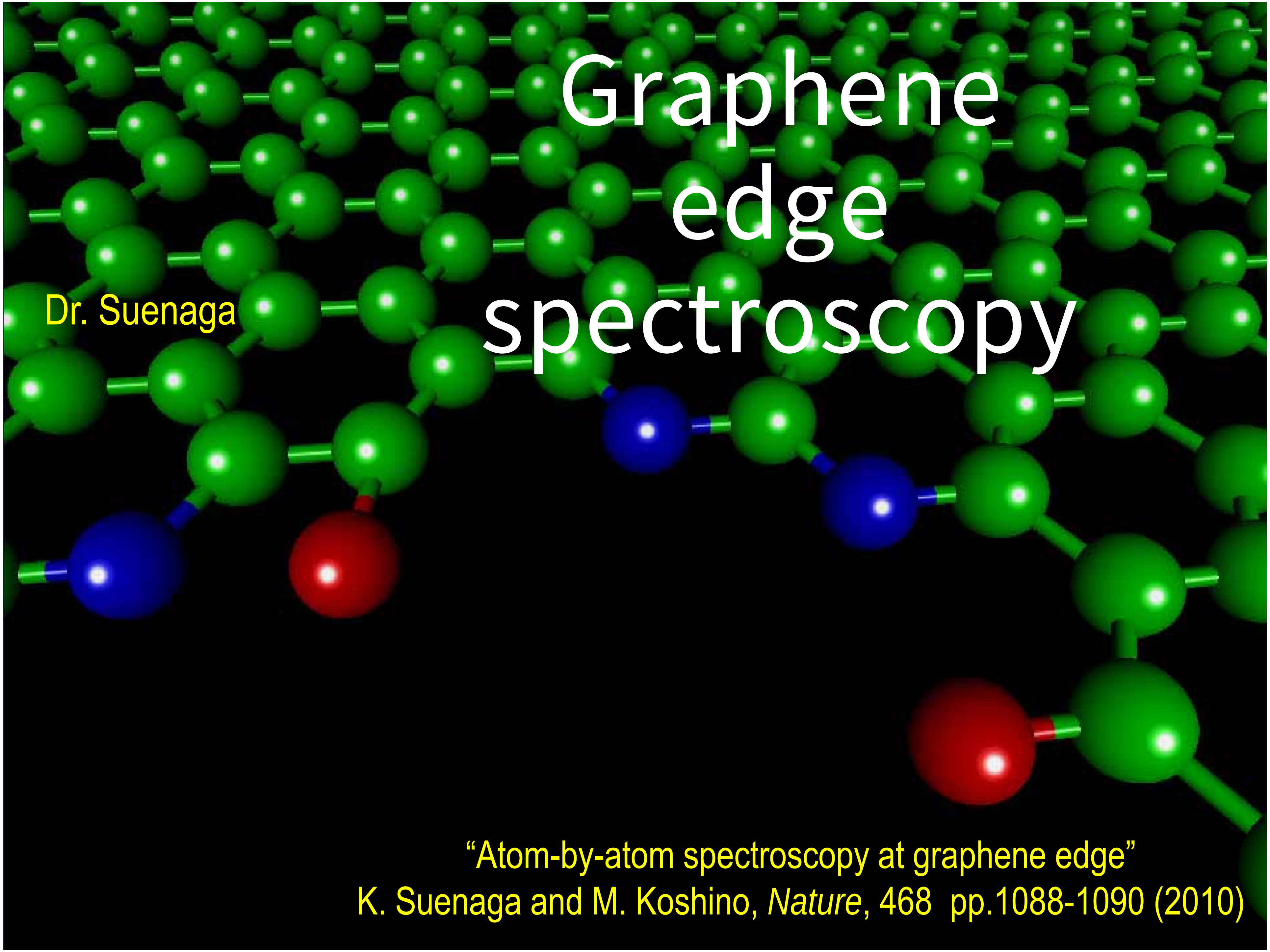
X=1



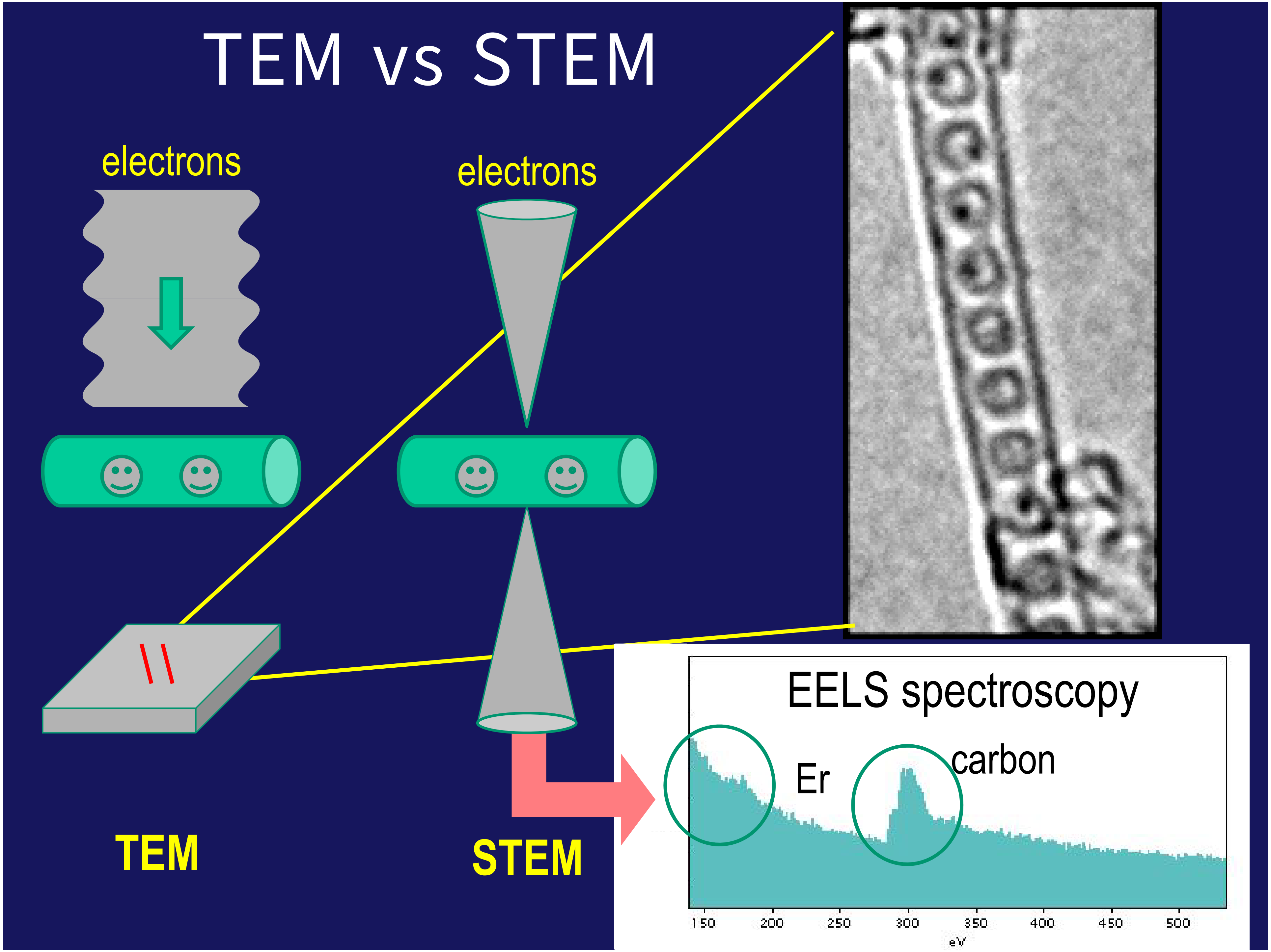
#0010

# Graphene edge spectroscopy

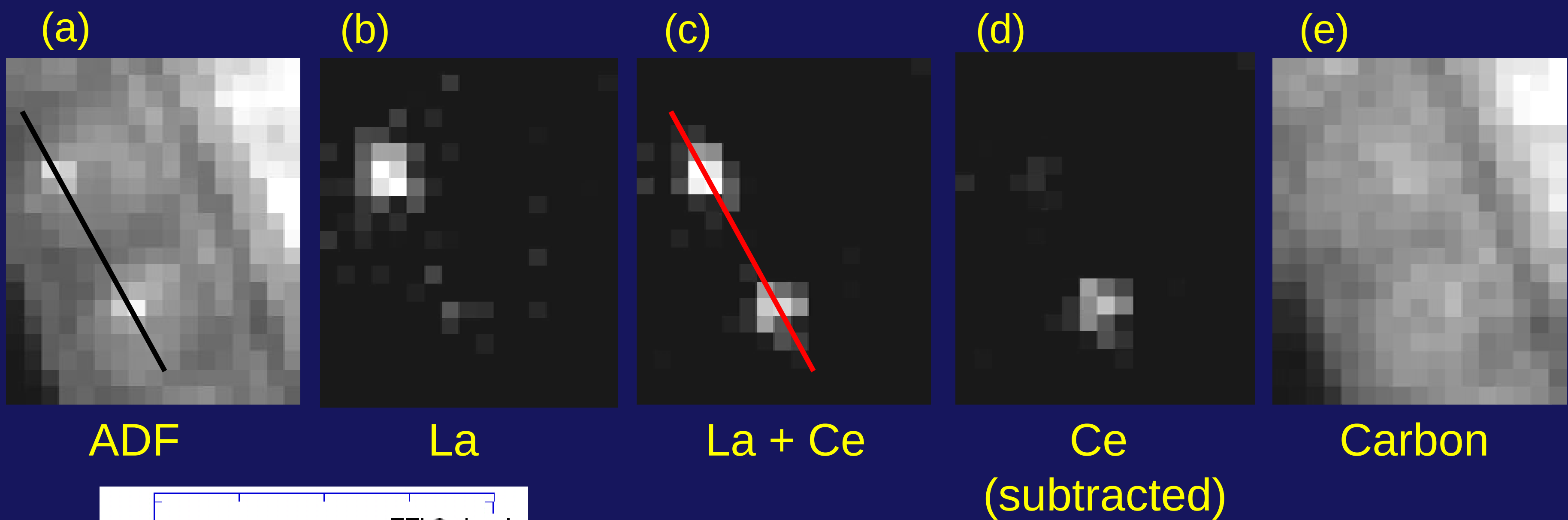
Dr. Suenaga

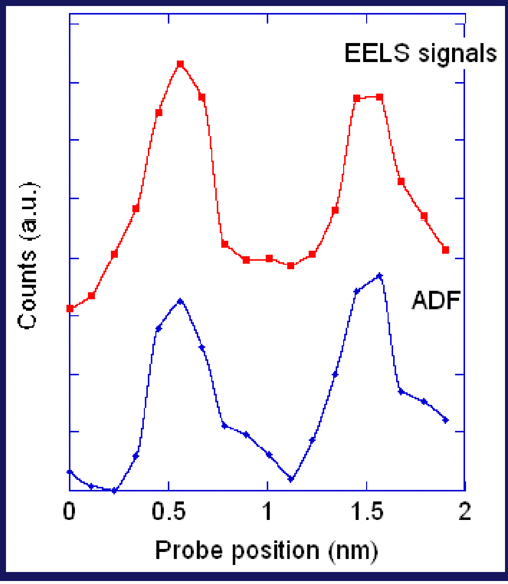


"Atom-by-atom spectroscopy at graphene edge"
K. Suenaga and M. Koshino, *Nature*, 468 pp.1088-1090 (2010)


TEM vs STEM
electrons
electrons
TEM
STEM
EELS spectroscopy
Er
carbon
150
200
250
300
350
400
450
500
eV

# Ultimate elemental mapping at individual atom basis

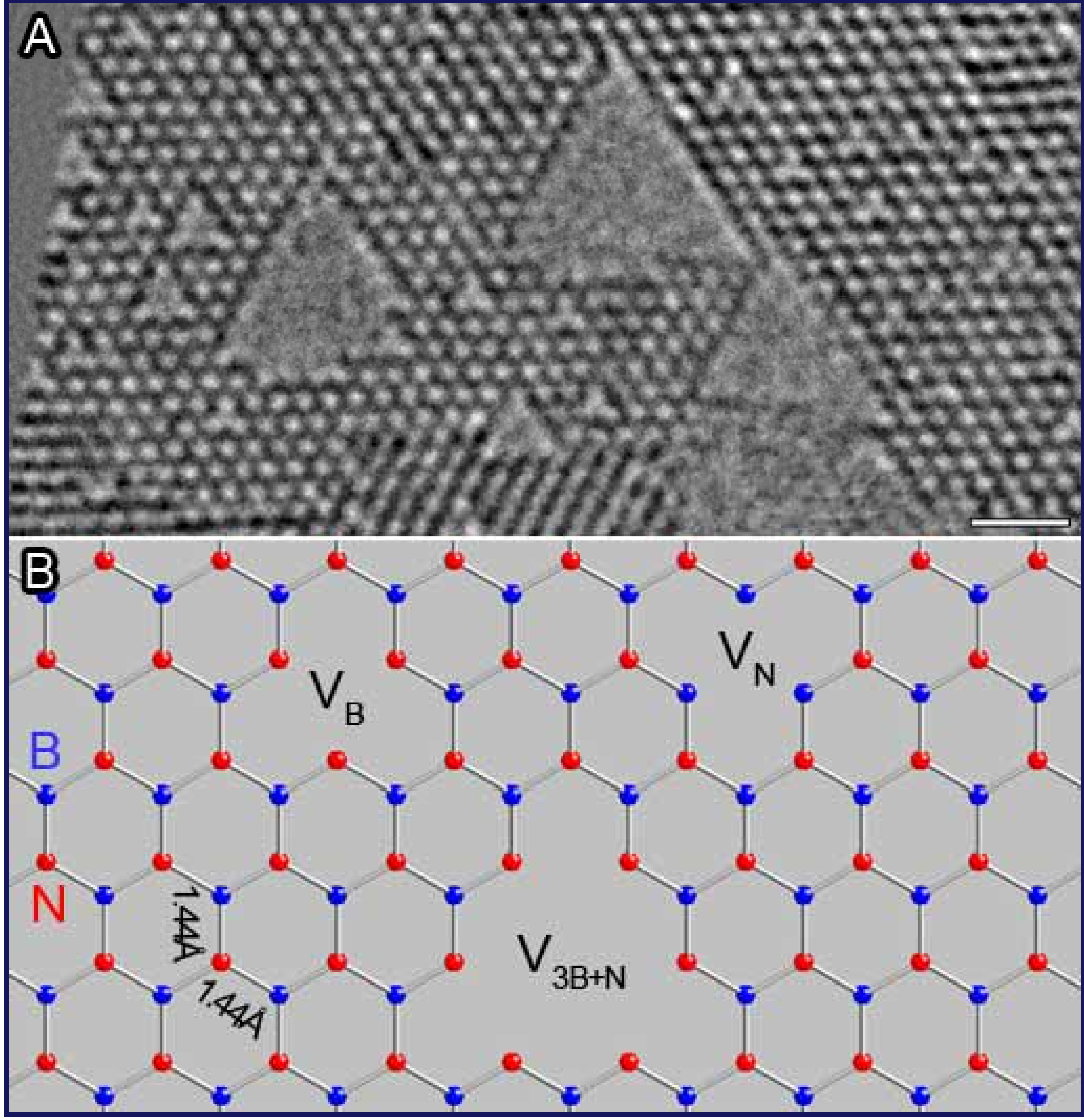



- Discrimination of La(Z=57) & Ce(Z=58)
- Discrimination of $Ce^{3+}$ & $Ce^{4+}$

# A defective *h*-BN mono-layer

Chaunhong. Jin, et al., *PRL* 2009




**The triangles:**

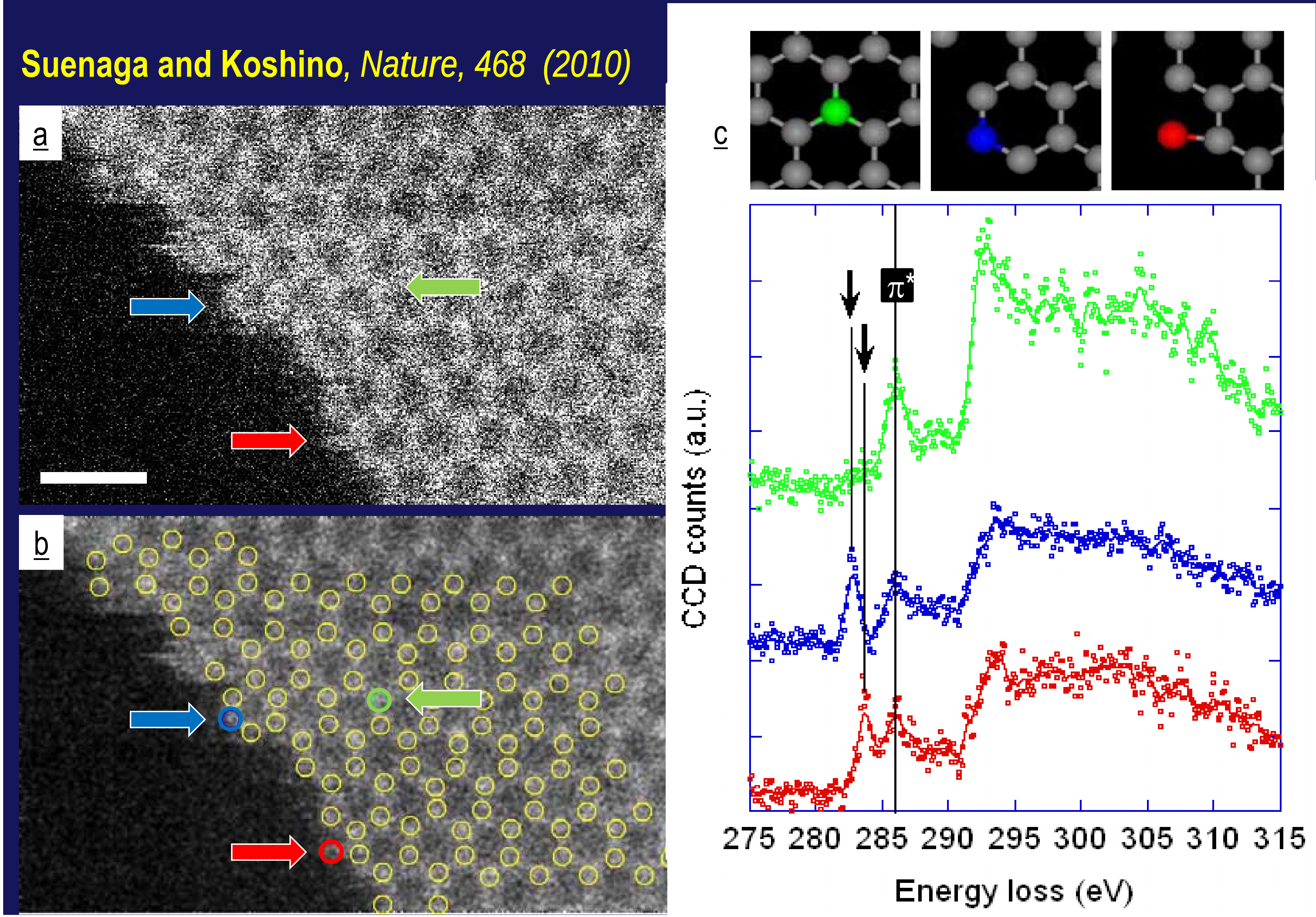
- *regular triangle shape*
- *discrete sizes*
- *in the same orientation*

**The smallest ones:**

*mono-vacancy of boron*

# EELS from an edge of a graphene sheet

**Suenaga and Koshino**, *Nature, 468 (2010)*



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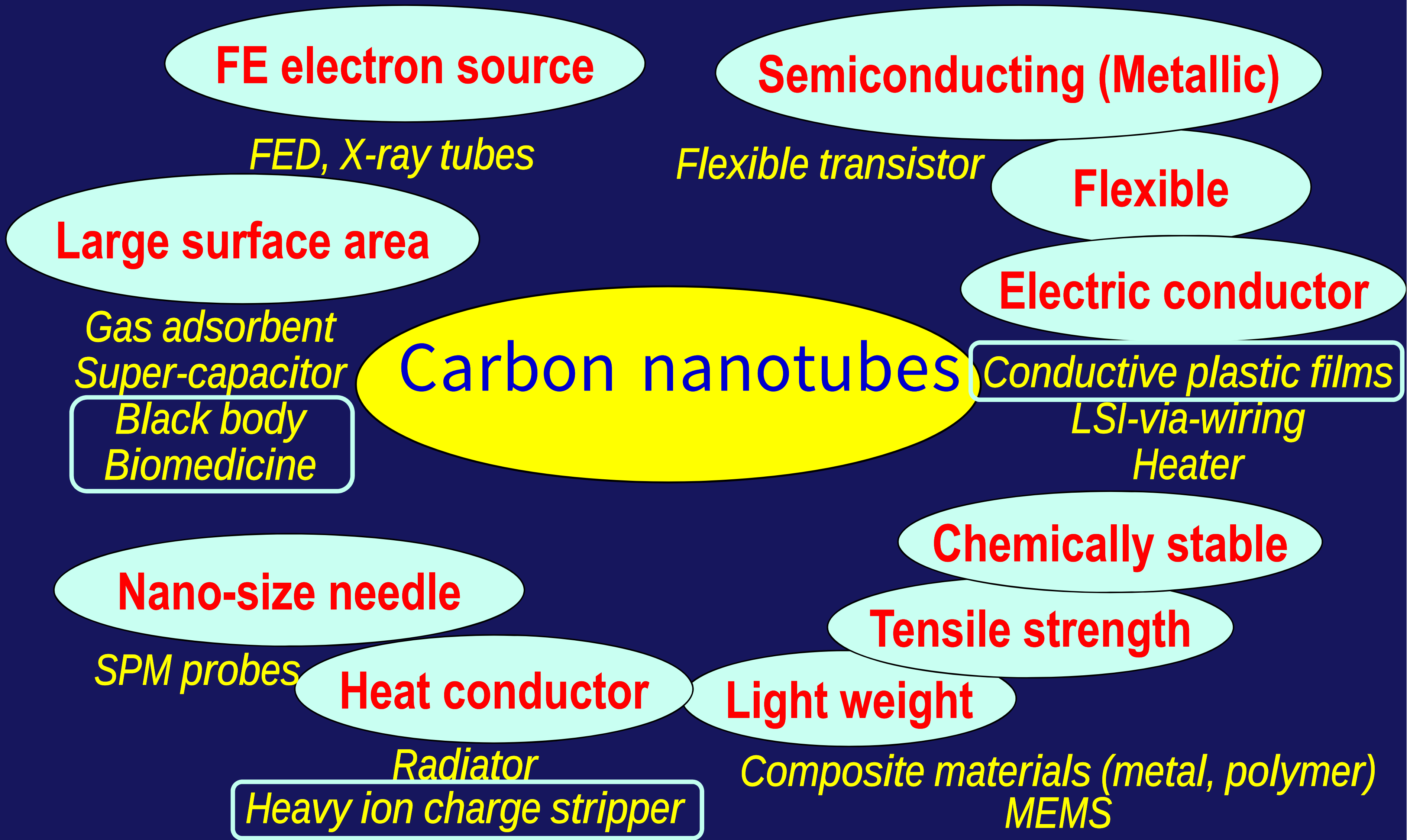
# Possible applications of CNT s



# Some examples of CNT applications

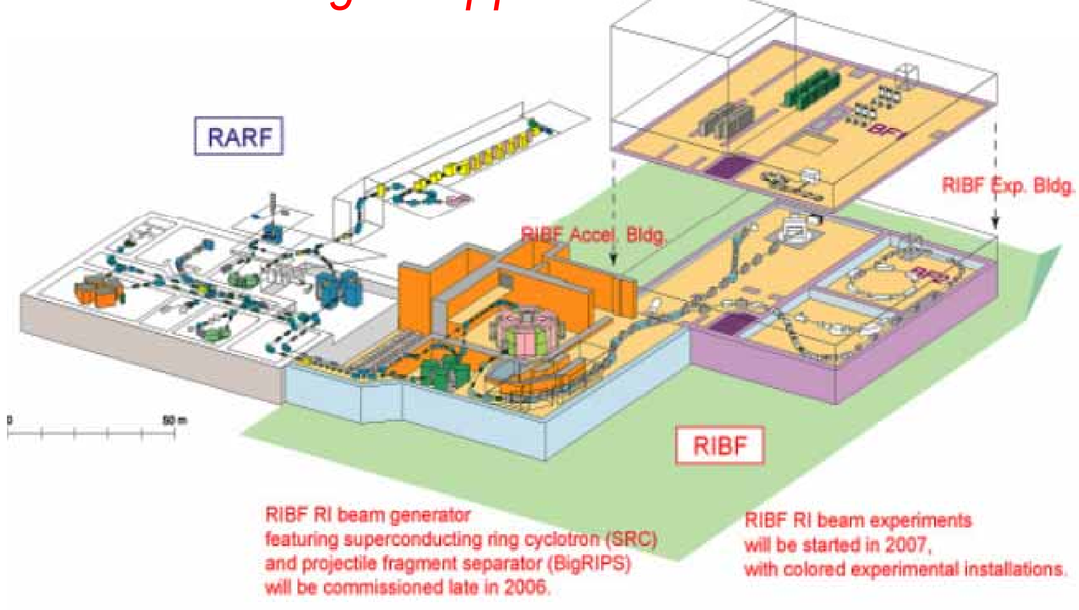
## CNT-Touch Screen Displays

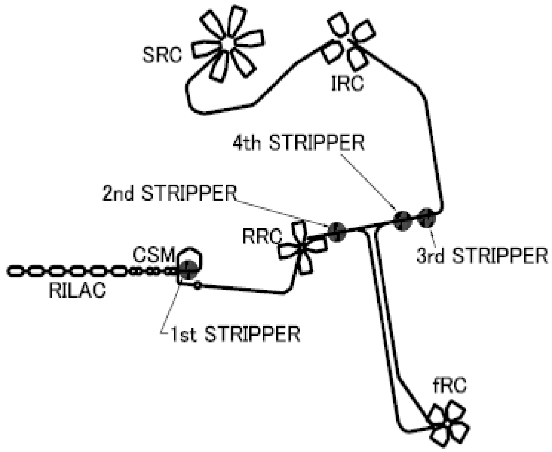
5 inch　　4 inch

**Smartphone**

http://www.gizchina.com/2011/11/20/ipad-nano-mini-carbon-nanotube

## CNT " *charge stripper*" for RIBF at RIKEN

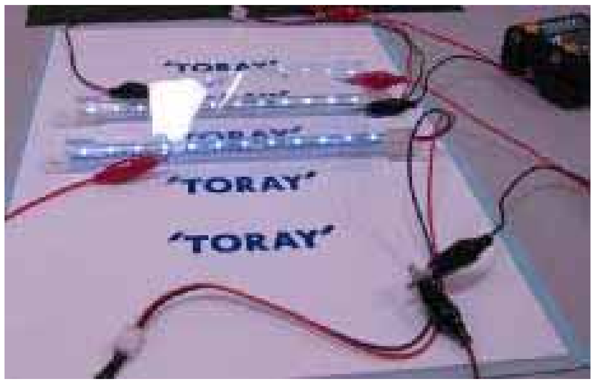


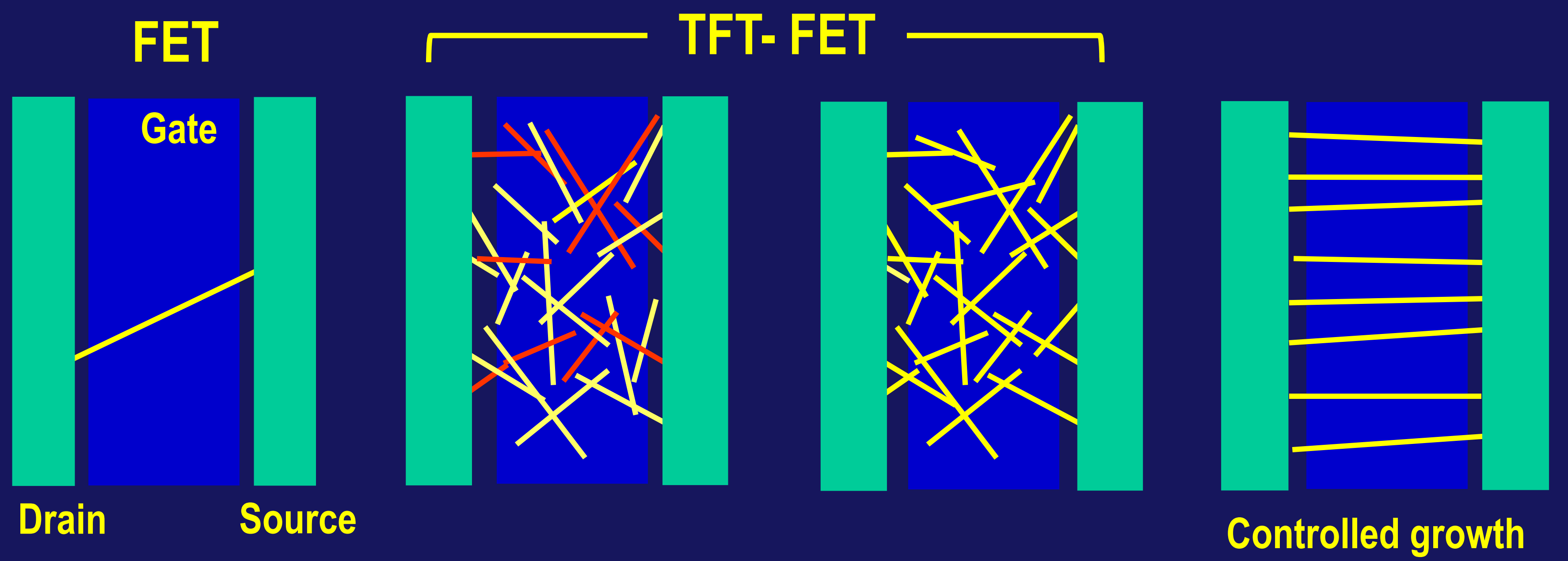

"史上最強の加速器"

史上最強のビーム強度を誇る超伝導リングサイクロトロン「SRC」。SRCは全体が純鉄のシールドで覆われた総重量8300トンの「鉄の塊」タイプです。この構造を採用する事によって「史上最強のイオンビーム偏向能力」（8Tm）を実現できるばかりか、自己漏えい磁気遮蔽、自己漏えい放射線遮蔽の機能を付加しています。
RIBFの加速器の最終段階で、ここを通過すると光速の70%までビームを加速できます。
また、超伝導という方式によって従来の方法に比べ100分の1の電力で動かせるようになり、大幅な省エネも実現しました。

## Electronic paper



# Flexible electronics industries of SWCNTs



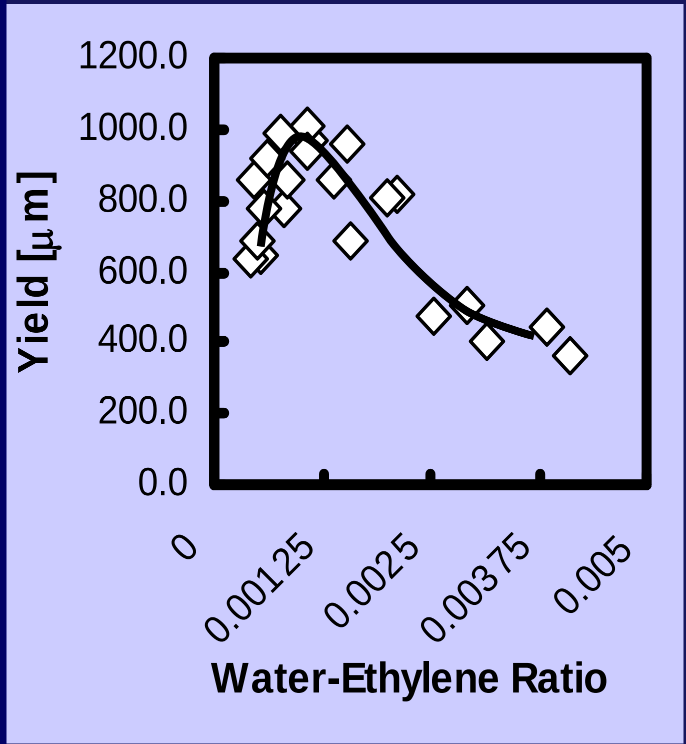


- S-M Separation
- Transparent & flexible conductive films
- Thin film transistors (printable-ink-jet)

# Super-Growth SWCNT technology

Hata et al. *Science* 2004

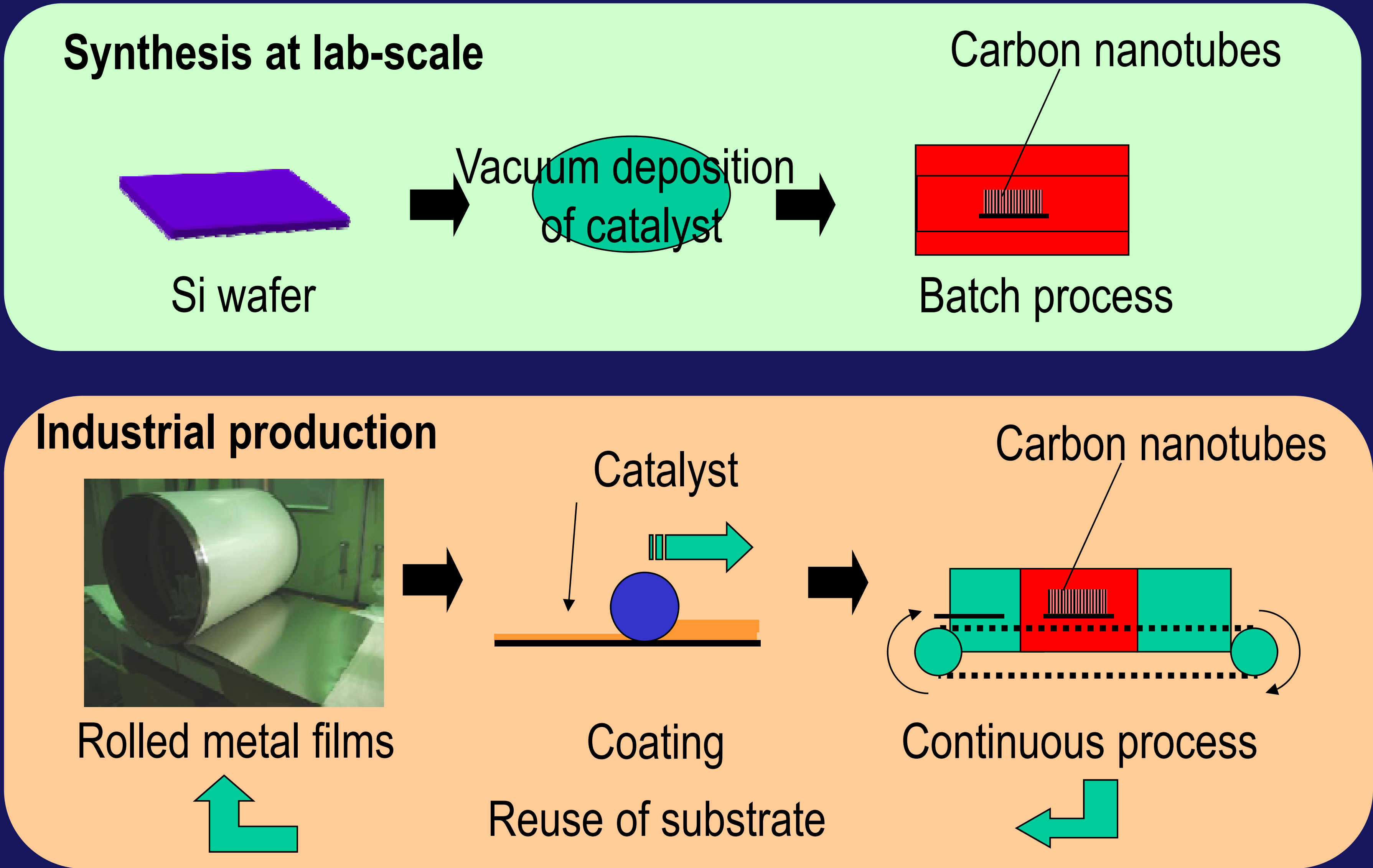

Futaba et al., *PRL* 2005



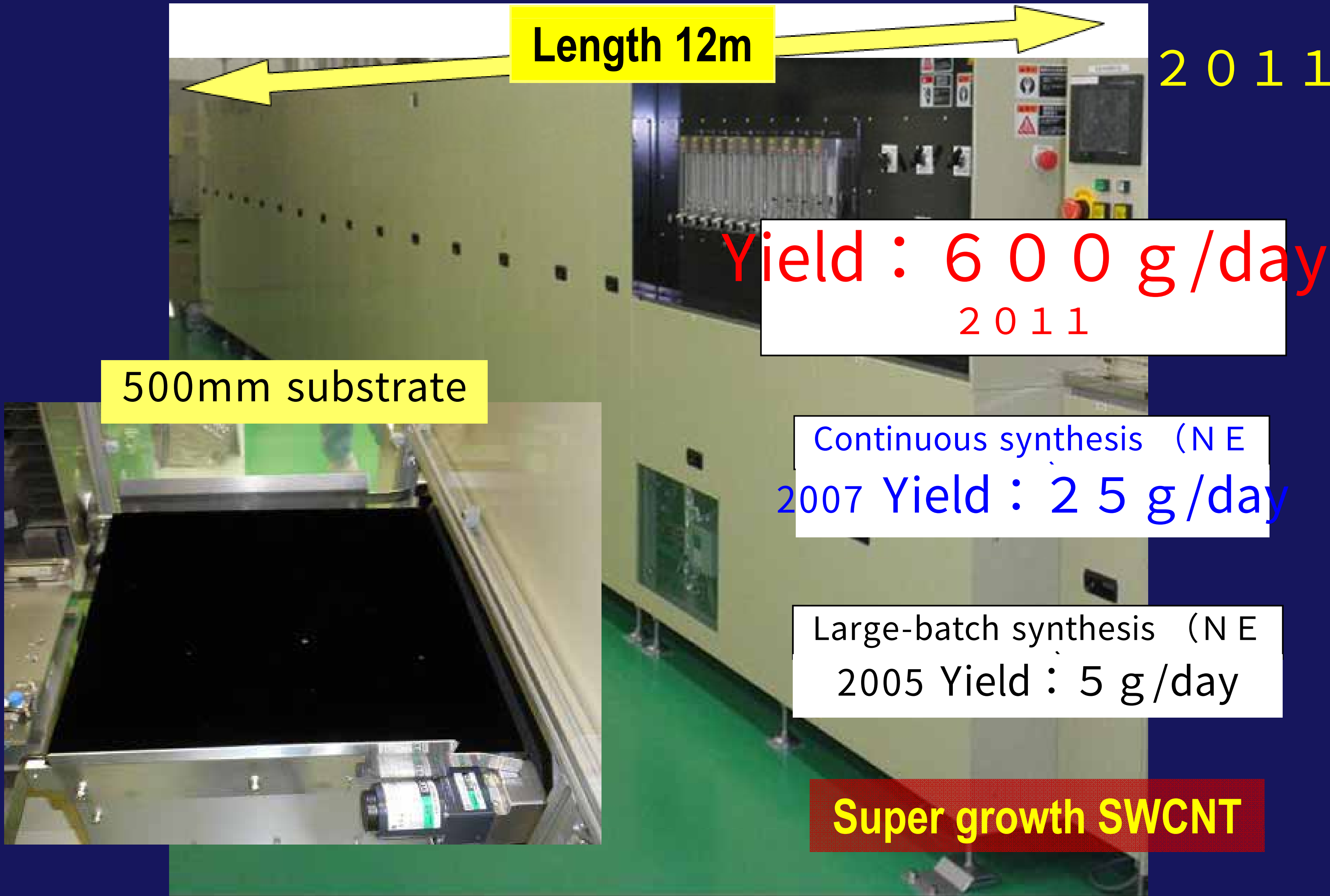

***Substantial cost down and efficiency!***

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

# Large-scale production of SWCNTs

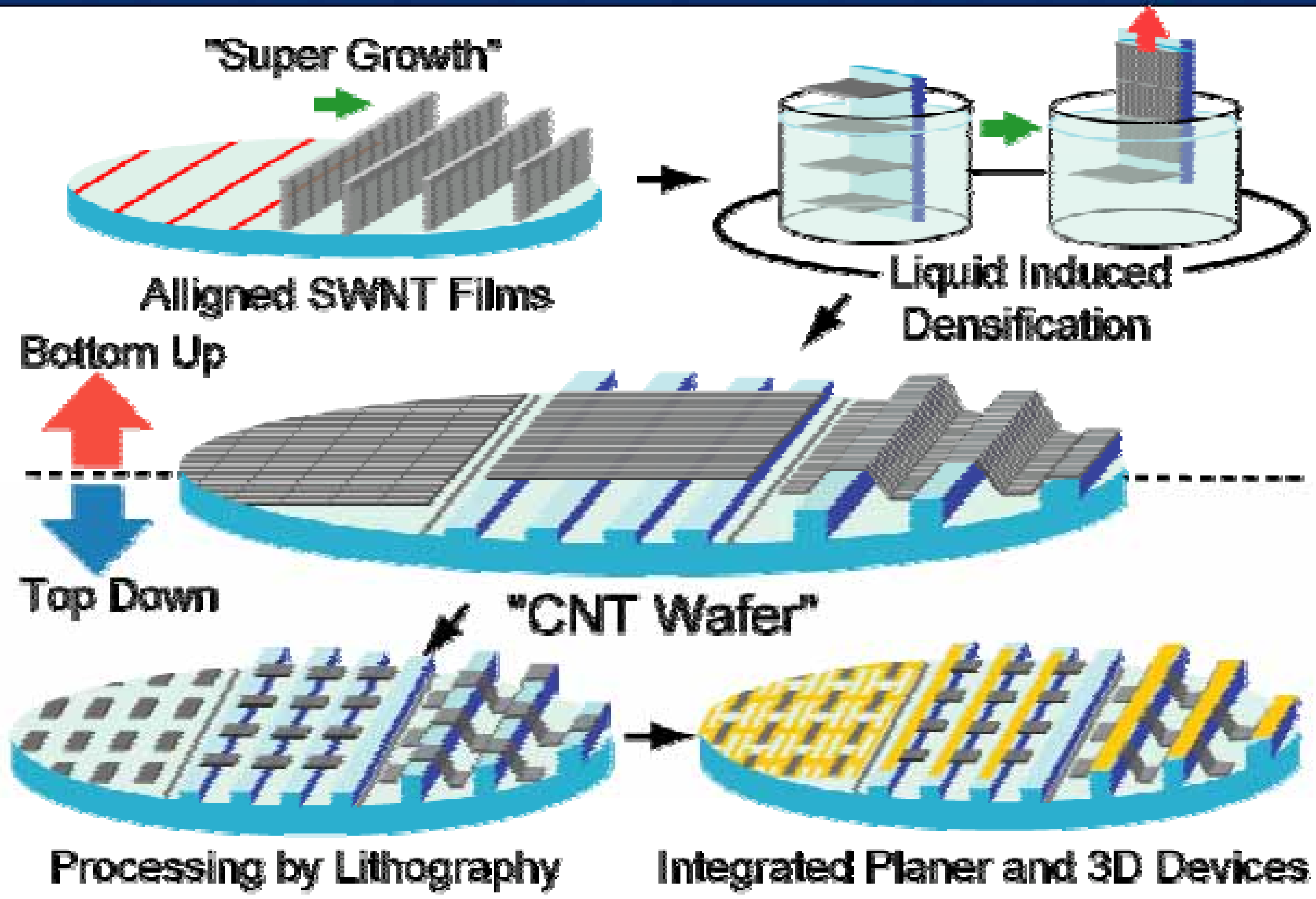


# Large-scale CVD synthesis of SWCNT

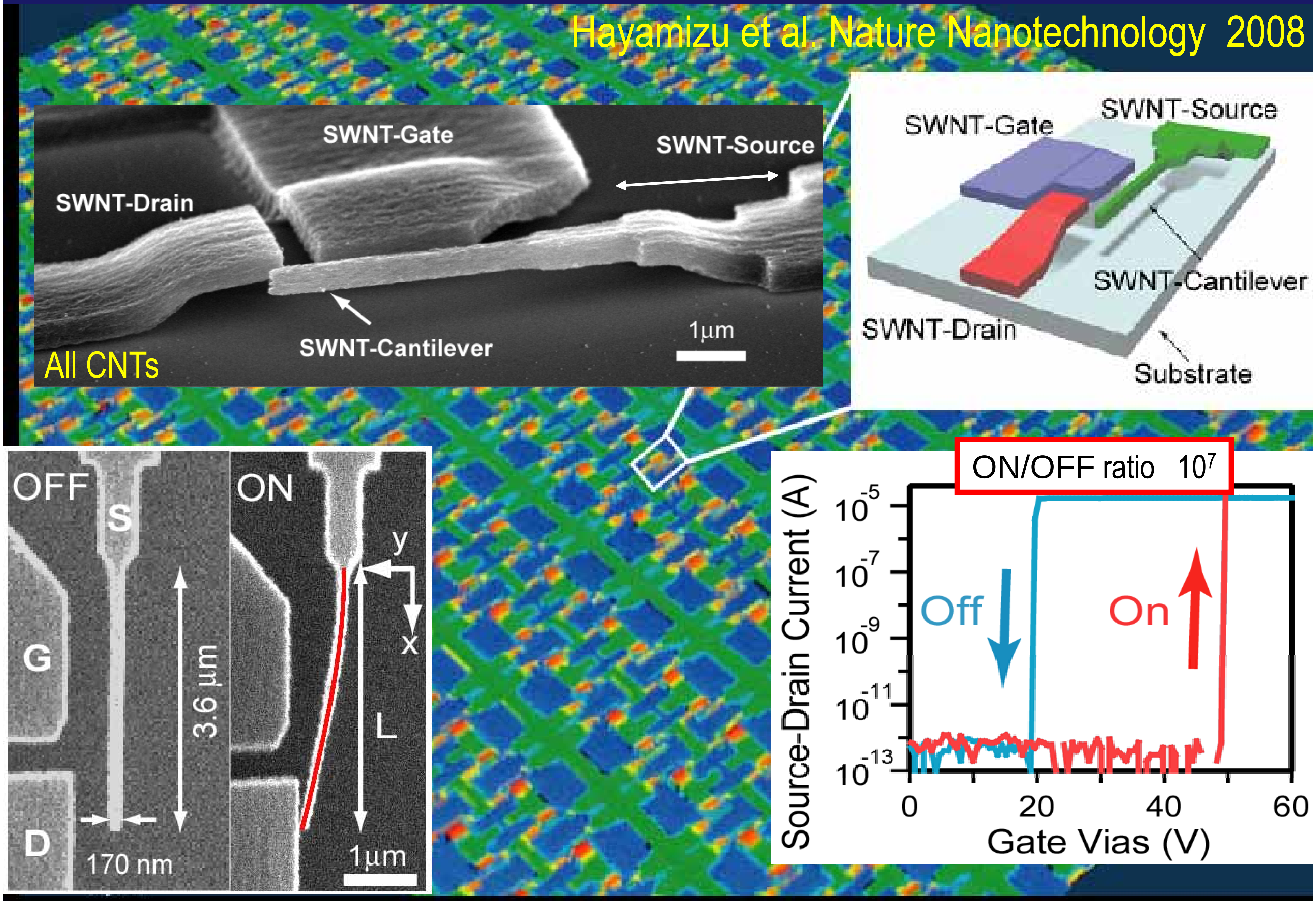



Sample will be supplied by AIST+ Nippon Zeon

# Concept of CNT Wafer

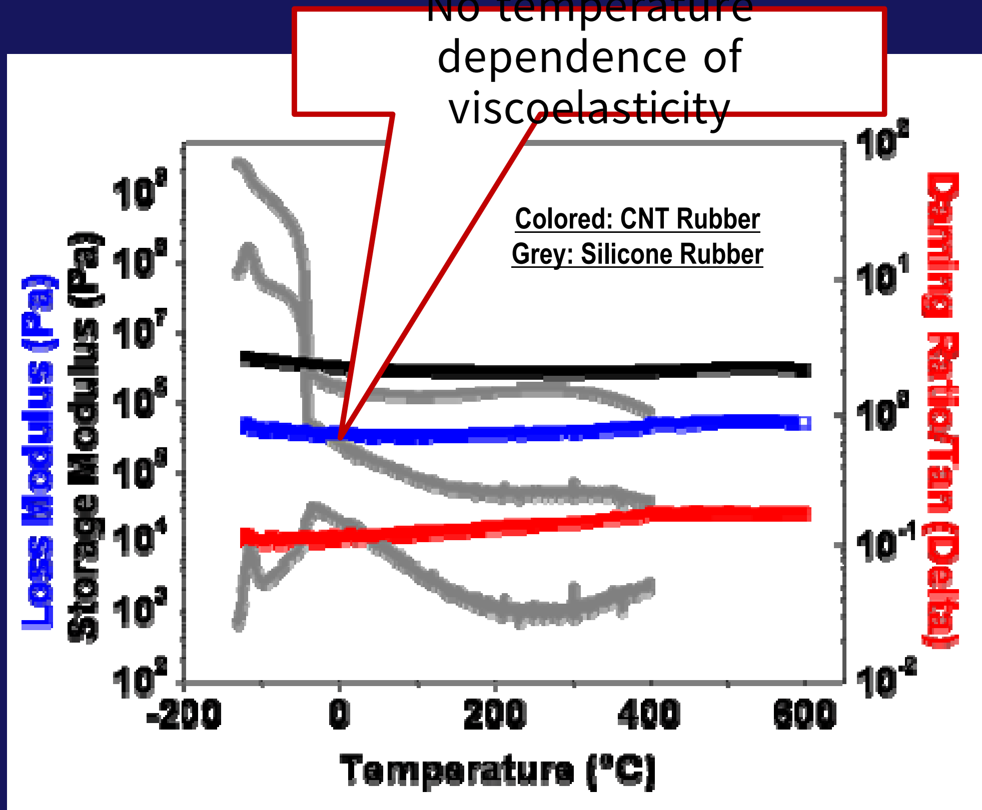


# Integration of 3D nanotube structures



# Viscoelastic SWCNT

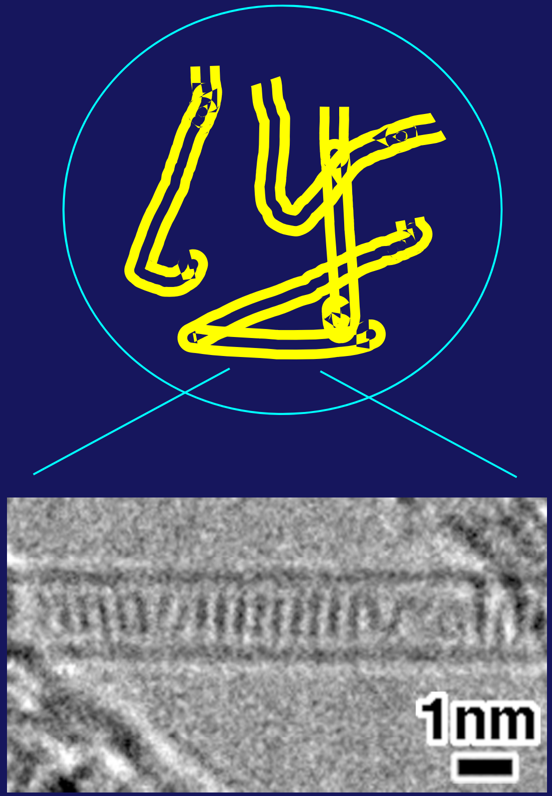
**K. Hata & Ming Xu, et al., *Science* 330 (2010)**

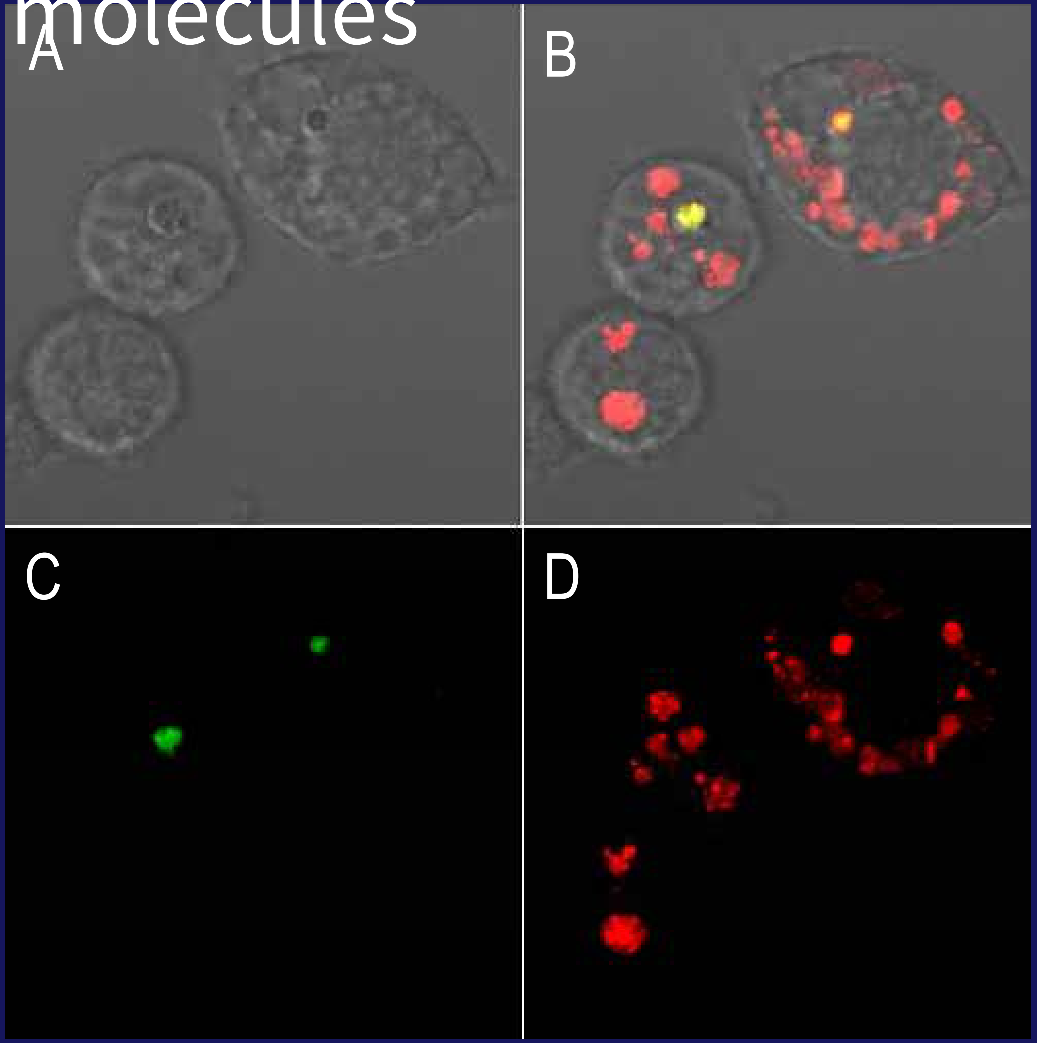




*Silcone-rubber like SWCNT mat between 96℃ & 1000℃*

# Luminescence from the encapsulated molecules

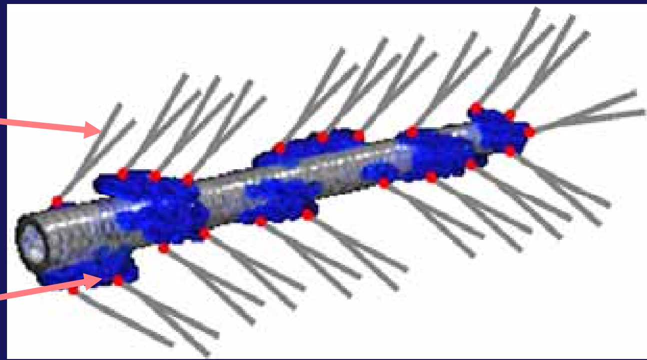
coronene@SWCNTs

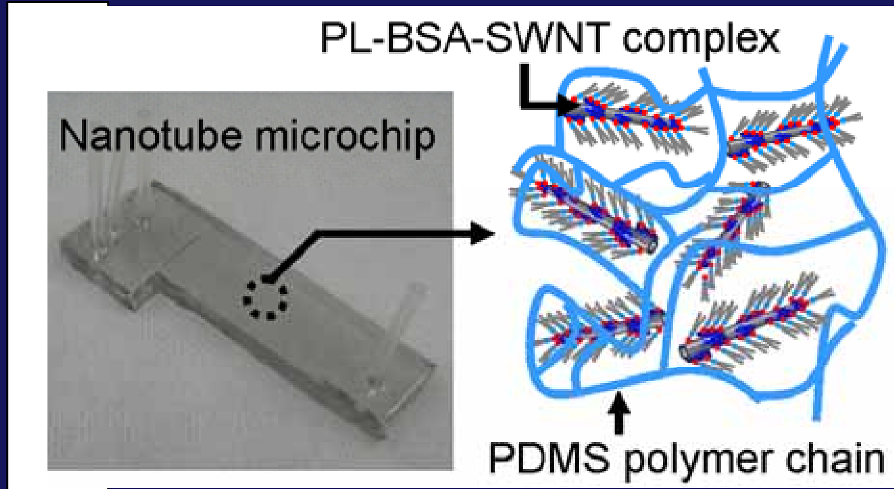


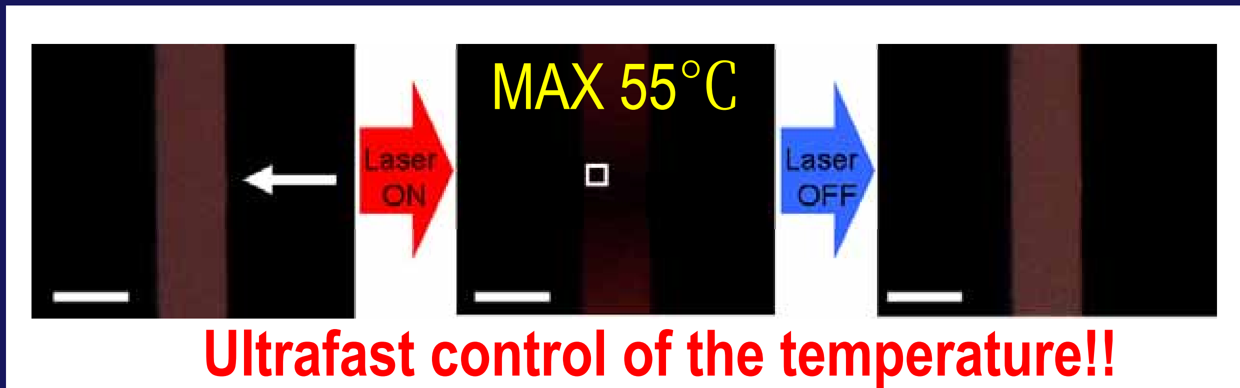

Confocal microscope images of muribe macrophage cell line RAW 264.7 after incubating with coronenes@SWCNTs wrapped with DSPE-mPEG. (A) Differential interference contrast (DIC) image. (B) Combined DIC and fluorescence images. Fluorescence images obtained from (C) coronenes@SWCNTs and (D) lysosomal markers (excitation wavelength = 488 nm, detection wavelength > 510 nm).

# CNT–polymer composite for light-driven microthermal control



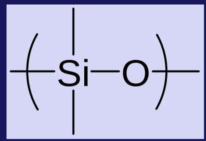

A phospholipid–BSA–-functionalized single-walled carbon nanotube complex (PL–BSA–SWNT) was synthesized and shown to be readily dispersible in poly dimethyl-siloxane (PDMS). A photoinduced PDMS microchip encapsulating the PL–BSA–SWNT complex is capable of ultrarapid control of the temperature of a solution in a microchannel in the chip. This system should be useful in various lab-on-a-chip applications.




E. Miyako et al. *Angew. Chem.* **47**, 3610-3613 (2008).

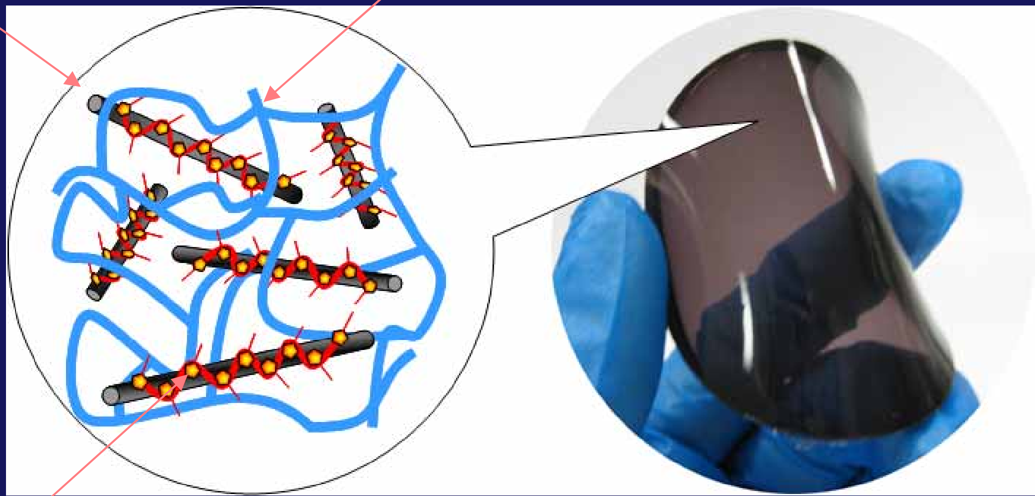
# CNT-based photo–thermal–electrical convertor for bionic applications

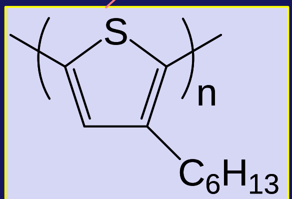
E. Miyako et al. *Angew. Chem. Int. Ed.* **50**, 12266 (2011) .




: Poly(dimethyl-siloxane) as a base polymer matrix

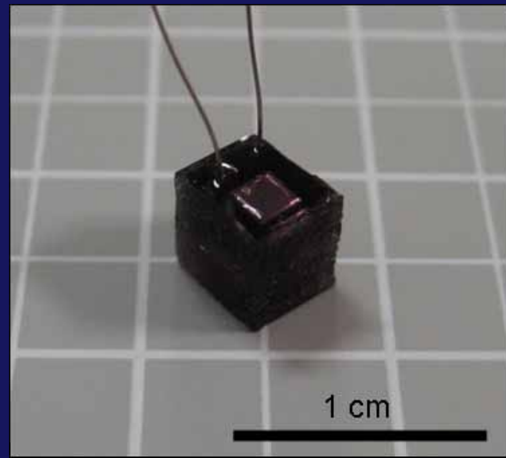
SWNT





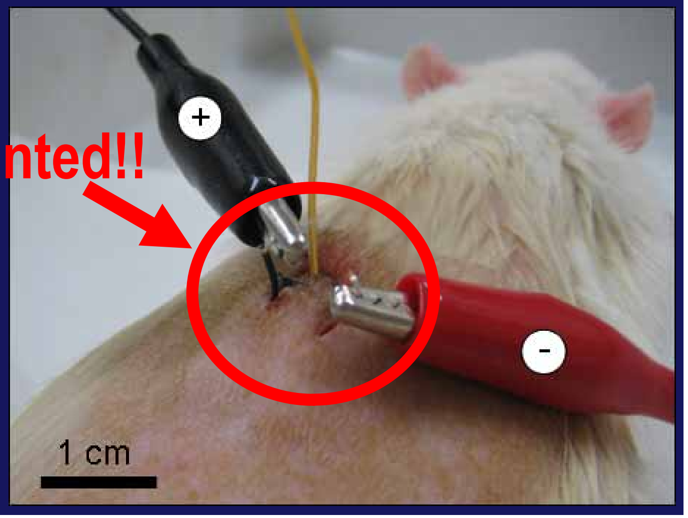

: Poly(3-hexylthiophene) (P3HT) as a dispersion agent

**Highly flexible CNT–polymer composite**



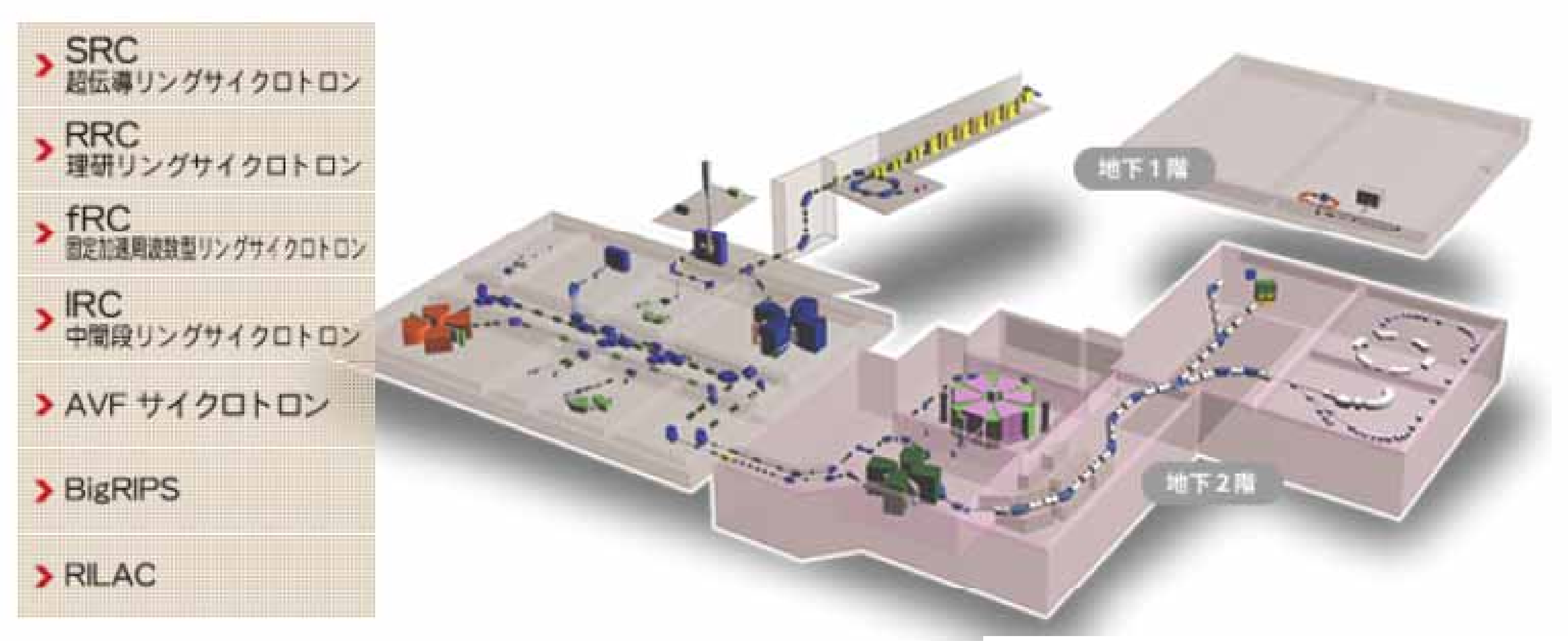

**CNT-based PTE convertor**

**Implanted!!**




We developed carbon nanotube (CNT)-based photo-thermal-electrical (PTE) converter that can be manipulated using a laser capable of transmission through a living body. Our present study represents important progress towards a wireless electrical power supply system for implantable medical devices as well as various bionic applications.

# SWCNT foil charge stripper for RIBF at RIKEN

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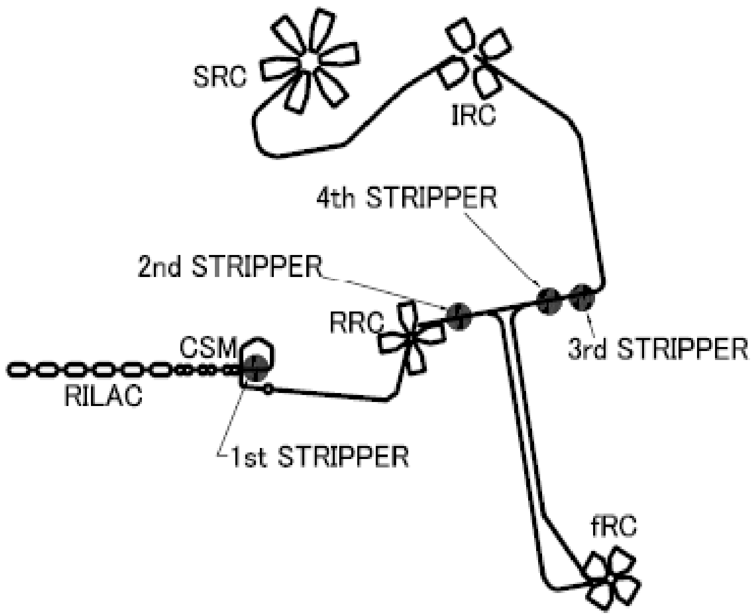
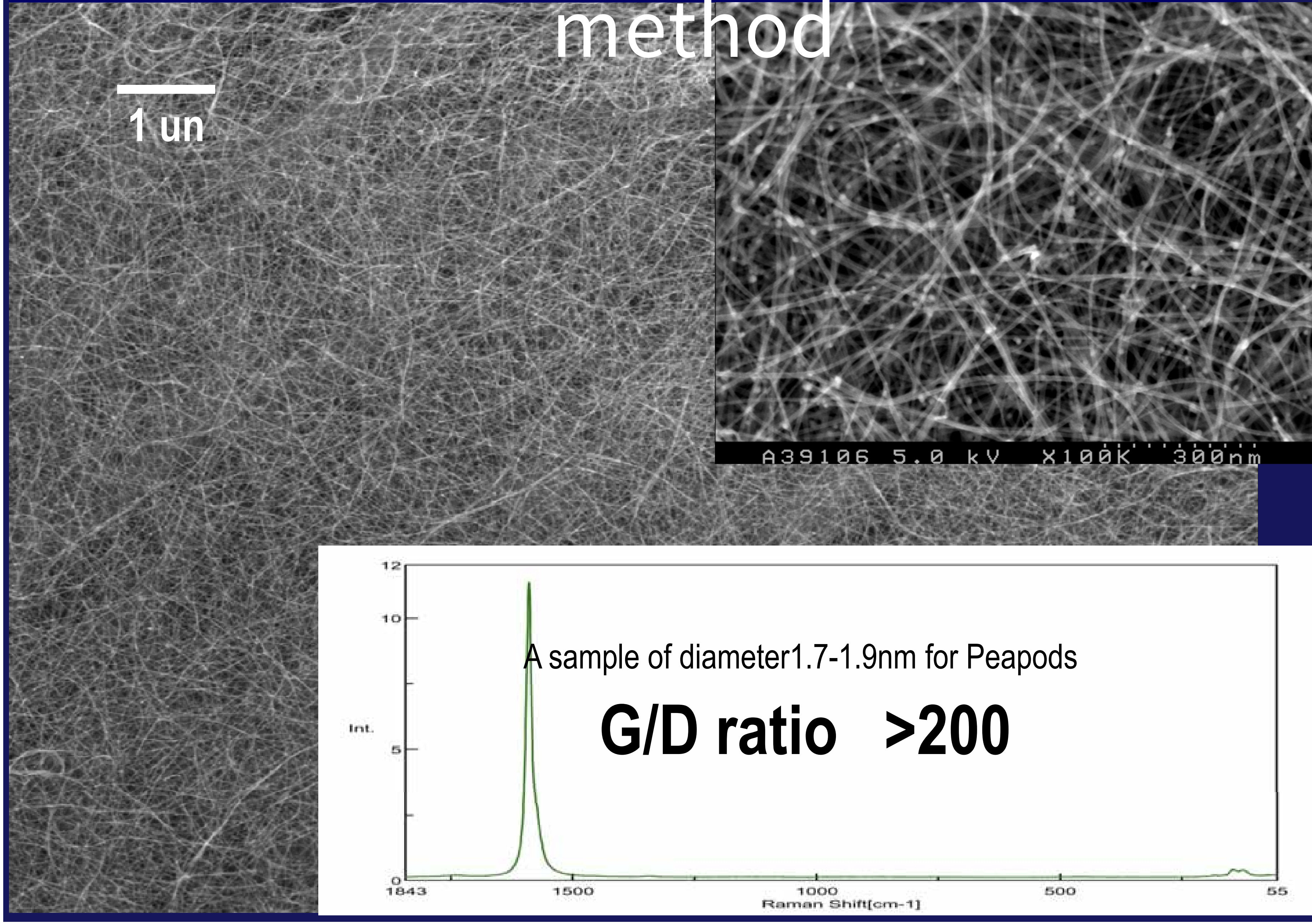


# High purity SWCNTs by DIPS method




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

# Helicity in Ropes of Chiral Nanotubes: Calculations and Observation

Tomanek, Iijima et al., *PRL* 108, 235501 (2012)

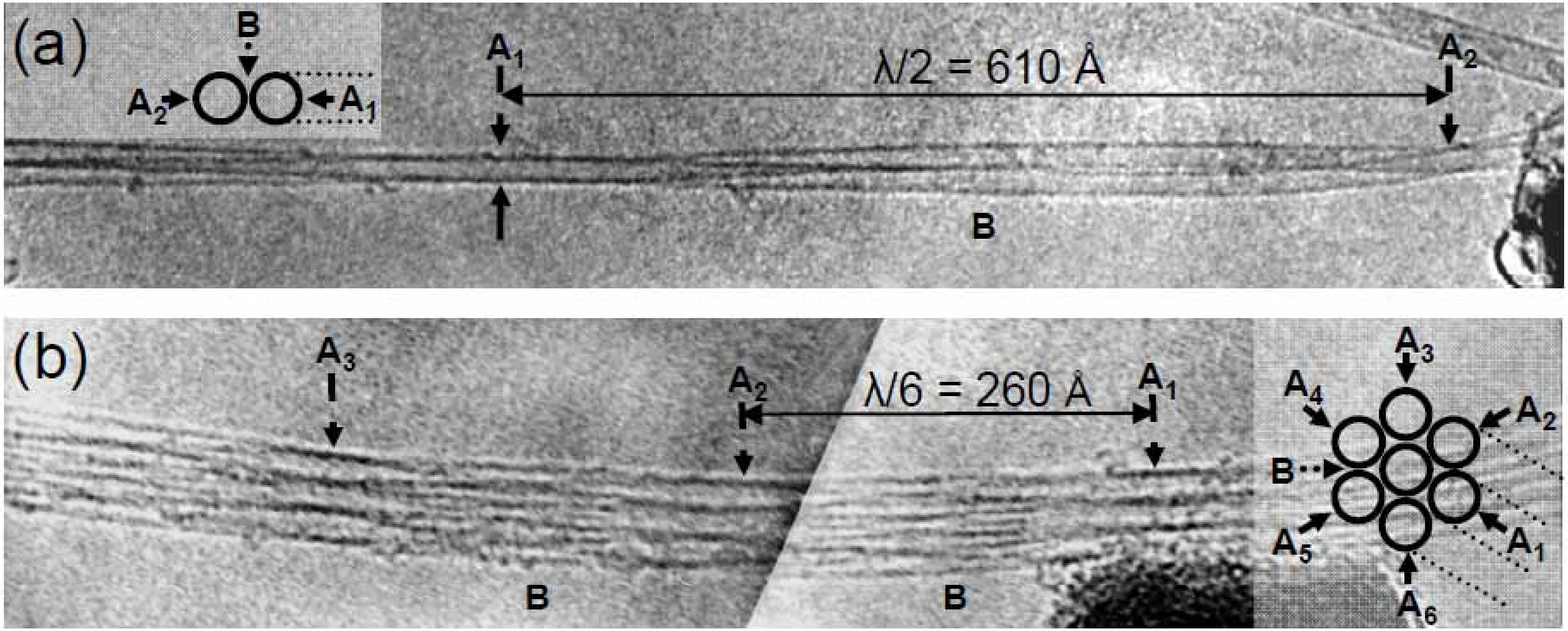



FIG. 1. High-resolution electron micrograph of a free-standing SWCNT rope containing (a) two and (b) six SWCNTs. The local rope orientation changes along the helix with respect to the electron beam direction, indicated by parallel dotted lines in the insets. Only two diffraction lines should occur in a two-tube rope for orientations labeled $A_1$ and $A_2$ in (a), shown also in Fig. 2(a), separated by half the pitch length. Only four such lines are observed in the 7-tube rope in (b) for rope orientations $A_1 - A_6$, separated by $\lambda/6$.

# Structure of CNT and bundles

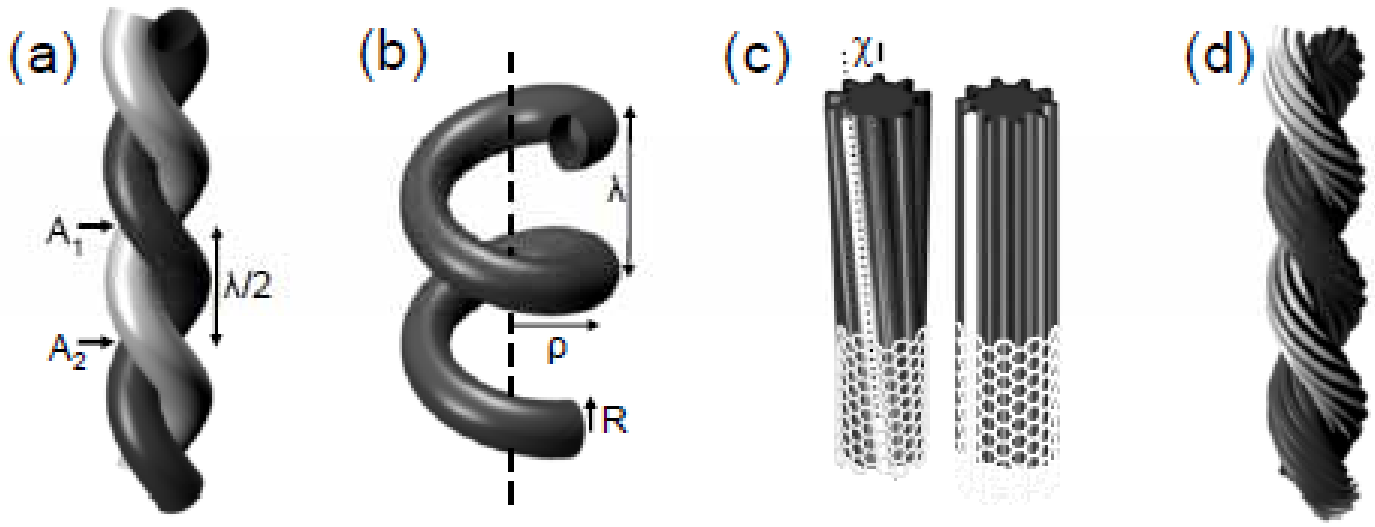



FIG. 2. Structure of carbon nanotubes and their bundles. (a) A pair of coiled nanotubes as the simplest example of a helical rope. Schematic views of (b) an individual nanotube coil (helix), (c) chiral and achiral nanotubes, with emphasis on the tilting angle $\chi$ associated with tilted lines of hexagons along the tube, shown by the white solid line, and (d) the optimum entanglement of two chiral nanotubes. The labeling in (a) refers to Fig. 1(a). The pitch length $\lambda$ and the radius $\rho$ of an individual helix, formed of a nanotube of radius $R$, are shown in (b).

# Energy for the formation of helical ropes

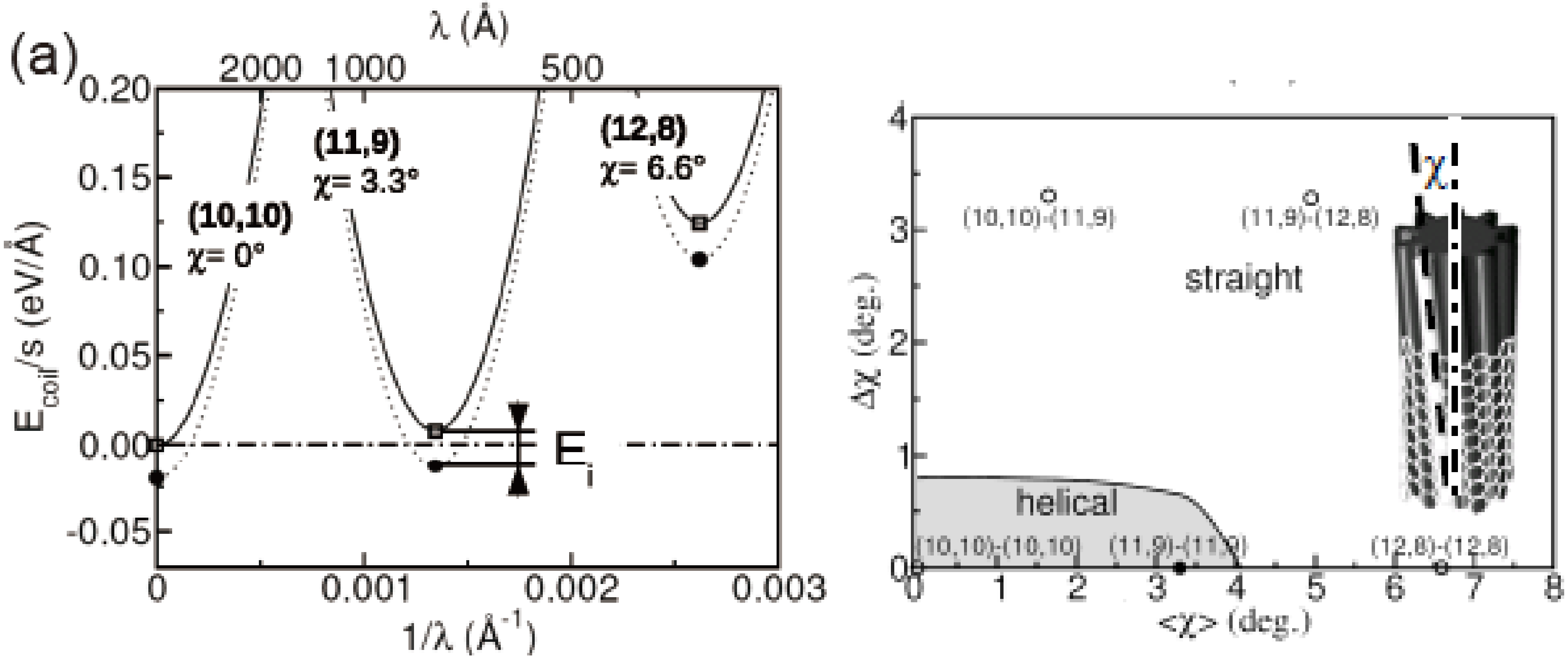
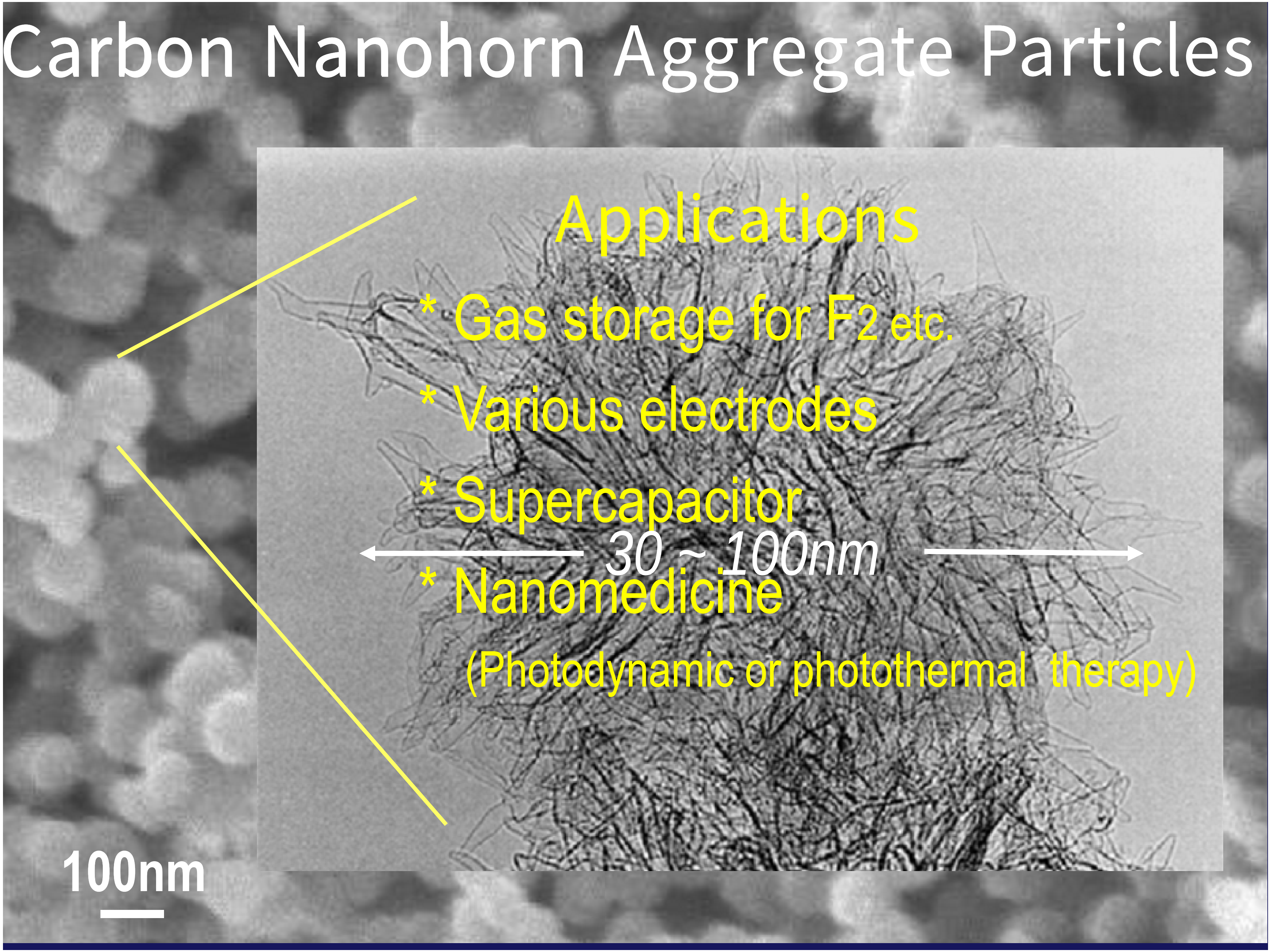



FIG. 4. Energy considerations for the formation of helical ropes. (a) Coiling energy $E_{coil}$ per nanotube length $s$ of two identical nanotubes in the case of ideal orientational alignment along the helix, shown by the solid lines. Presence of the inter-tube interaction $E_i$ stabilizes the helix, as indicated by the dotted lines. The energy reference is a pair of non-interacting (10,10) nanotubes. (b) Phase diagram, indicating conditions, under which two nanotubes with pitch angles $\chi_1$ and $\chi_2$ should form a helix. $<\chi>= (\chi_1+\chi_2)/2$ is the average pitch angle and $\Delta\chi = |\chi_1+\chi_2|$ is the pitch angle difference.

# Carbon Nanohorn Aggregate Particles

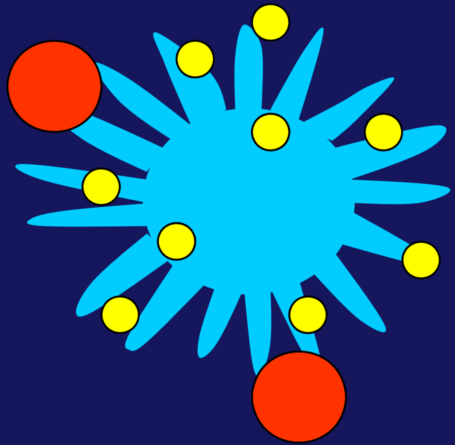


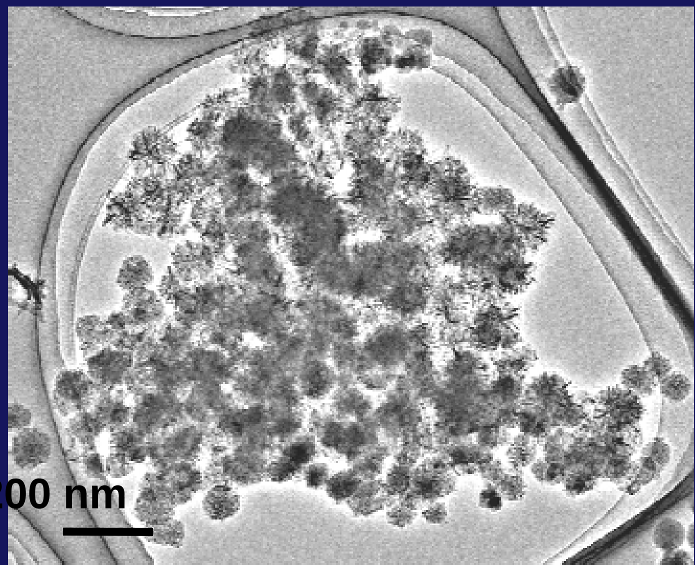

## Applications

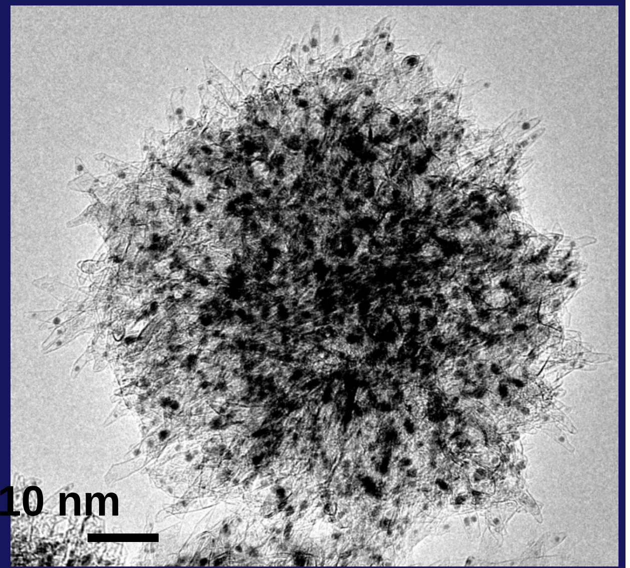
* Gas storage for $F_2$ etc.
* Various electrodes
* Supercapacitor
* Nanomedicine
  (Photodynamic or photothermal therapy)

# Drug delivery carrier

Ajima et al. *Molecular Pharmaceutics* 2005

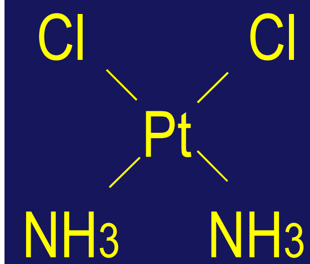


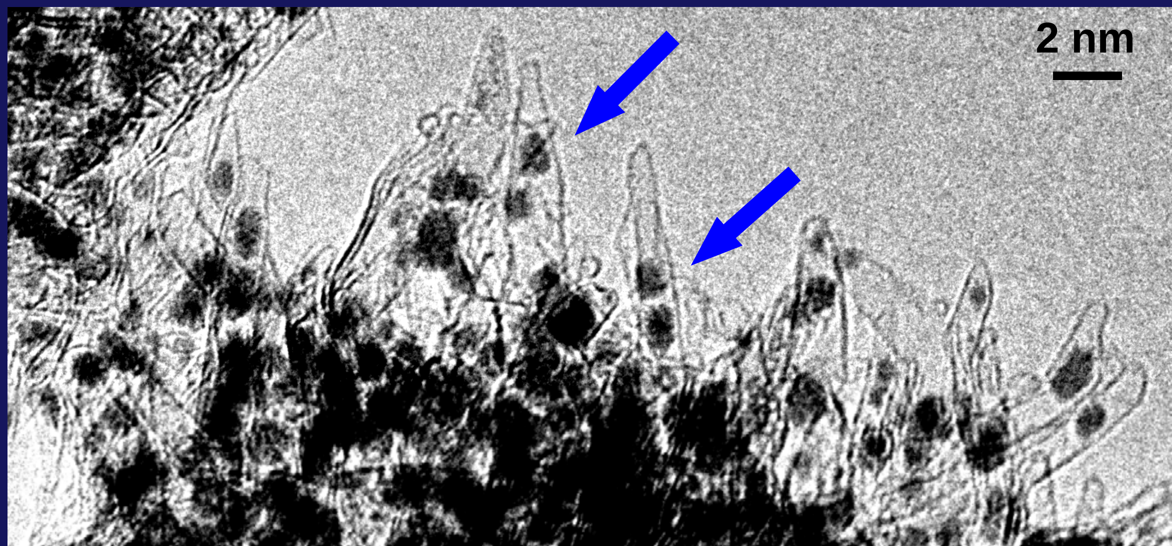


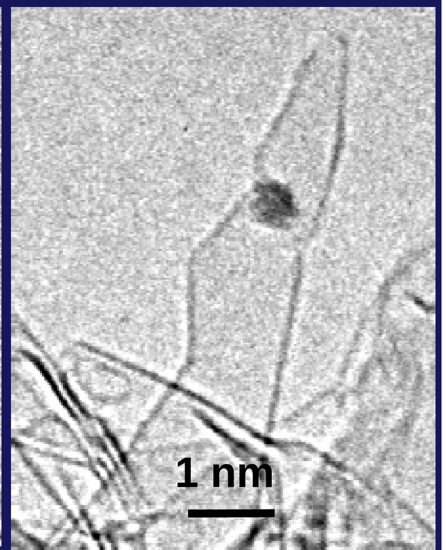




- **Drug:** Cisplatin, Dexamethasone (anti- inflammatory agent )
- **Targeting Material**
- **Drug carrier**

CDDS

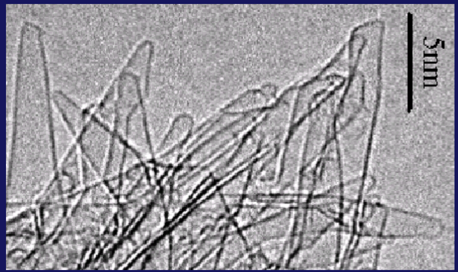


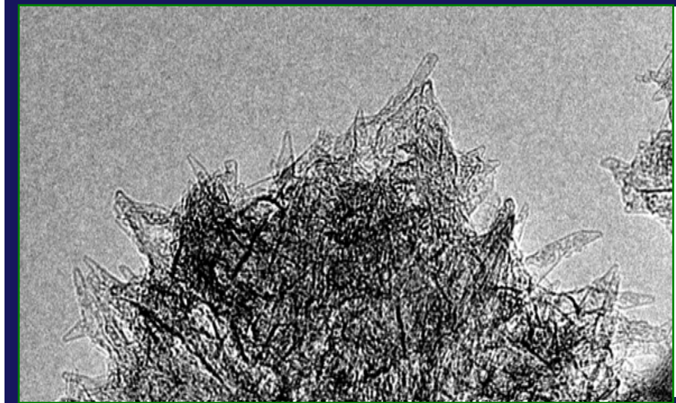



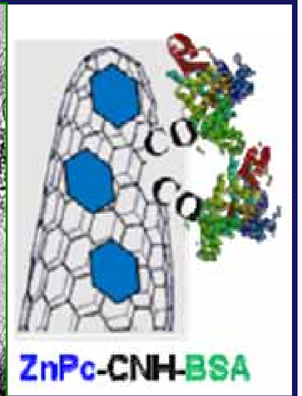



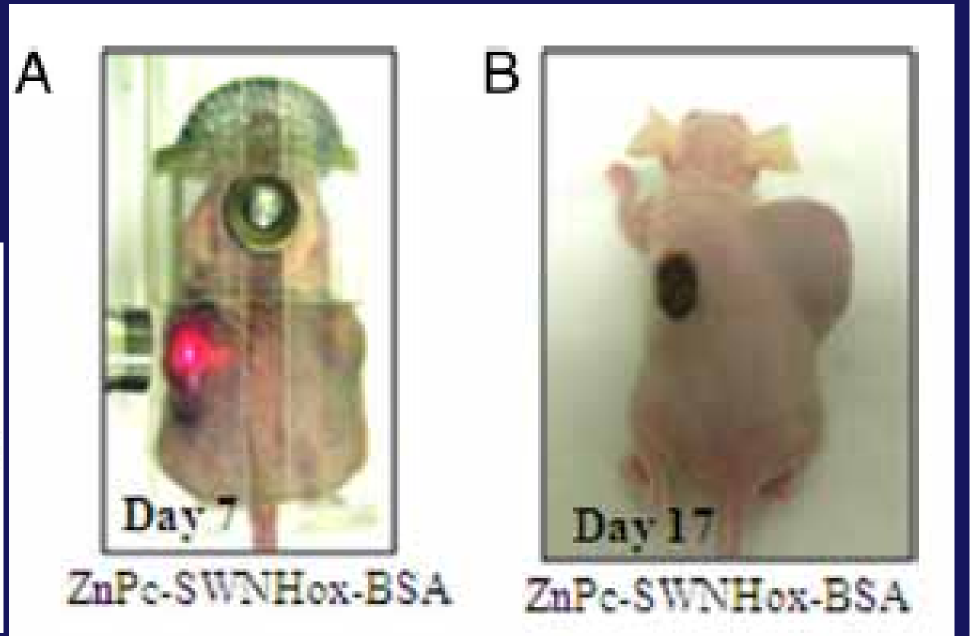
# ZnPc/protein nanohorns for Photodynamic Therapy (PDT)

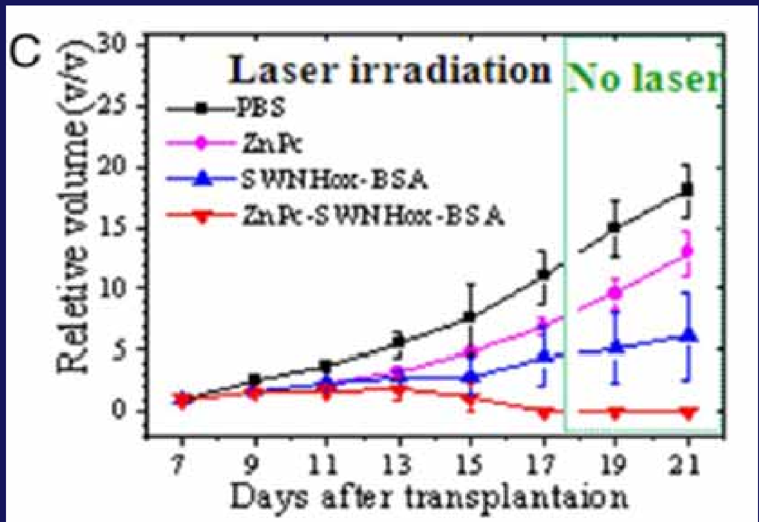
Yudasaka et al., *PNAS*, 105, 14775(2008)

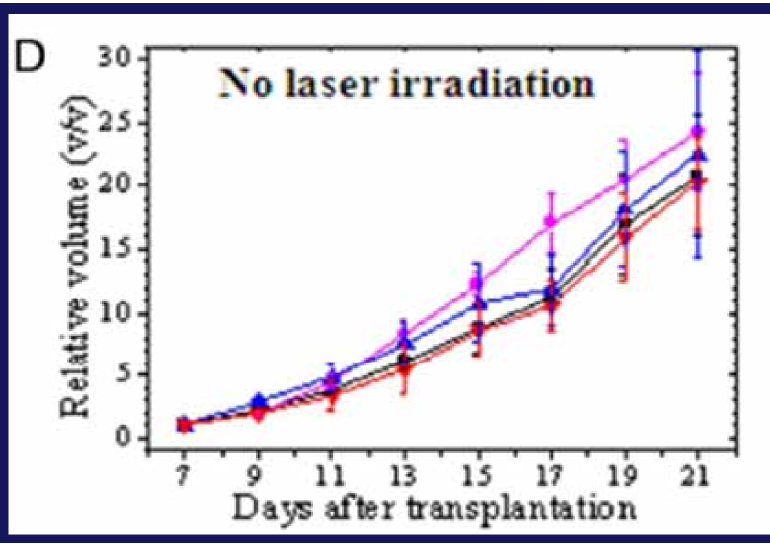




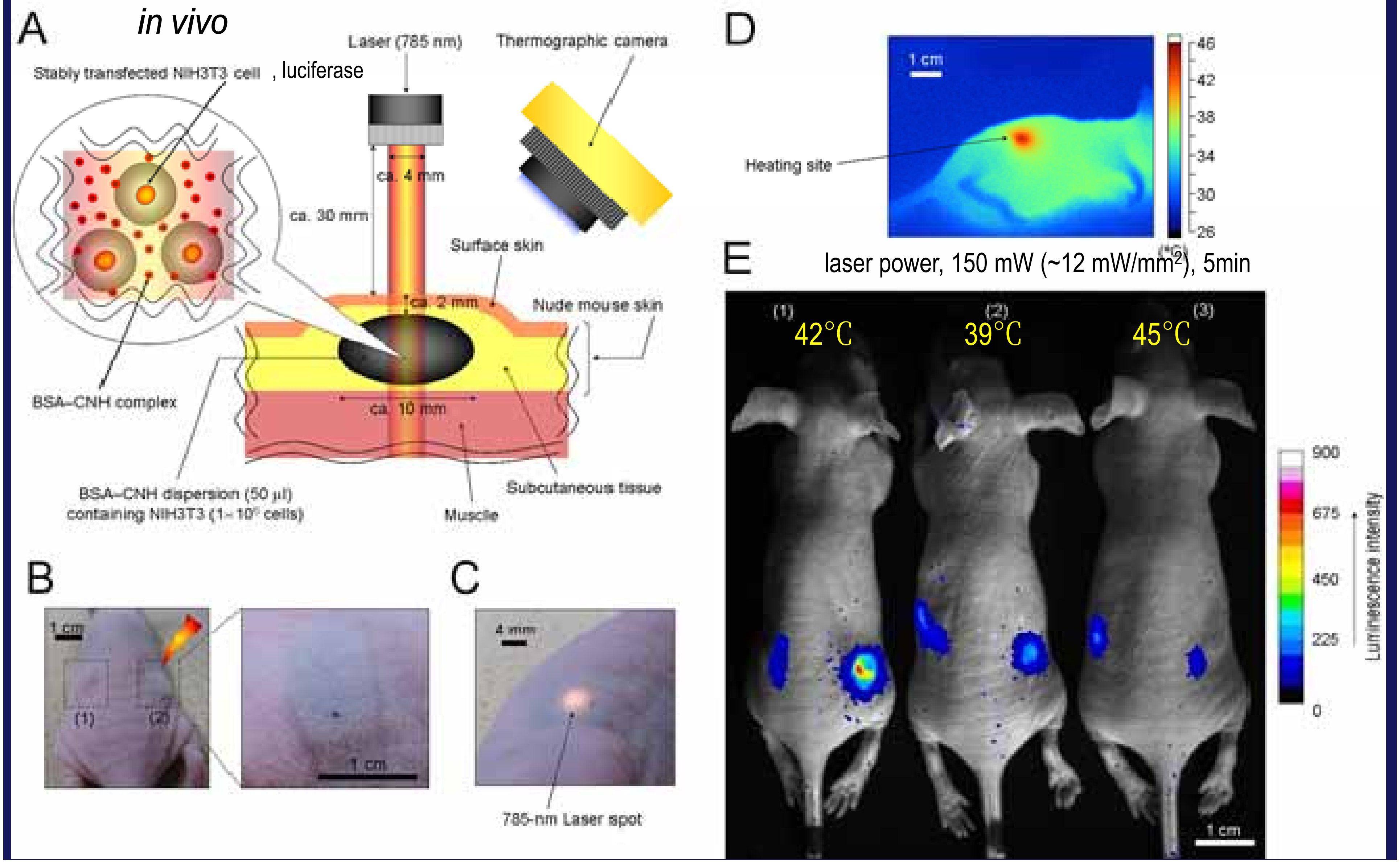



# Photo-Thermo-Genetics by CNH

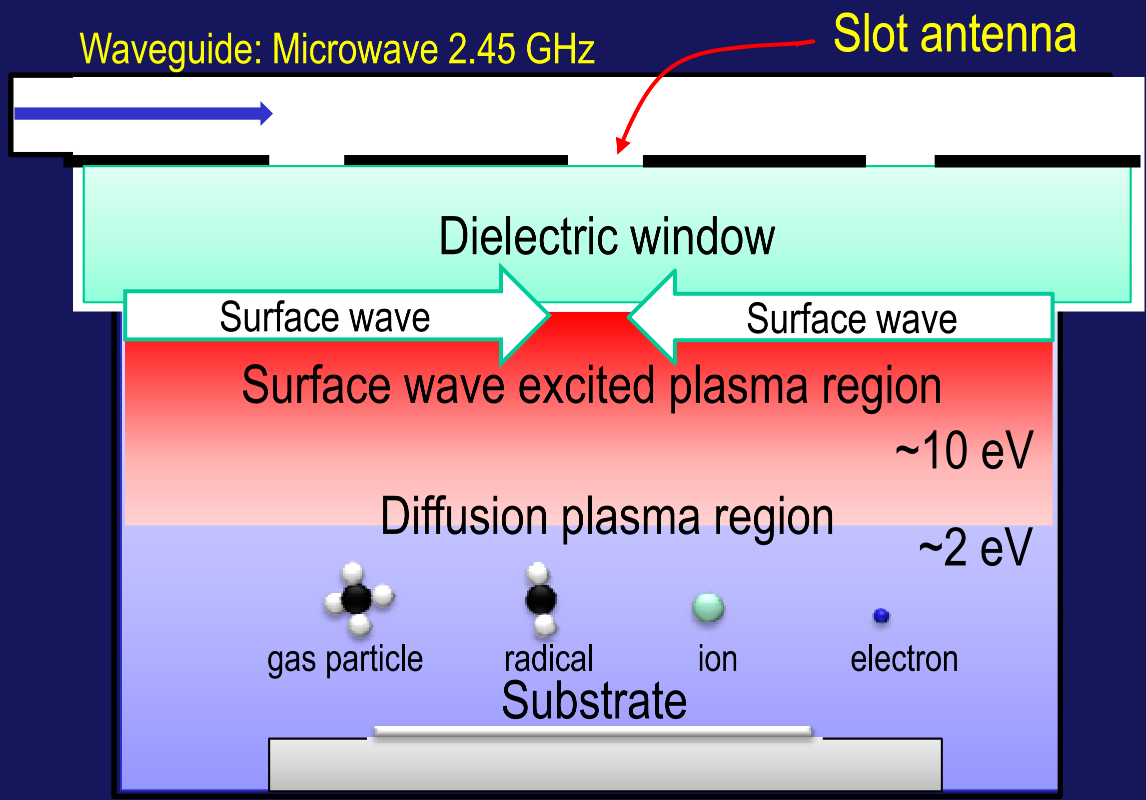
Heat shock promoter-mediated gene expression
triggered by laser-induced carbon nanohorns

Miyako et al. *PNAS* 2012.



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

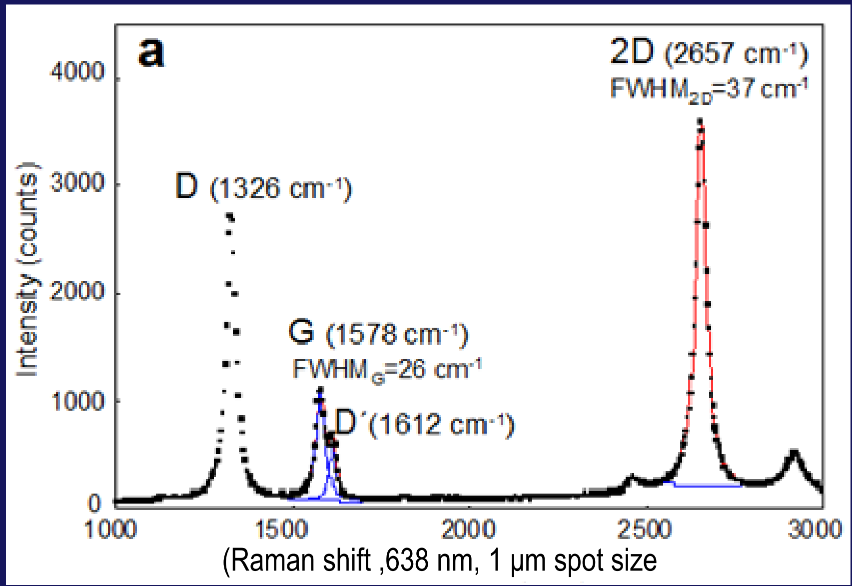
CVD area: 60 cm × 40 cm



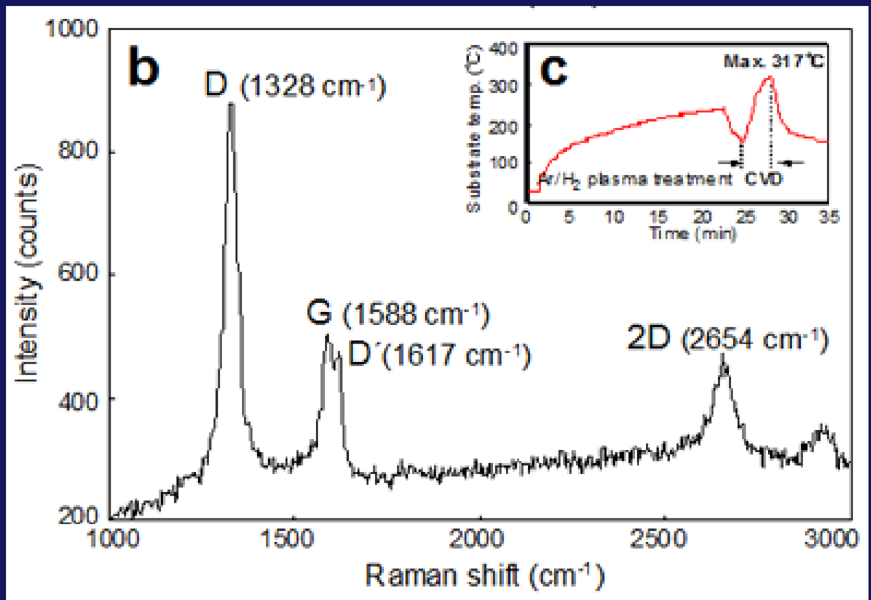

- MW power: 3-5 kW per a MW generator
- Gas: H2/CH4 /Ar
- Substrate: Cu (t30 μm) and Al (t12 μm) foils
- Gas pressure: 3-5 Pa
- Substrate temperature: below 400 ℃
- Deposition time: 30-180 s

# Characteristics of graphene-based films as transparent electrodes

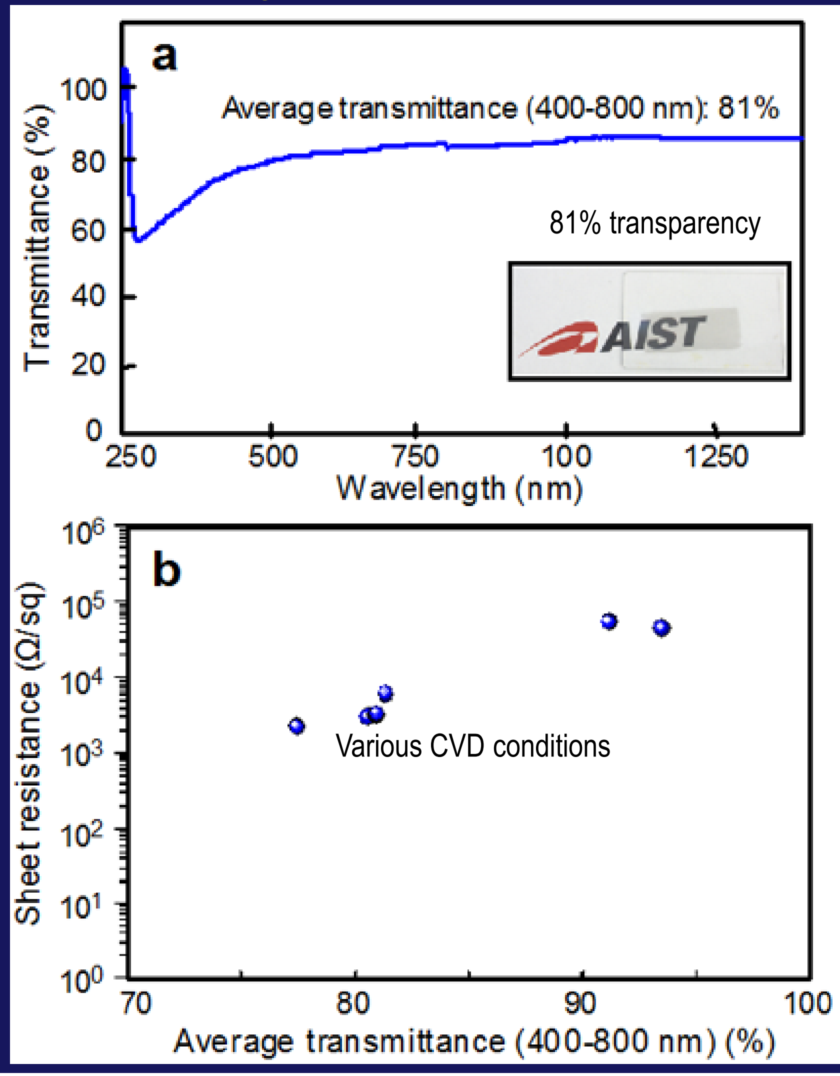
Hasegawa et al., JAP, 2010



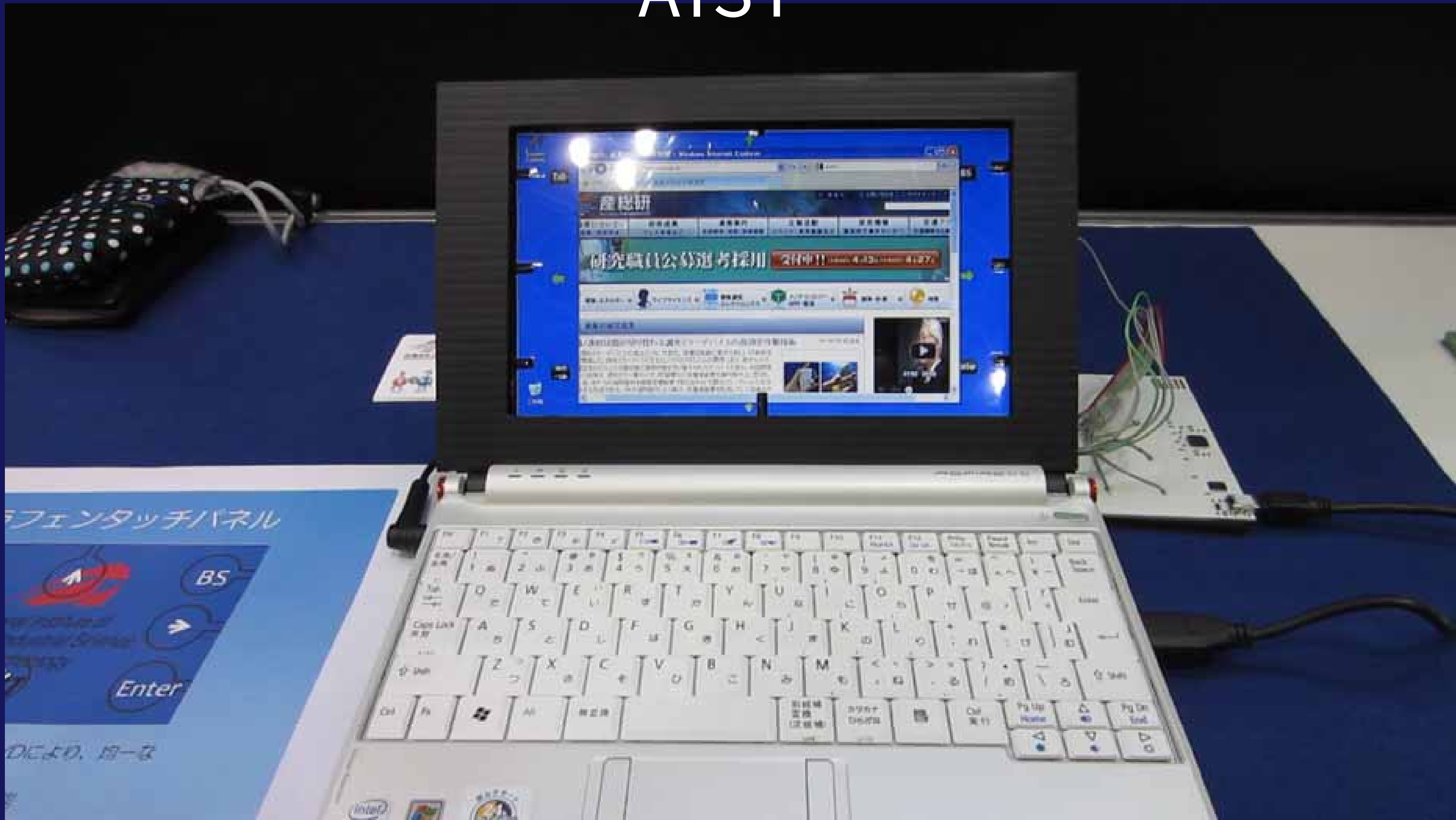

(a) Cu foil (CVD conditions: 5 Pa, $CH_4/Ar/H_2$=30/20/10 sccm, 3 kW per a MW generator, 30 s) substrate temperatures below 400 ˚C




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



# Touch panel made of graphene sheets by AIST




- Capacitave type
- Surface resistance **1～3**kΩ/sq
- Transparency 80% (with PET film, 90% only for Graphene)
- Number of graphene sheets : 4~5 sheets

# 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**