Introduction to Nanotechnology

Carbon Nanotubes

Jason C.S. Chang

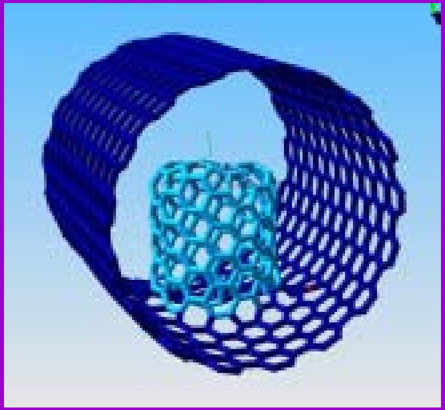
Institute of Physics, Academia Sinica

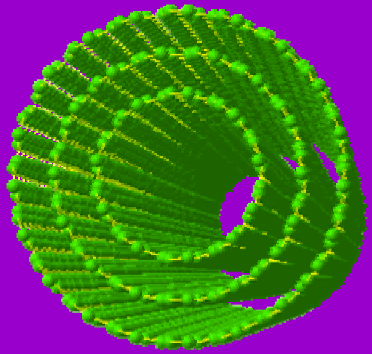
Taipei, Taiwan

December 10, 2007 TIGP Nano Program, Academia Sinica Taipei

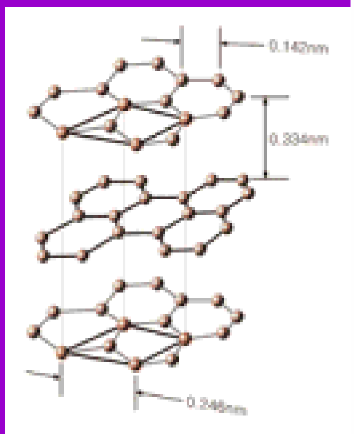
Outline

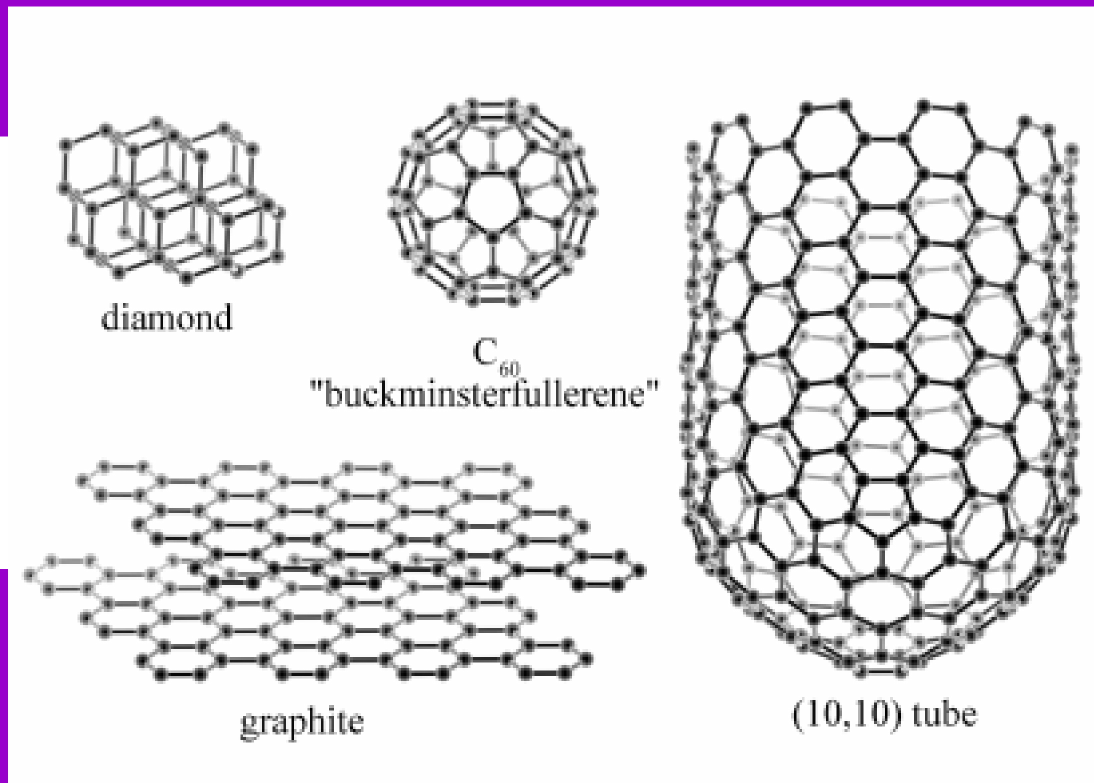
- Types of carbon nanotubes
- Growth of carbon nanotubes
- Physical properties of carbon nanotubes
- Applications of carbon nanotubes
- Manipulation of carbon nanotubes

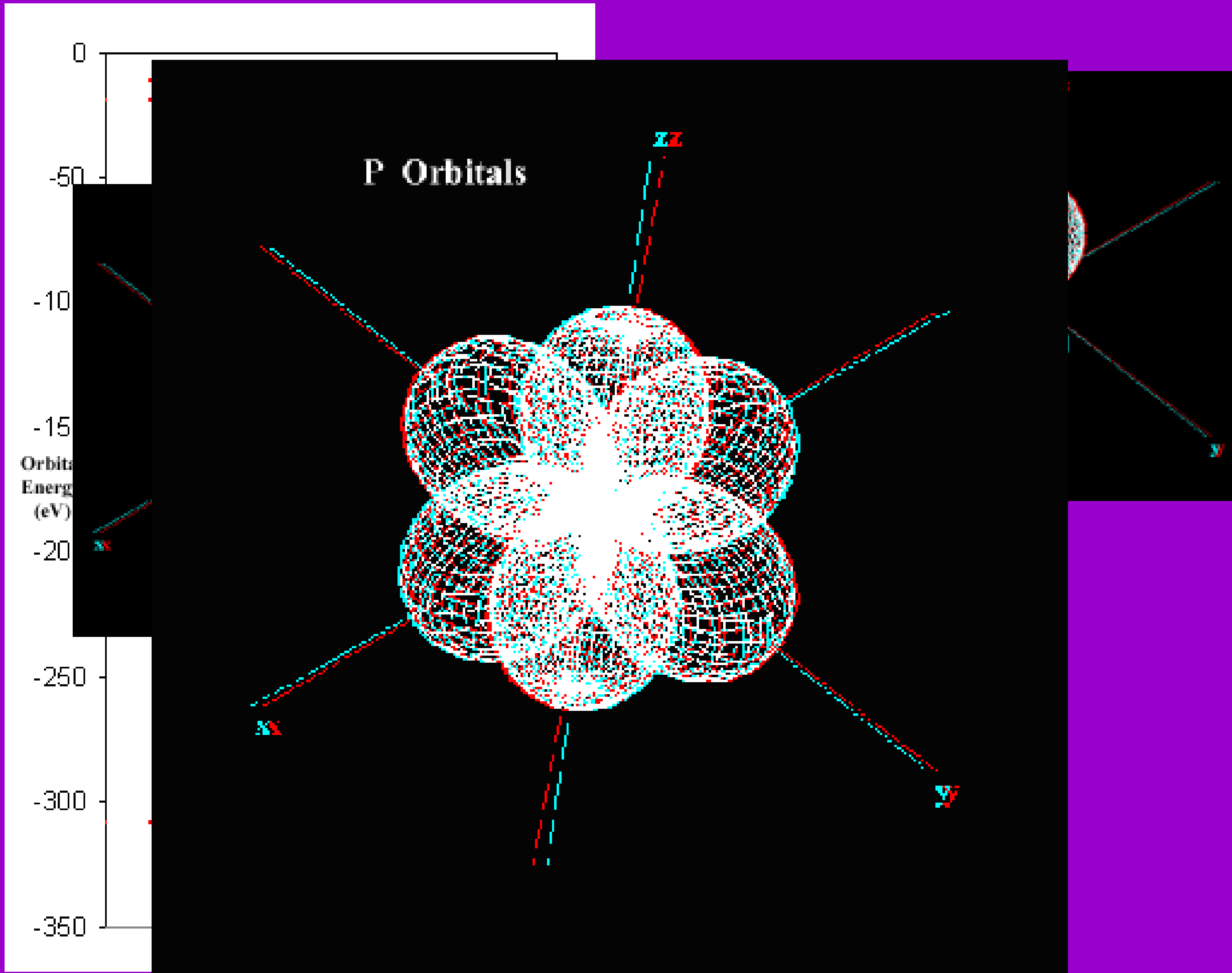




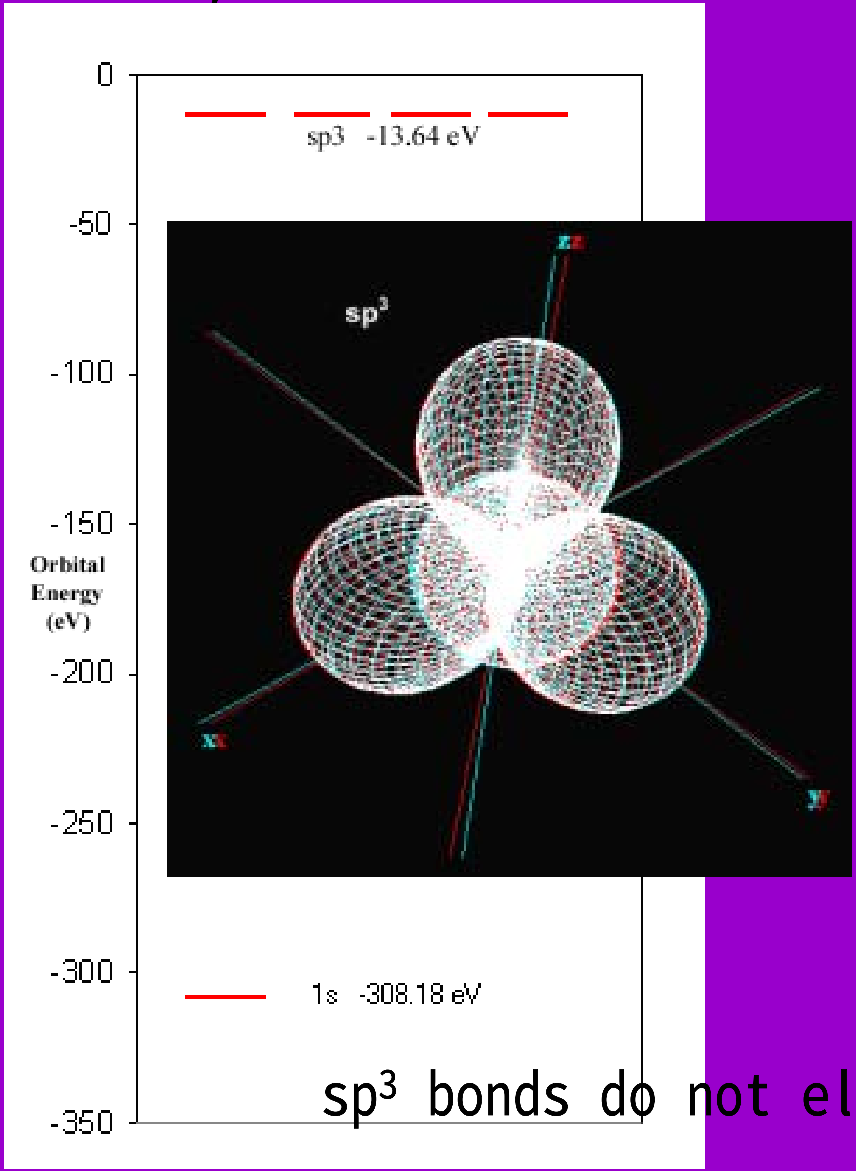
Structures of carbon

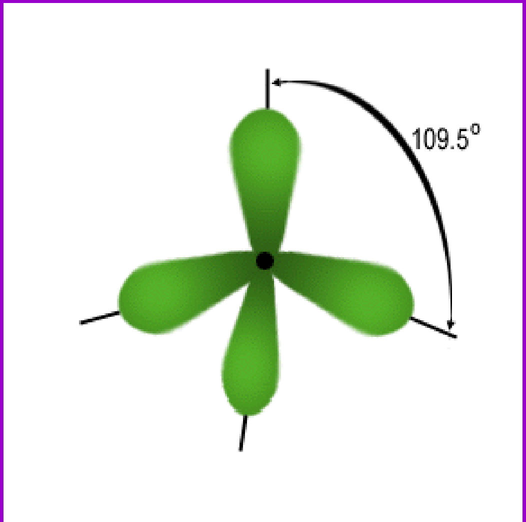




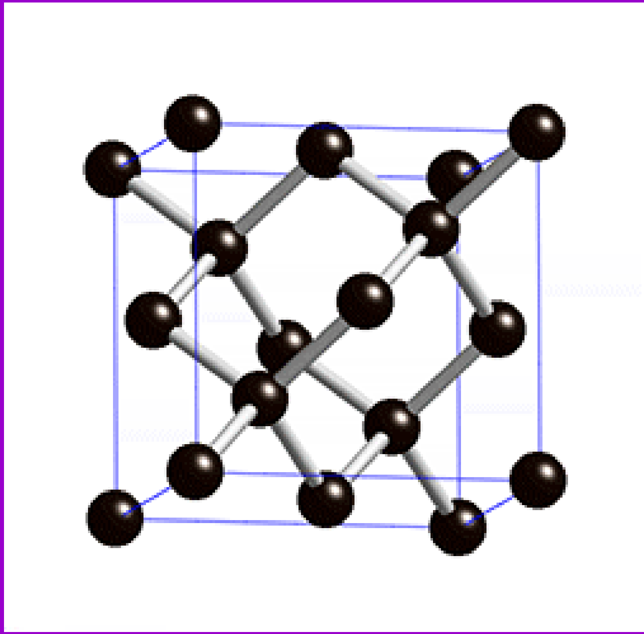

P Orbitals
zz
xx
yy
0
-50
-10
-15
-20
-250
-300
-350
Orbit
Energ
(eV)

Hybridization of Carbon Atomic Orbitals

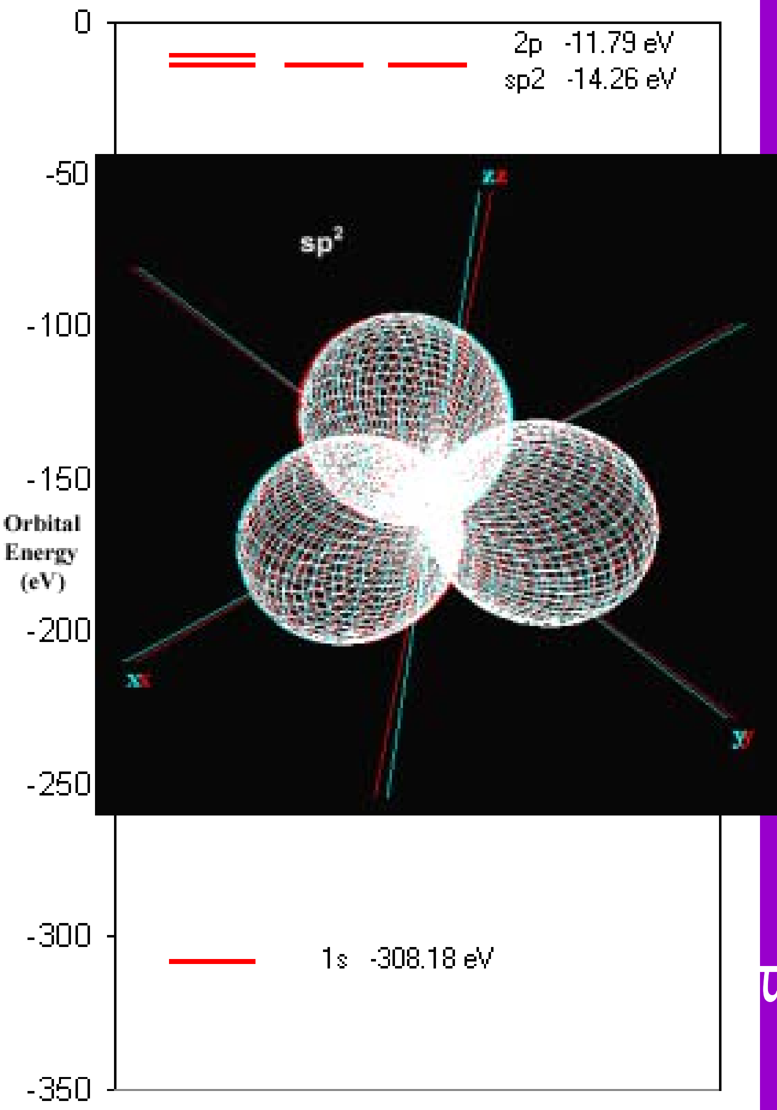


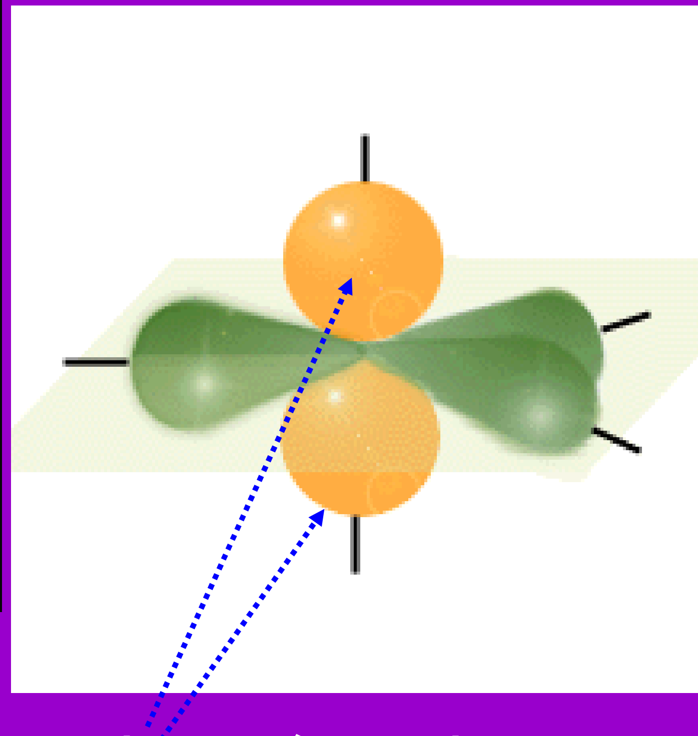


sp^3 bonds do not electrically conduct

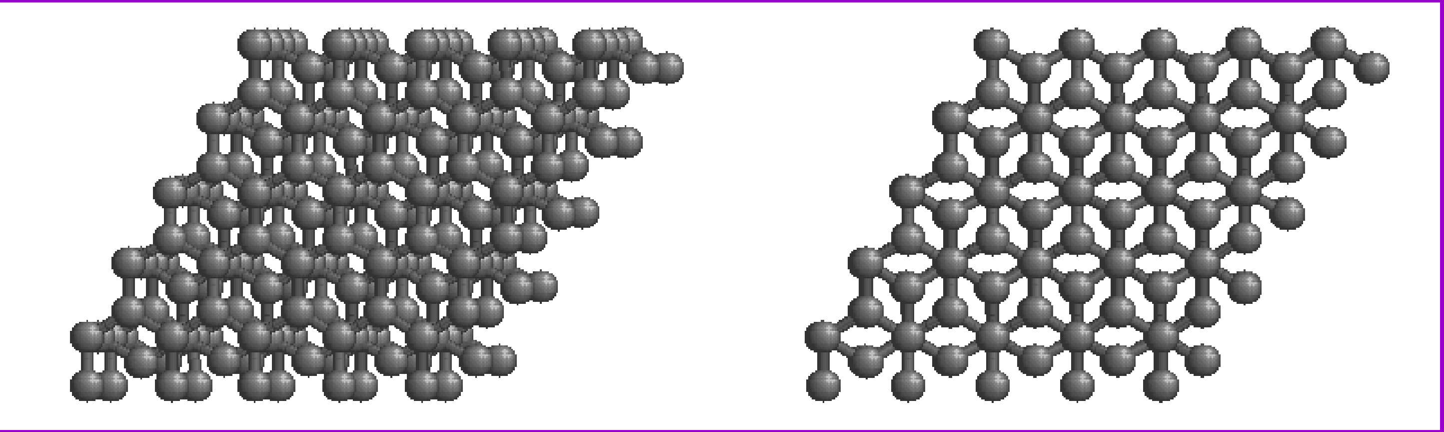


Diamond





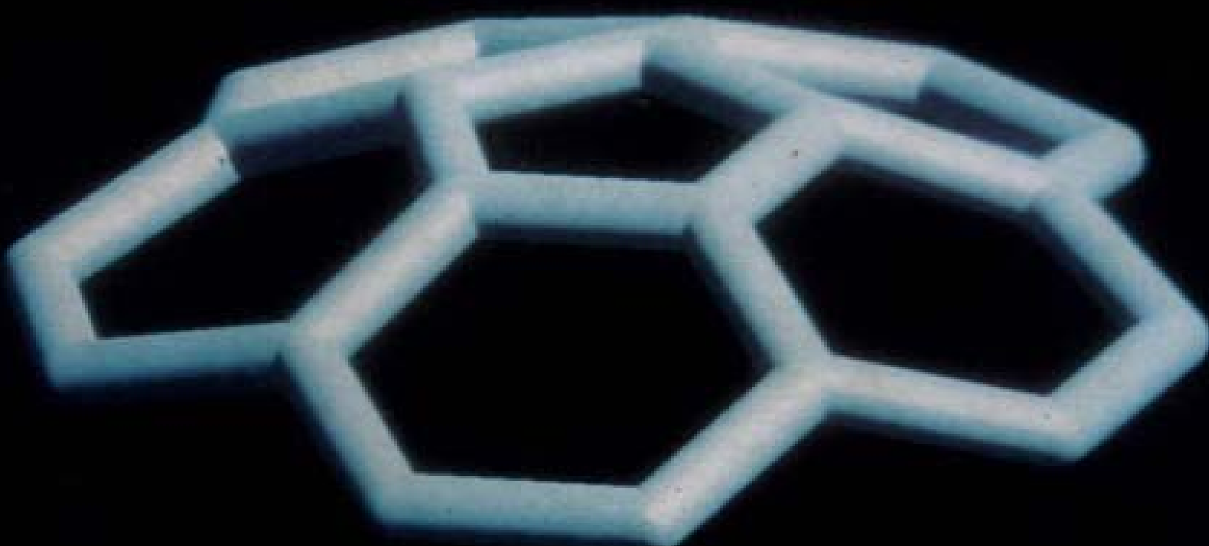
π-orbit (conducting)

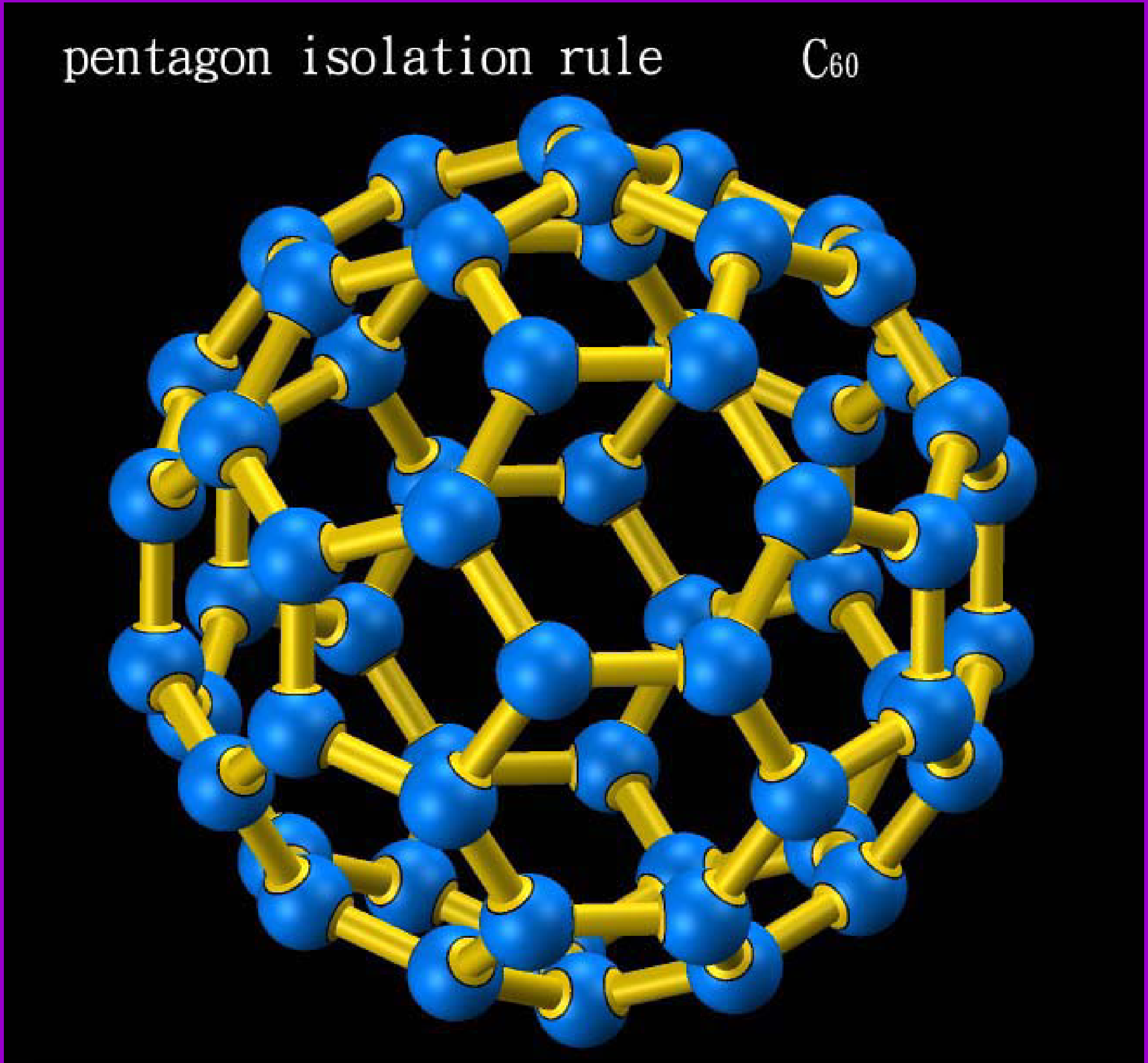


Graphite

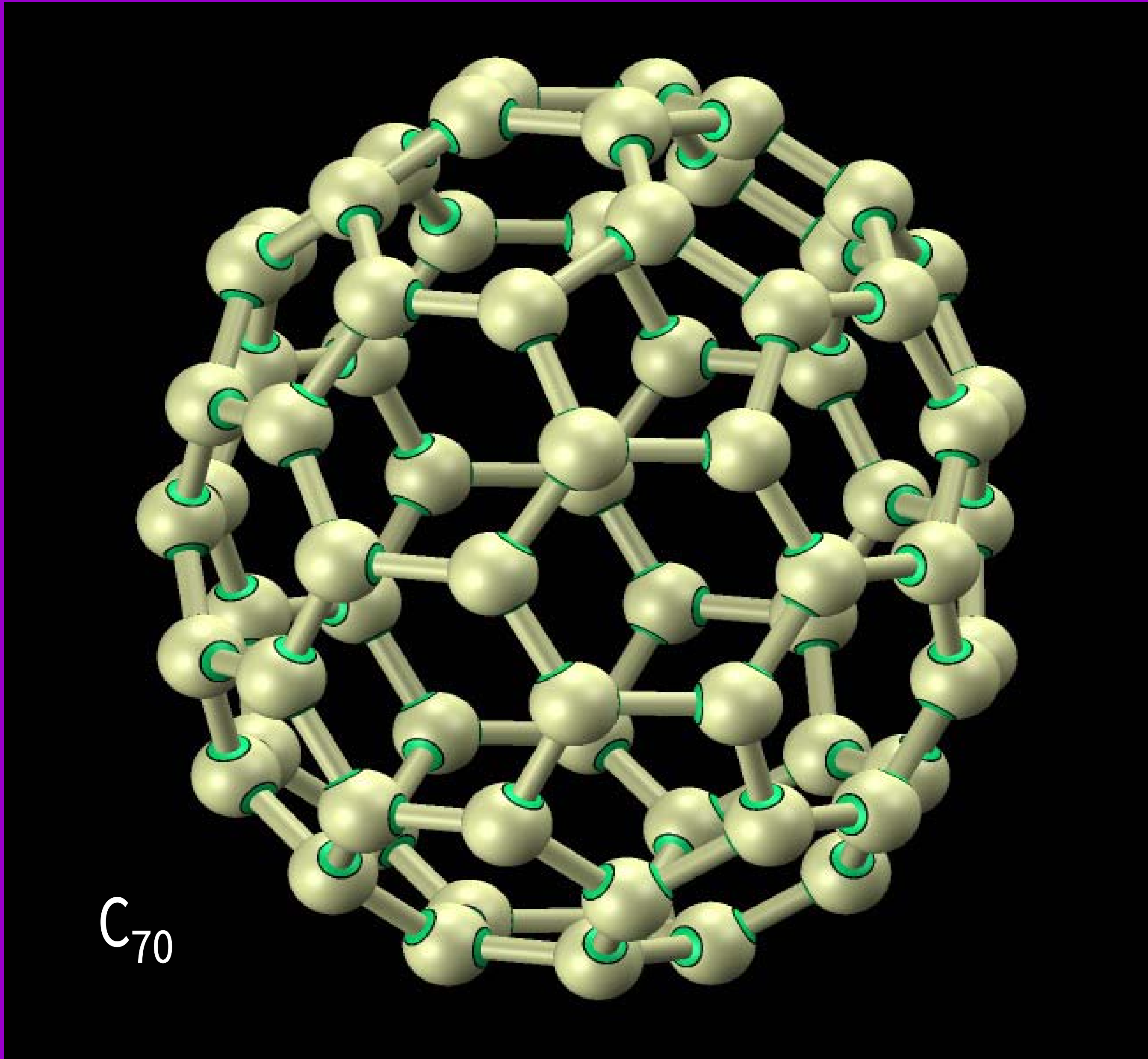
一個五連環形成正30度曲面

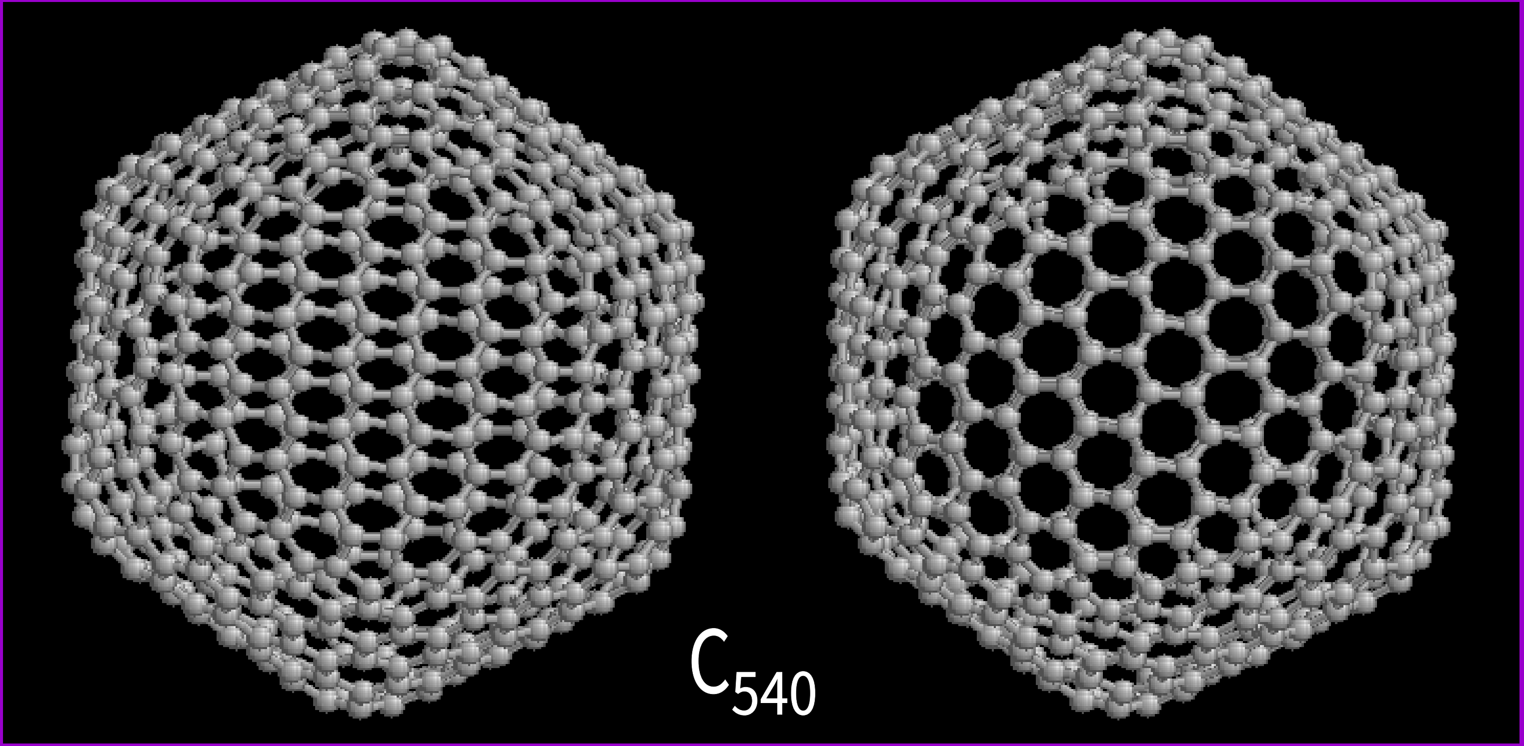
(五連環可視為六連環平面之defect).

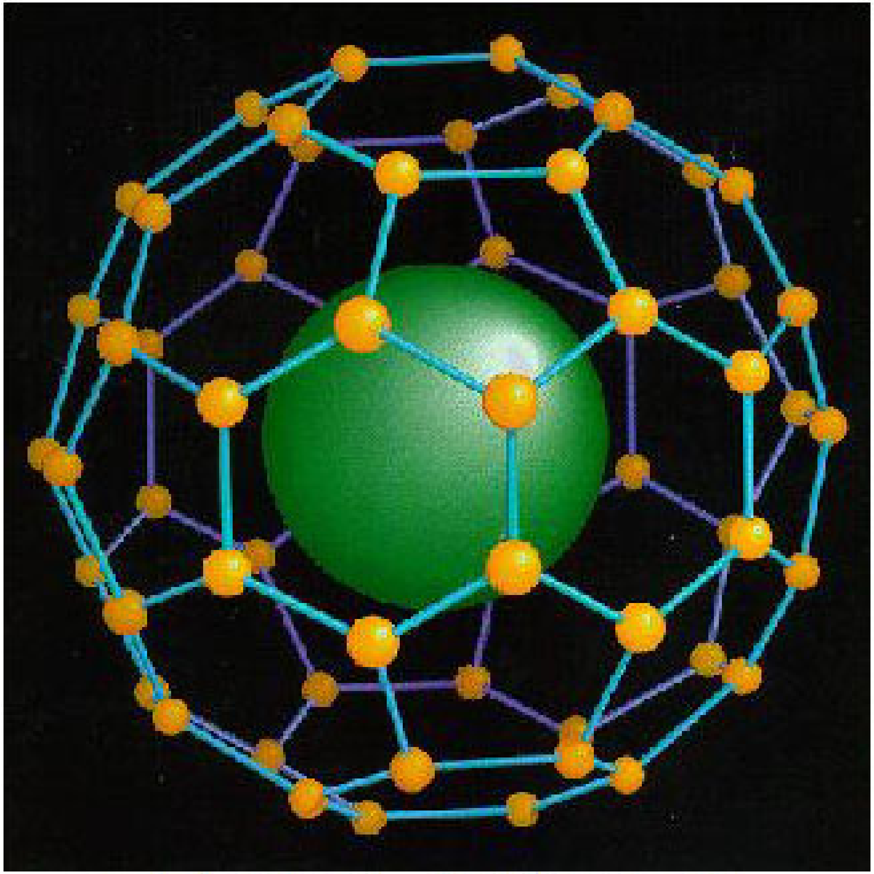




C60 consists of 12 pentagons and 20 hexagons


C_{70}

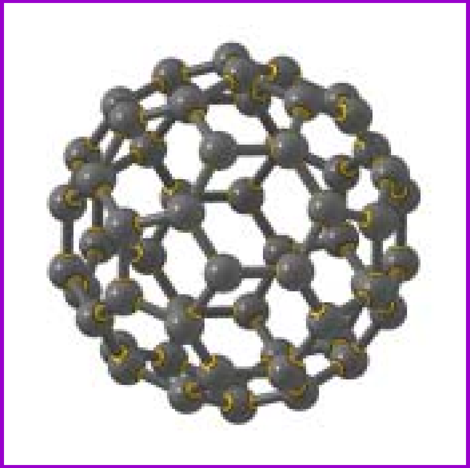

C_{540}



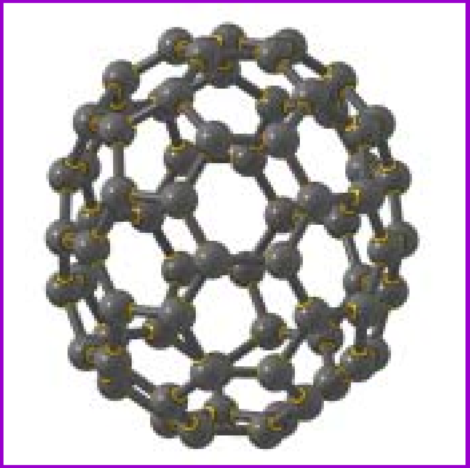
endohedral fullerenes

$M@C_{60}$, $La@C_{60}$, LaC_{70}

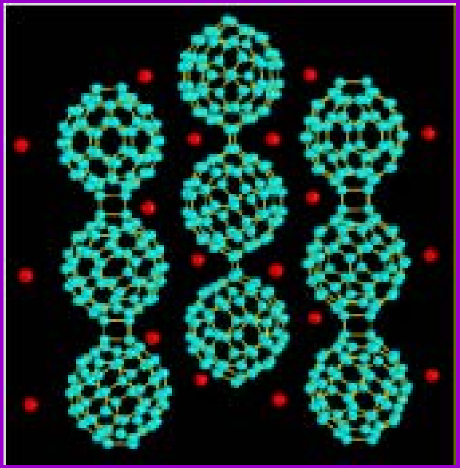
Fullerenes



C_{60}

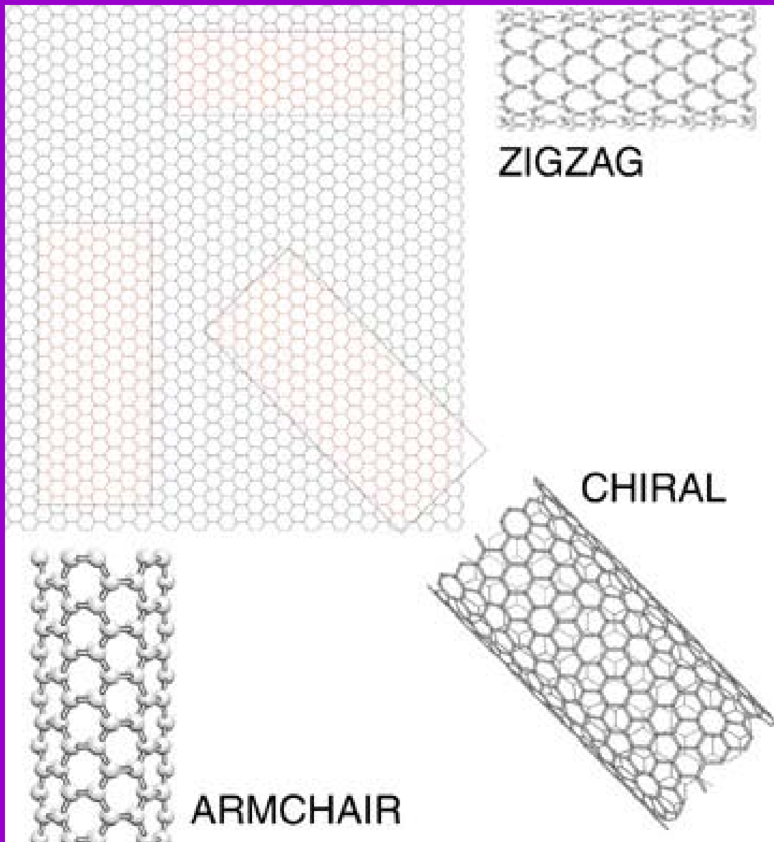


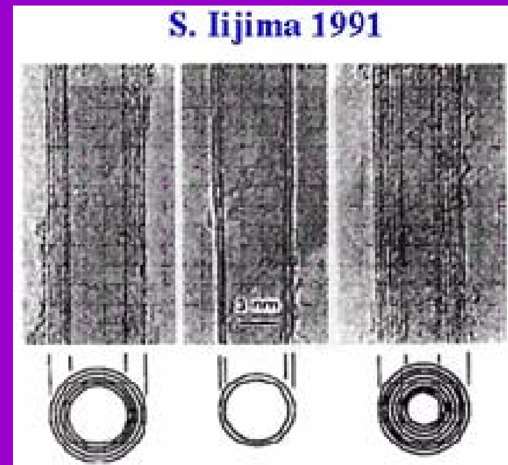
C_{70}

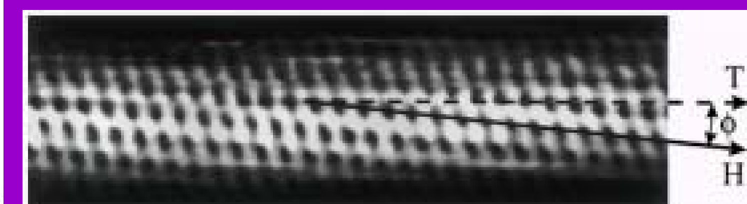


RbC_{60}

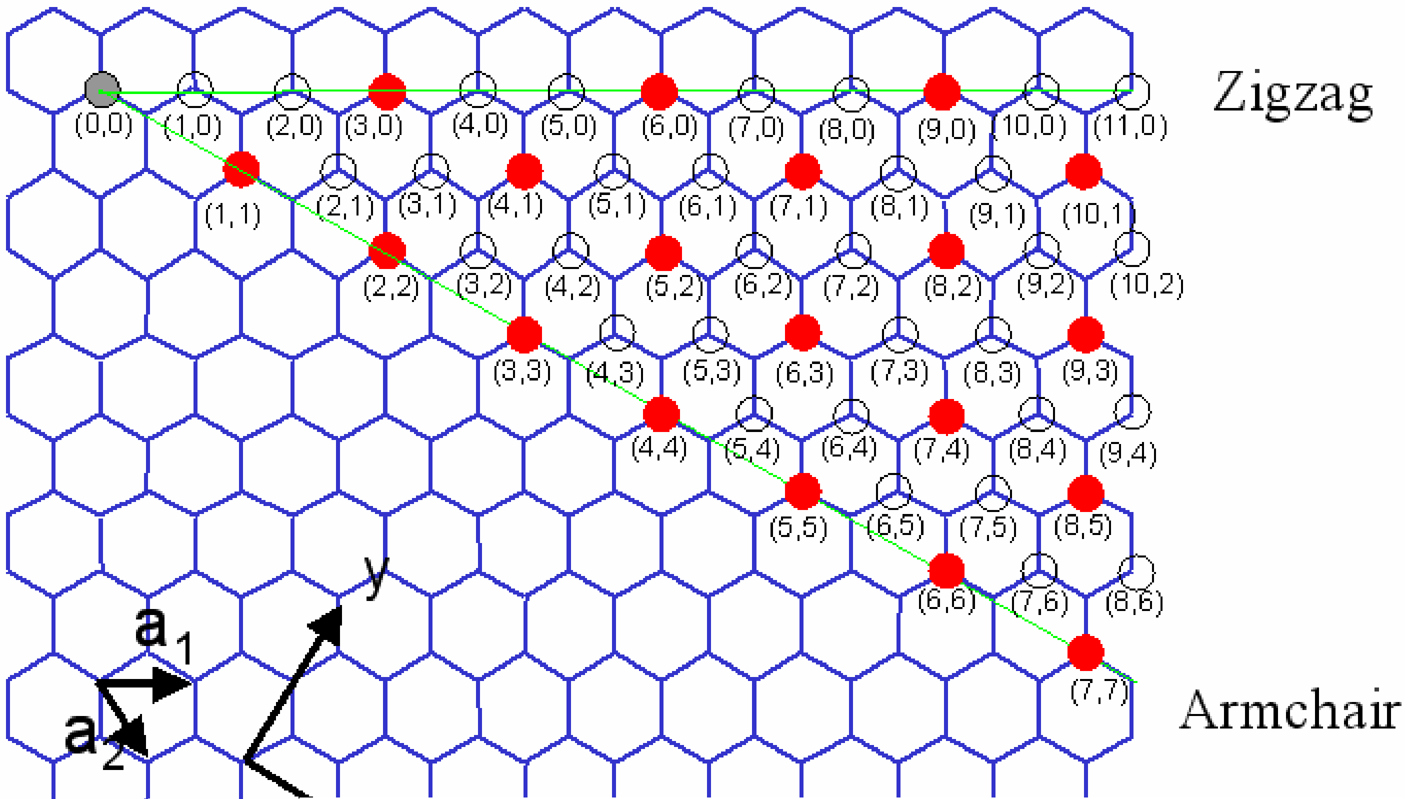
Types of carbon nanotubes







Structure of carbon nanotubes (CNT)



Metallic nanotube is: 2n+m=3q (q: integer), red solid point

black open circle represents semiconductor nanotubes

Appl. Phys. Lett. 60 (18), 1992

Structure of carbon nanotubes (CNT)

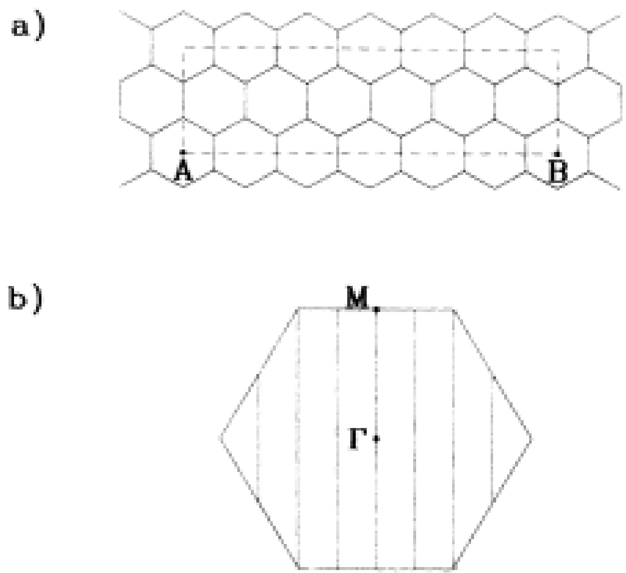


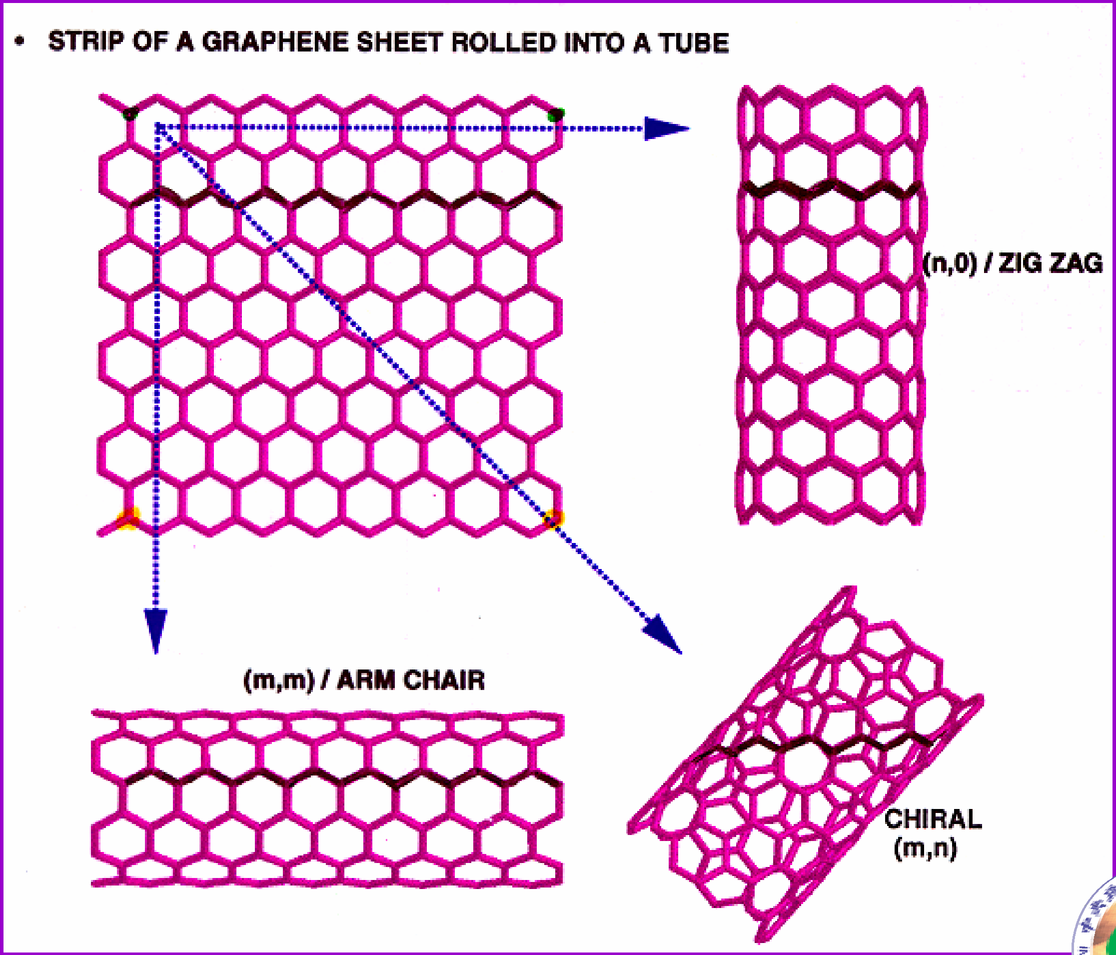
FIG. 1. (a) Unit cell of the (6,0) tube mapped onto the graphite sheet. For the tube, point *A* is rolled onto point *B*. (b) Brillouin zone of the graphite sheet. The vertical lines mark the set of allowed *k* vectors for the tube.

Metallic nanotube is: 2n+m=3q (q: integer), red solid point

black open circle represents semiconductor nanotubes

Phys. Rev. Lett. 72, 1878 (1994)

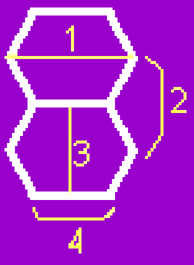
Structure of carbon nanotubes (CNT)



Physical constants of SWNT

Equilibrium Structure

Average Diameter of SWNT's	1.2-1.4 nm
Distance from opposite Carbon Atoms (Line 1)	2.83 Å
Analogous Carbon Atom Separation (Line 2)	2.456 Å
Parallel Carbon Bond Separation (Line 3)	2.45 Å
Carbon Bond Length (Line 4)	1.42 Å
C - C Tight Bonding Overlap Energy	~ 2.5 eV
Group Symmetry (10, 10)	C_{5V}



Density:

(10, 10) Armchair	1.33 g/cm3
(17, 0) Zigzag	1.34 g/cm3
(12, 6) Chiral	1.40 g/cm3

Physical constants of SWNT

Optical Properties (Fundamental Gap)

For (n, m); n-m is divisible by 3	[Metallic]	0 eV
For (n, m); n-m is not divisible by 3	[Semi-Conducting]	~ 0.5 eV

Electrical Transport

Conductance Quantization	n x (12.9 kΩ)$^{-1}$
Resistivity	10^{-4} Ω-cm
Maximum Current Density	10^{13} A/m^2

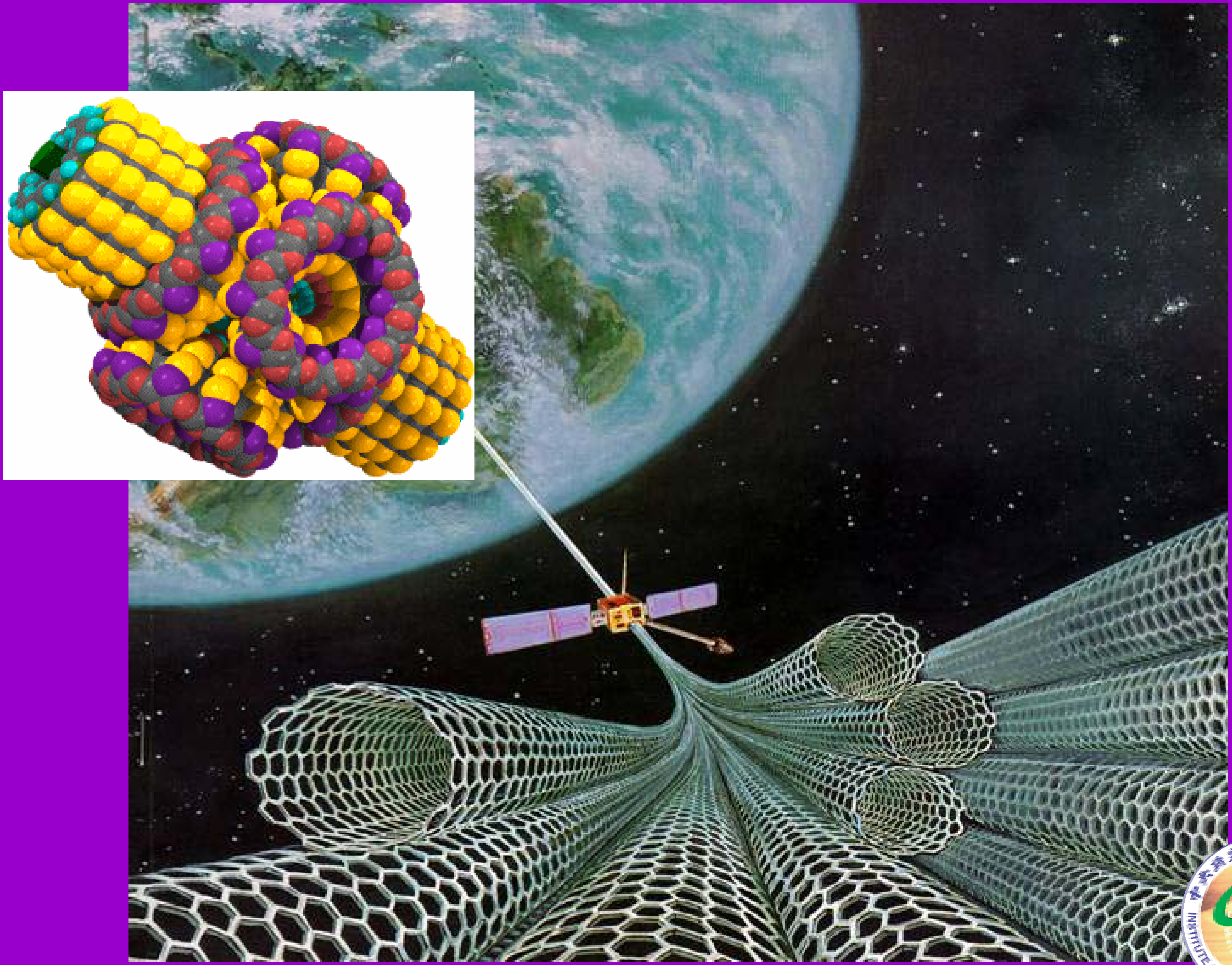
Thermal Transport

Thermal Conductivity	~ 2000 W/m/K
Phonon Mean Free Path	~ 100 nm
Relaxation Time	~ 10^{-11} s

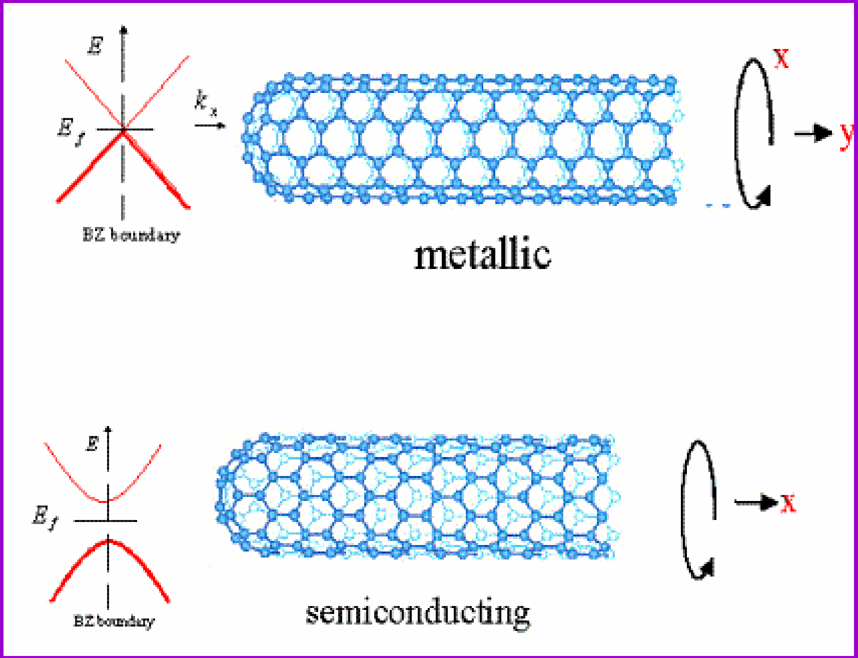
Elastic Behavior

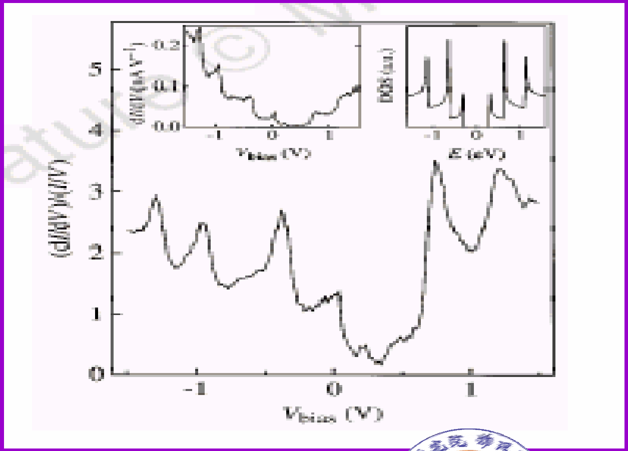
Young's Modulus (SWNT)	~ 1 TPa
Young's Modulus (MWNT)	~ 1.28 TPa
Maximum Tensile Strength	~ 30 GPa

Mechanical properties of CNT

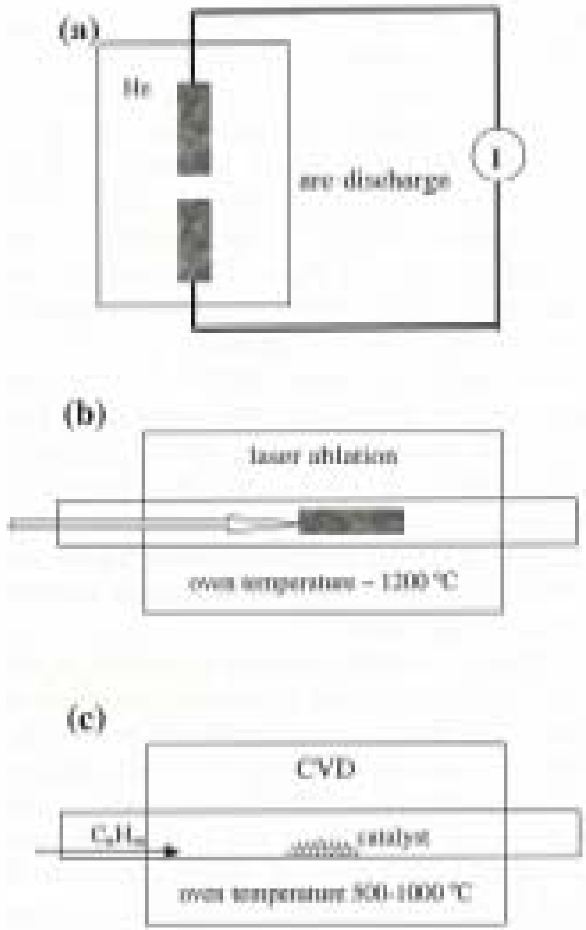


Electronic properties of carbon nanotubes





Growth methods of carbon nanotubes



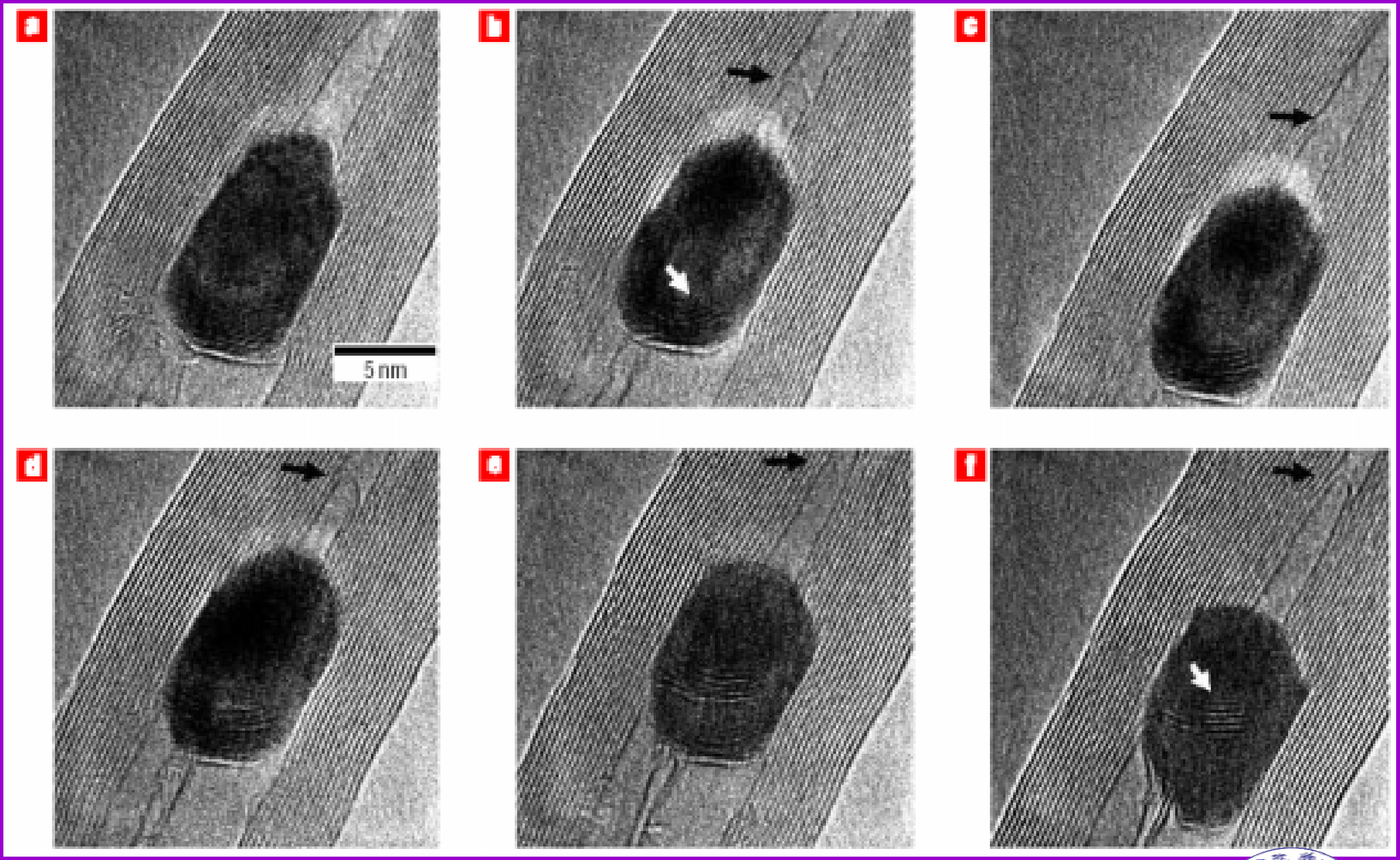
Arc-discharge

Laser ablation

CVD

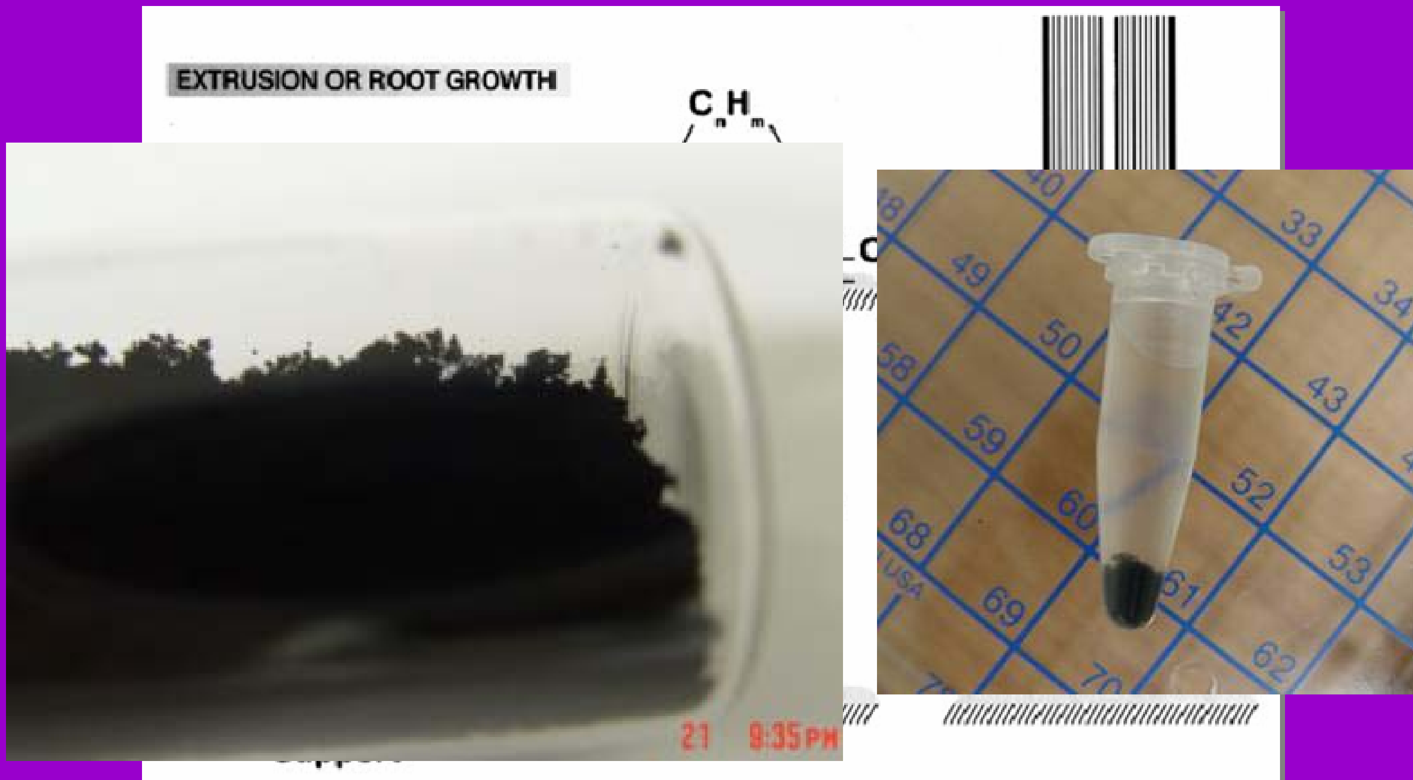
Fig. 1 a–c. Schematic experimental setups for nanotube growth methods

In situ growth of CNT

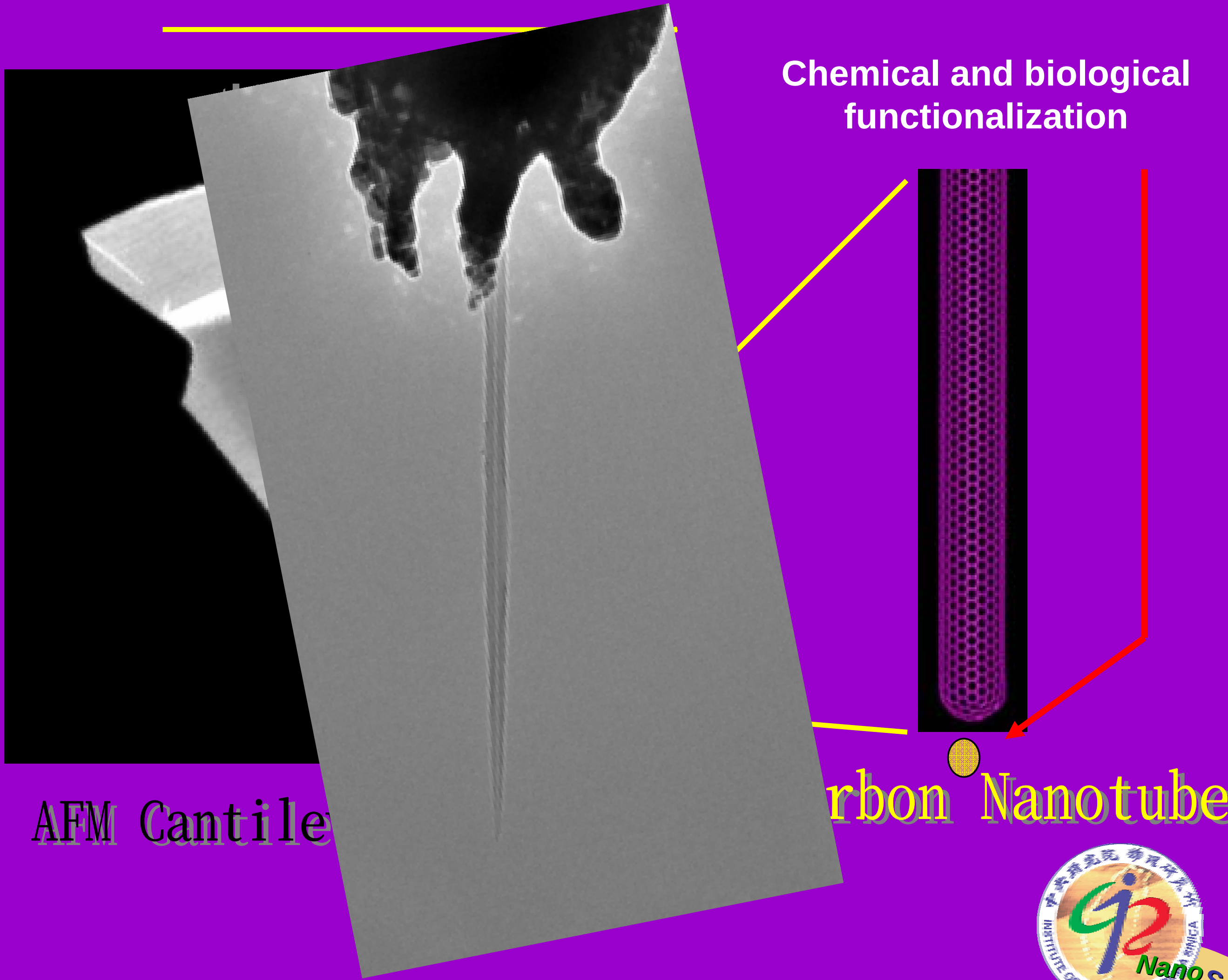


Nature Nanotechnology 2007

Growth mechanism of carbon nanotubes

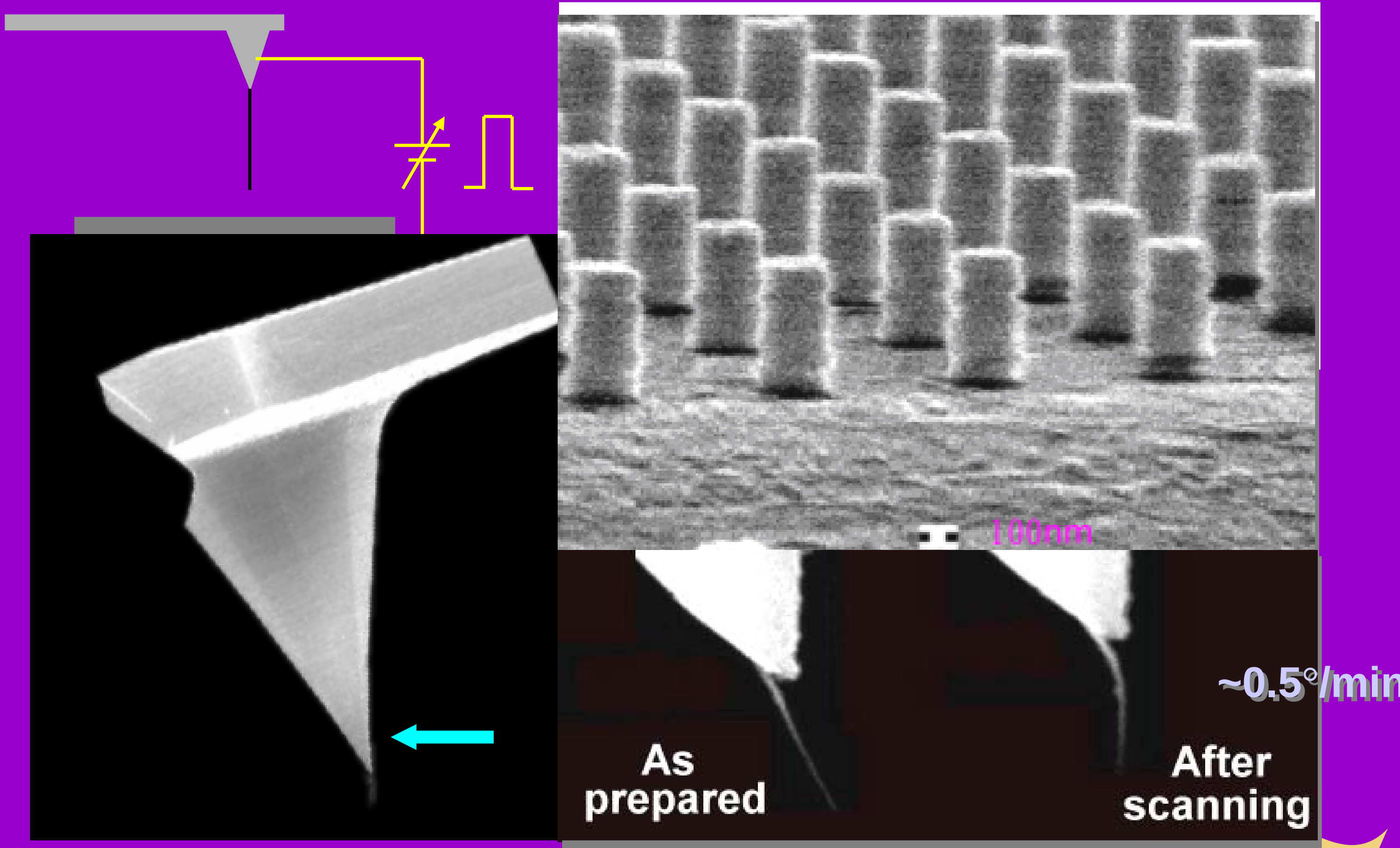


Carbon Nanotube tip for AFM

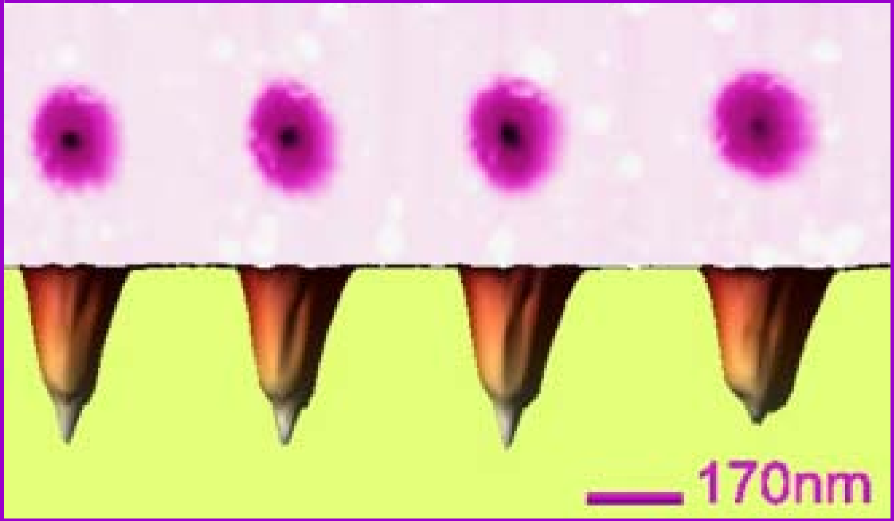


Modification of CNT probe

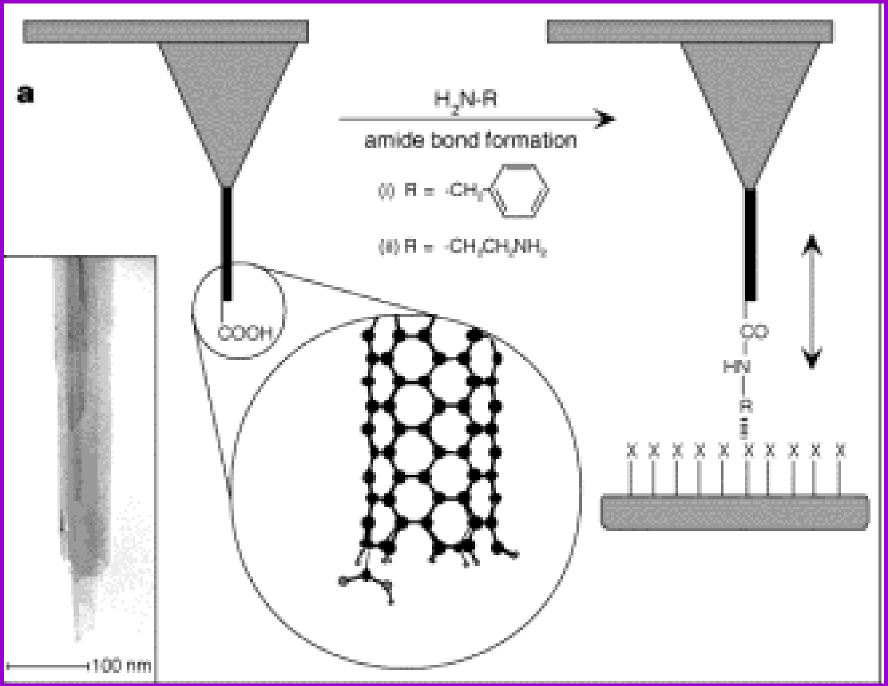
15V 800μs

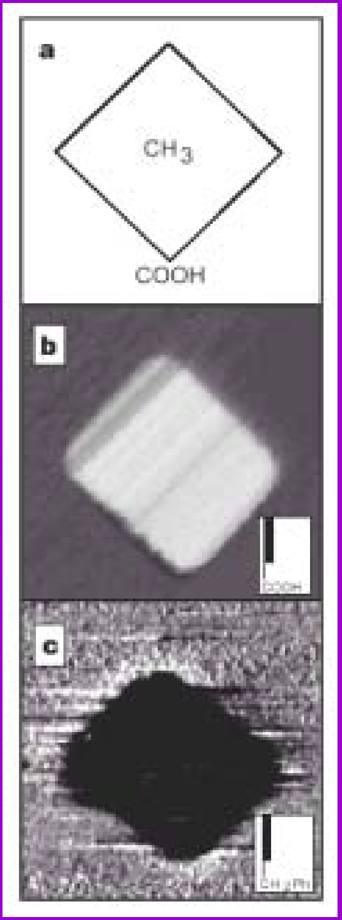


In-depth imaging



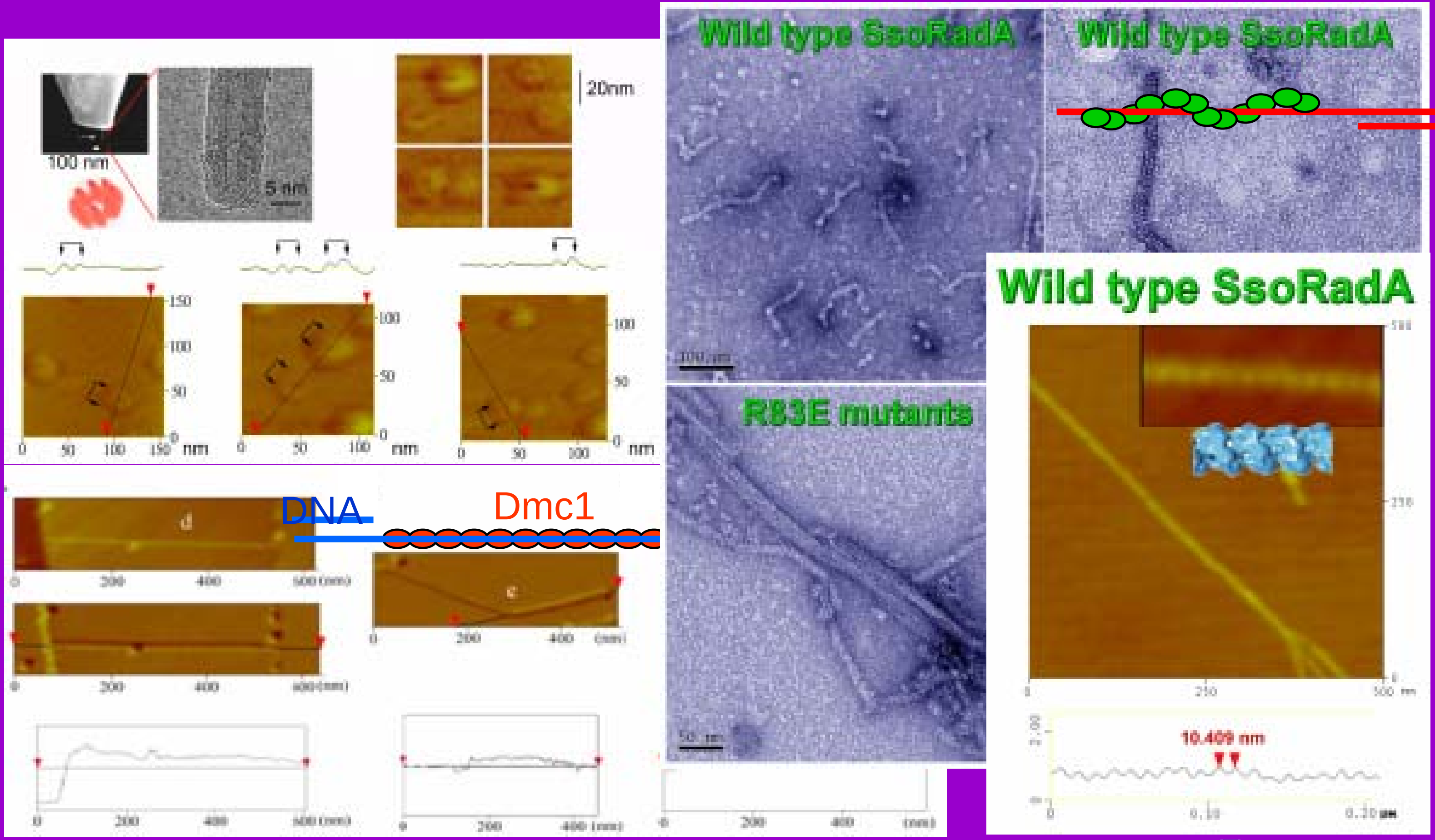
Chemical Probe





S. S. Wong *et al., Nature* 394, 52 (1998).

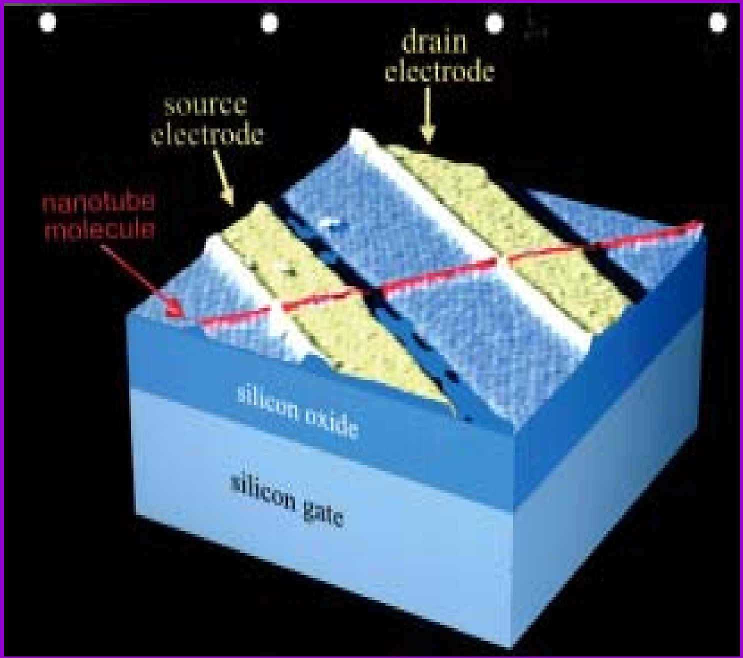
Bio-imaging using CNT tip

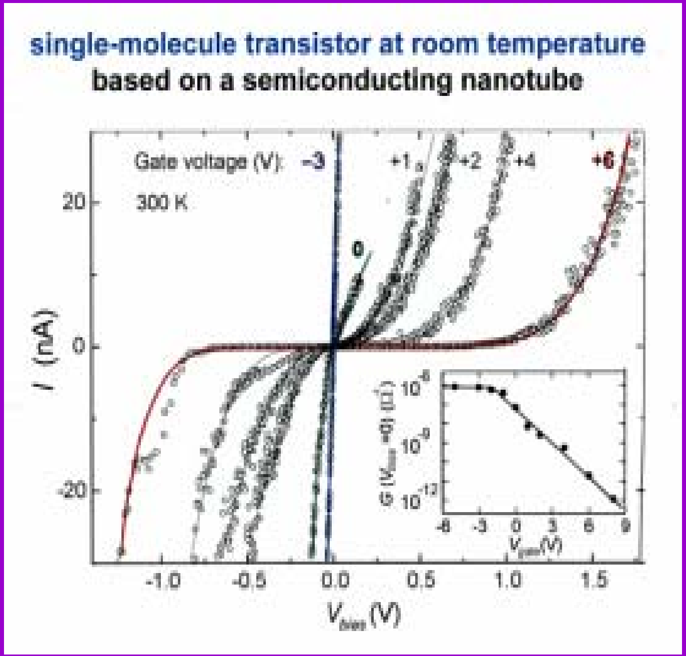


Biochemical and Biophysical Research Communication 323, 845-851 (2004)
Biochemsitry 44, 6052-6058 (2005)
Journal of Biological Chemistry 280, 40980-40984 (2005)
Nucleic Acids Research 35,1787-1801(2007)

NanoSci Lab

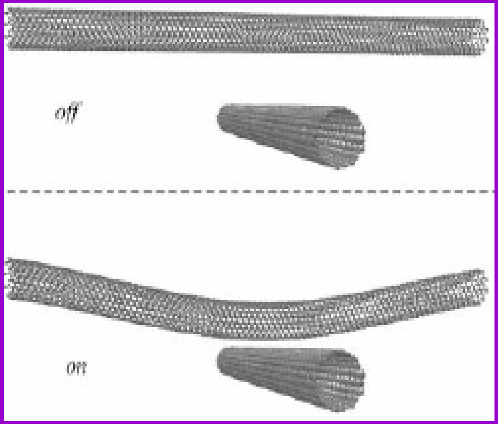
SWNT transistor

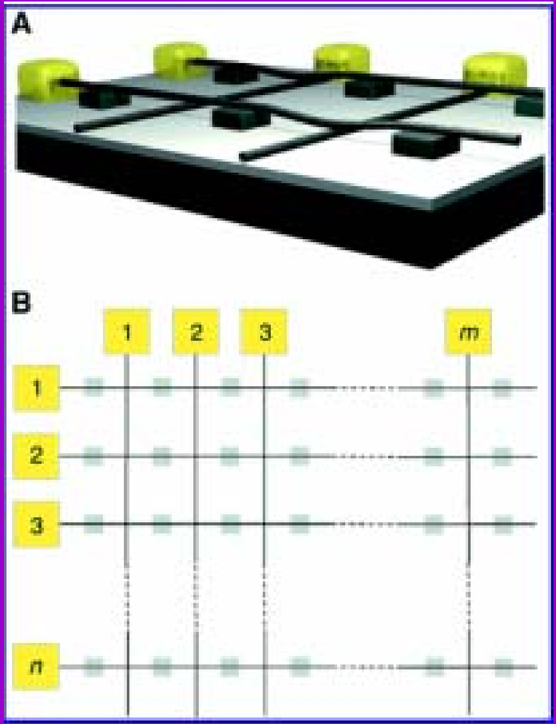


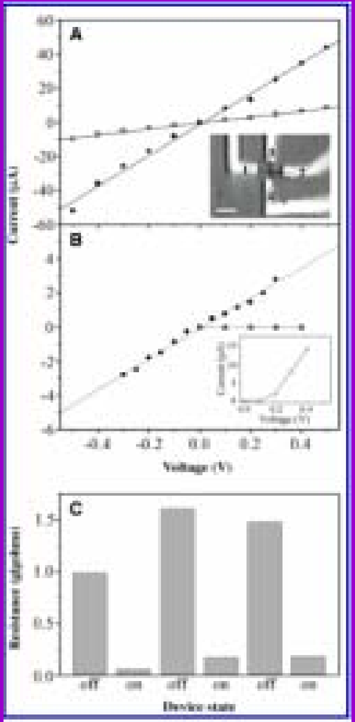


S.J. Tans *et al., Nature* 393, 49 (1998).

RAM by carbon nanotubes

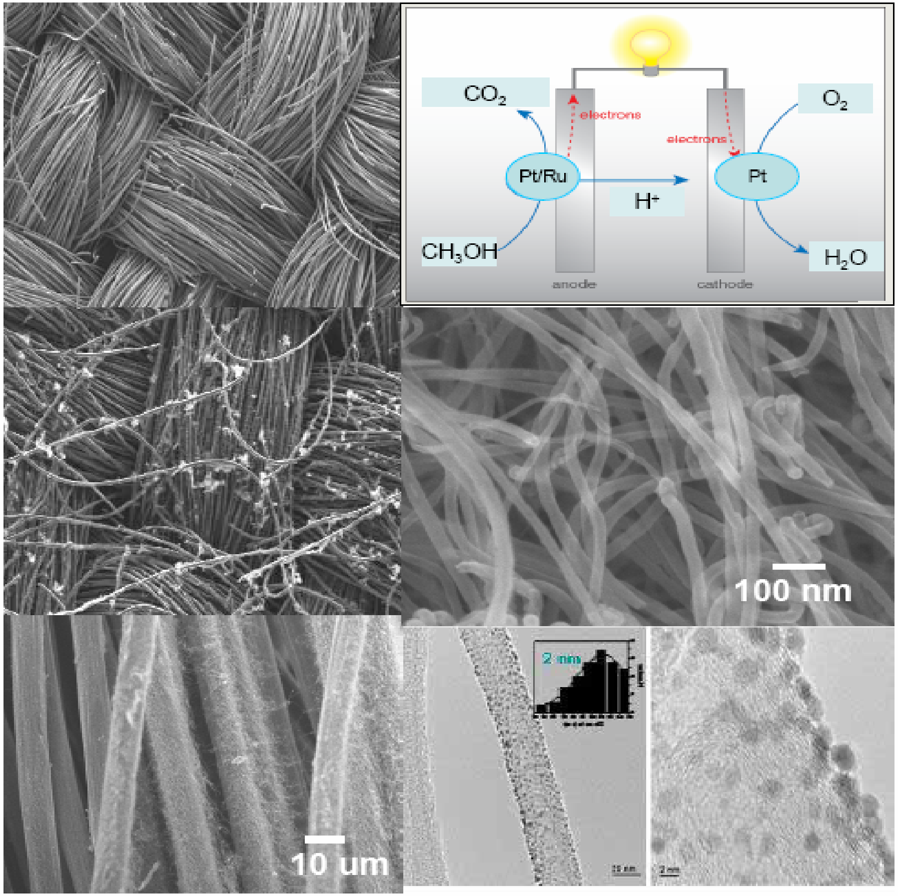


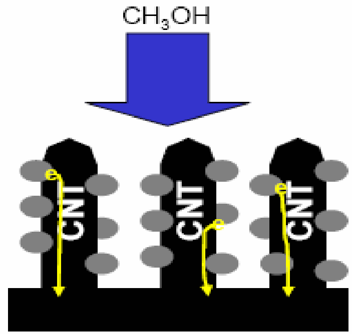


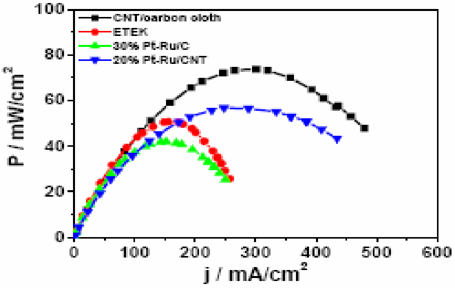


T. Rueckes *et al.*,
Science 289, 94 (2000).

CNT for Fuel Cell Applications

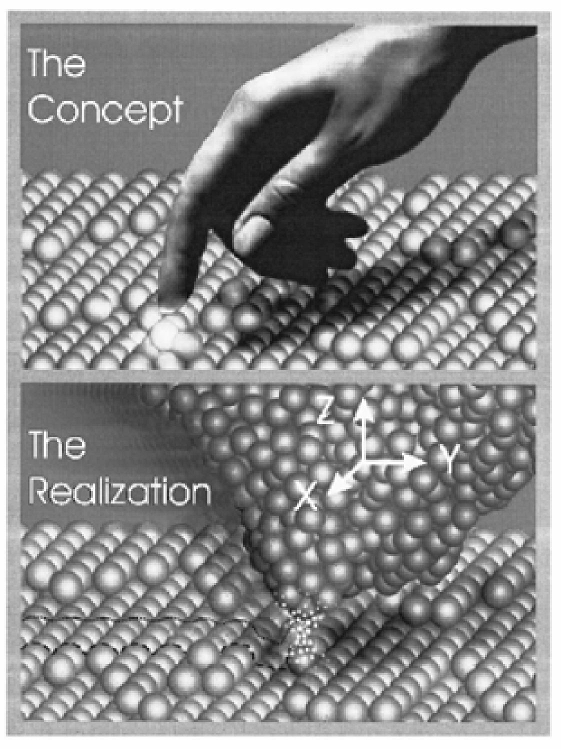




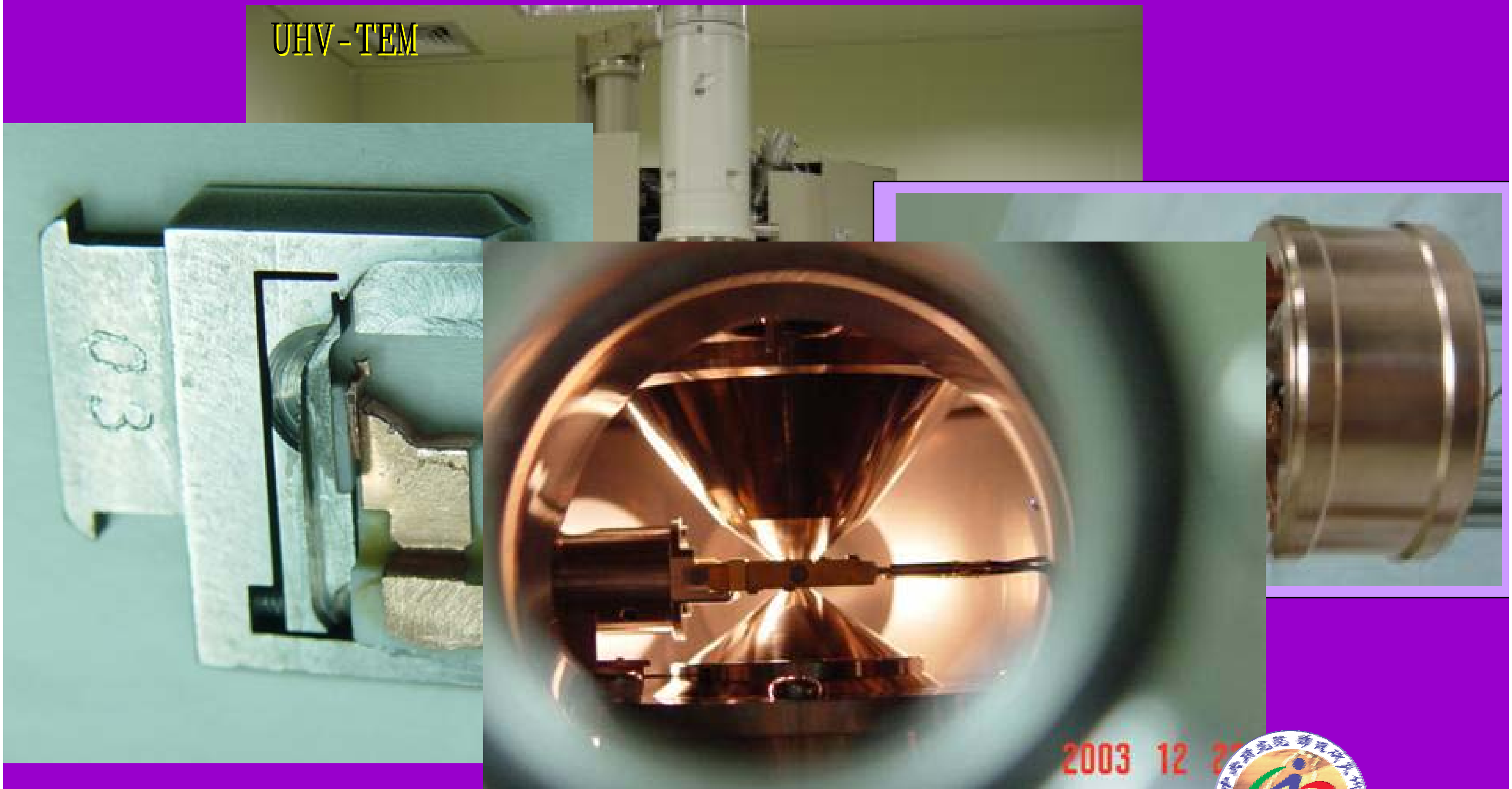


Dr. K. H. Chen, IAMS, AS

Concept of eye and finger

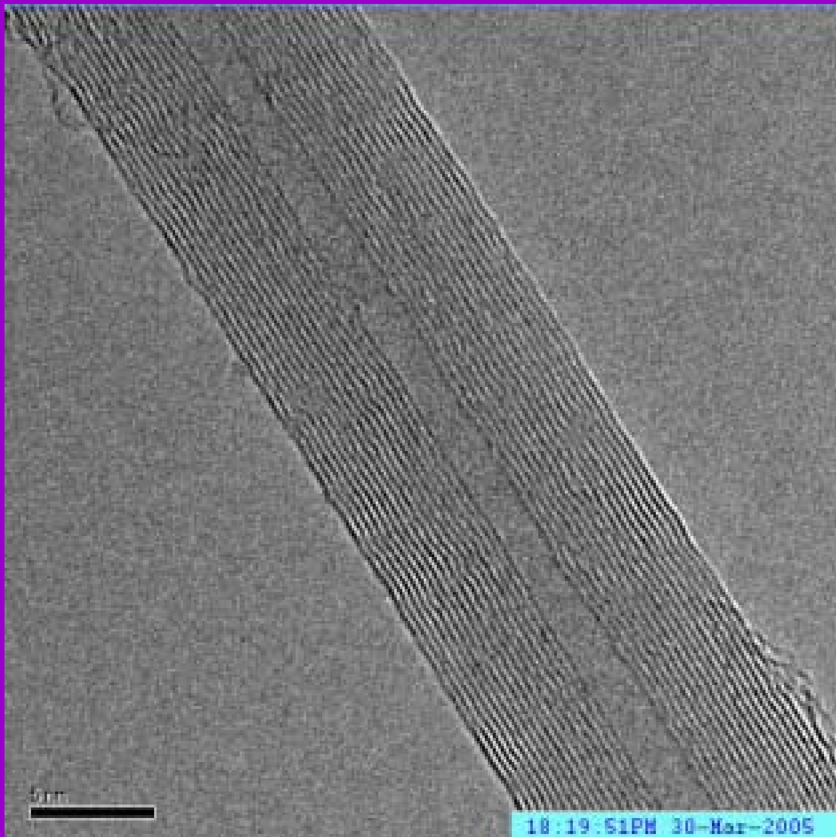


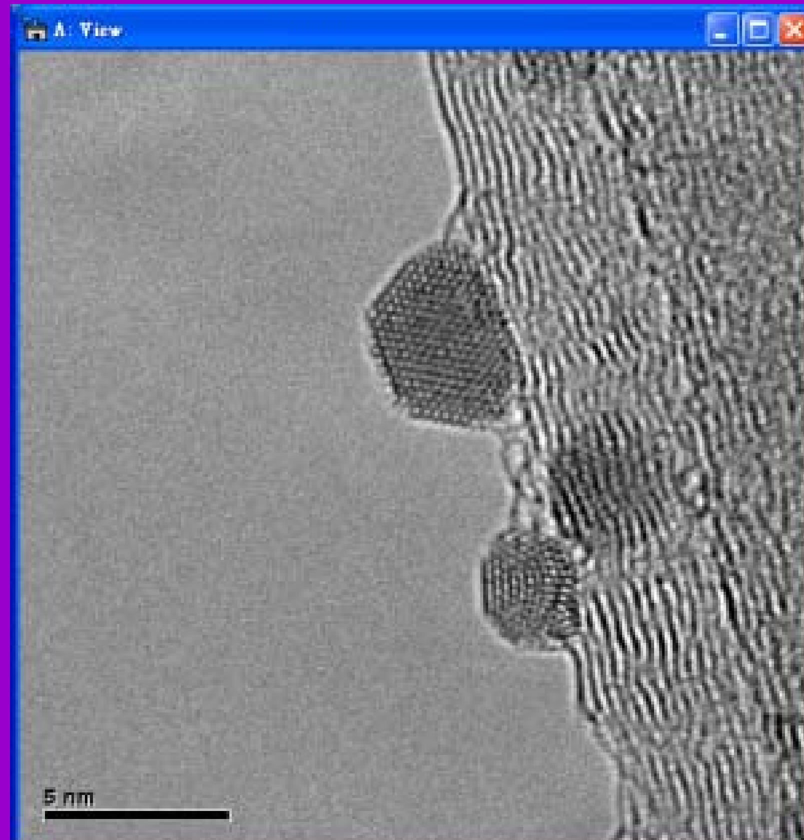
STM@UHV - TEM



Base pressure 2 x 10^{-10} torr

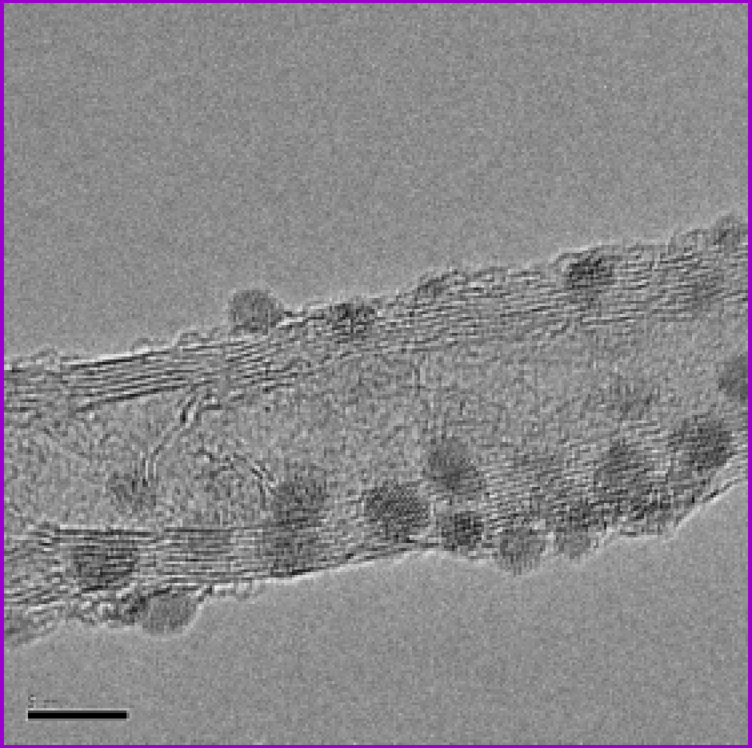
In situ deposition



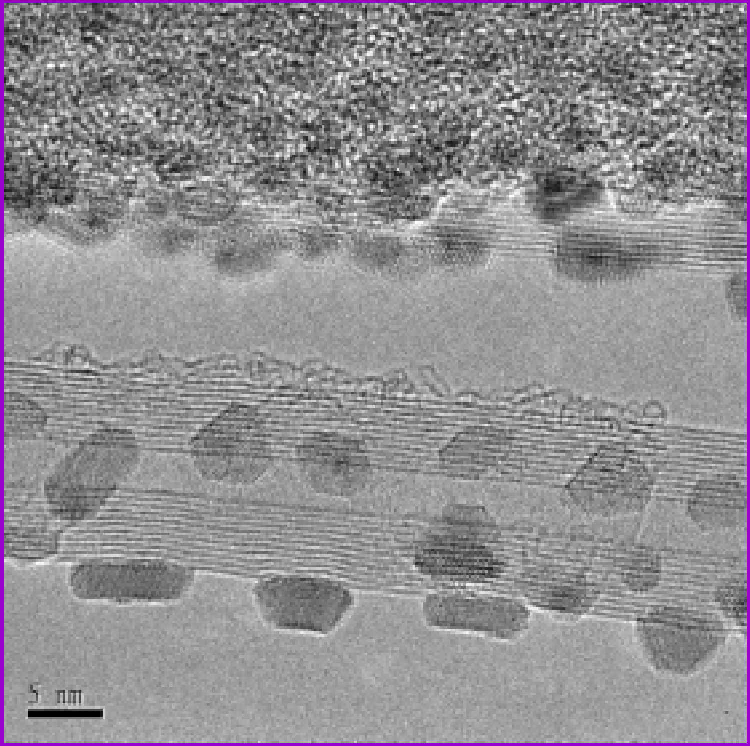


PHYSICAL REVIEW B **74**, 125424 (2006)

Growth of metal clusters on CNT

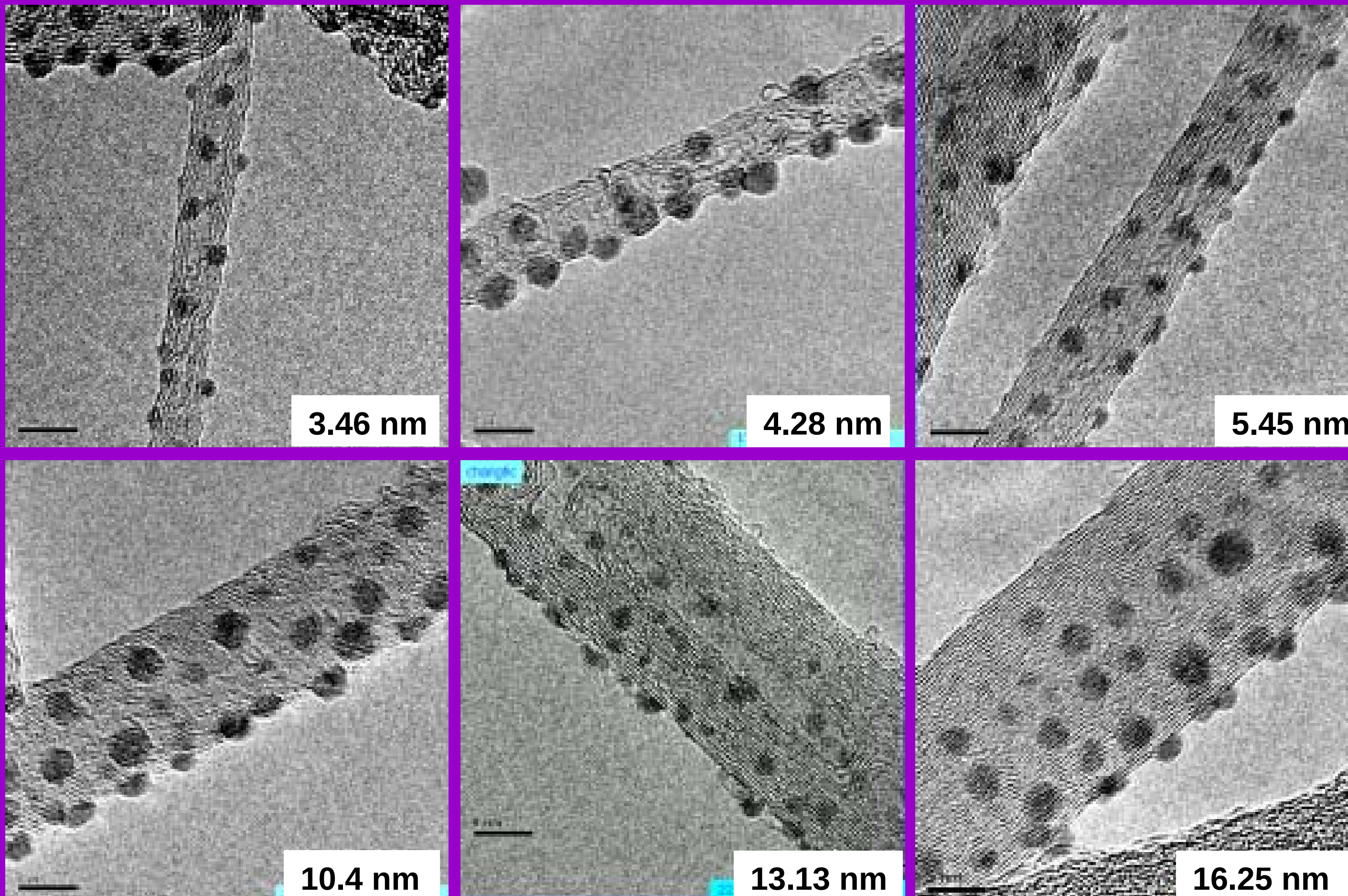


Ag on CNT

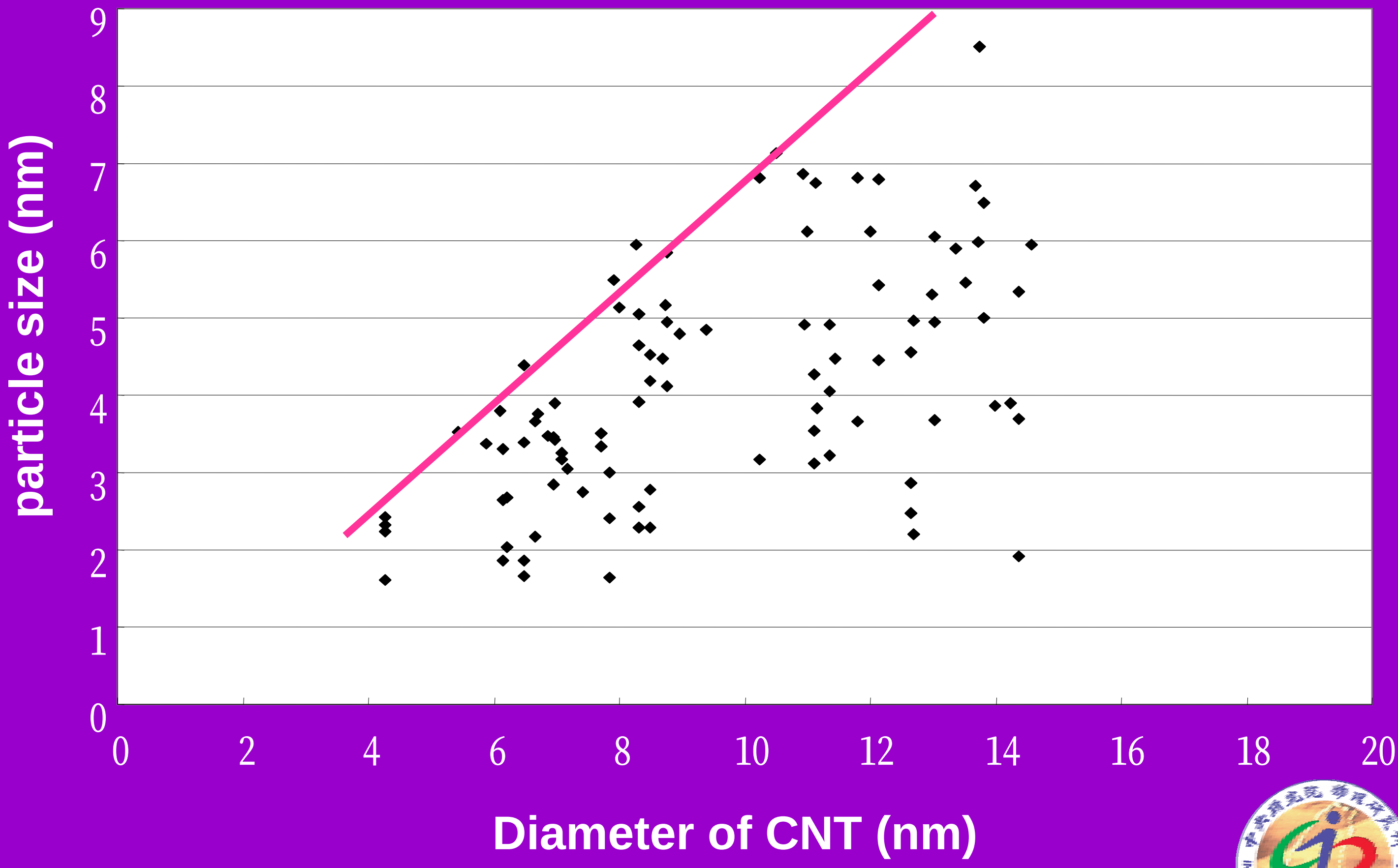


Pd on CNT

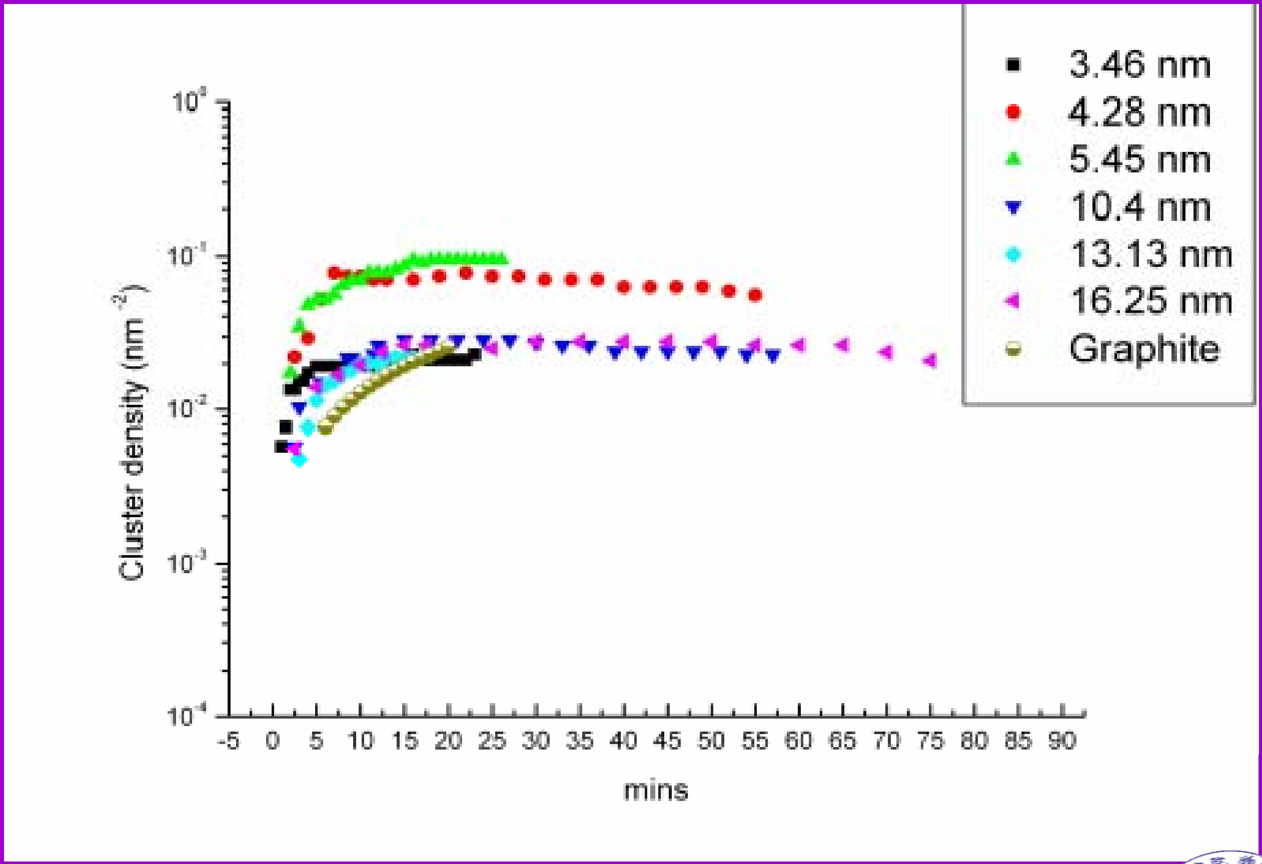
Growth of Ag clusters on carbon nanotubes



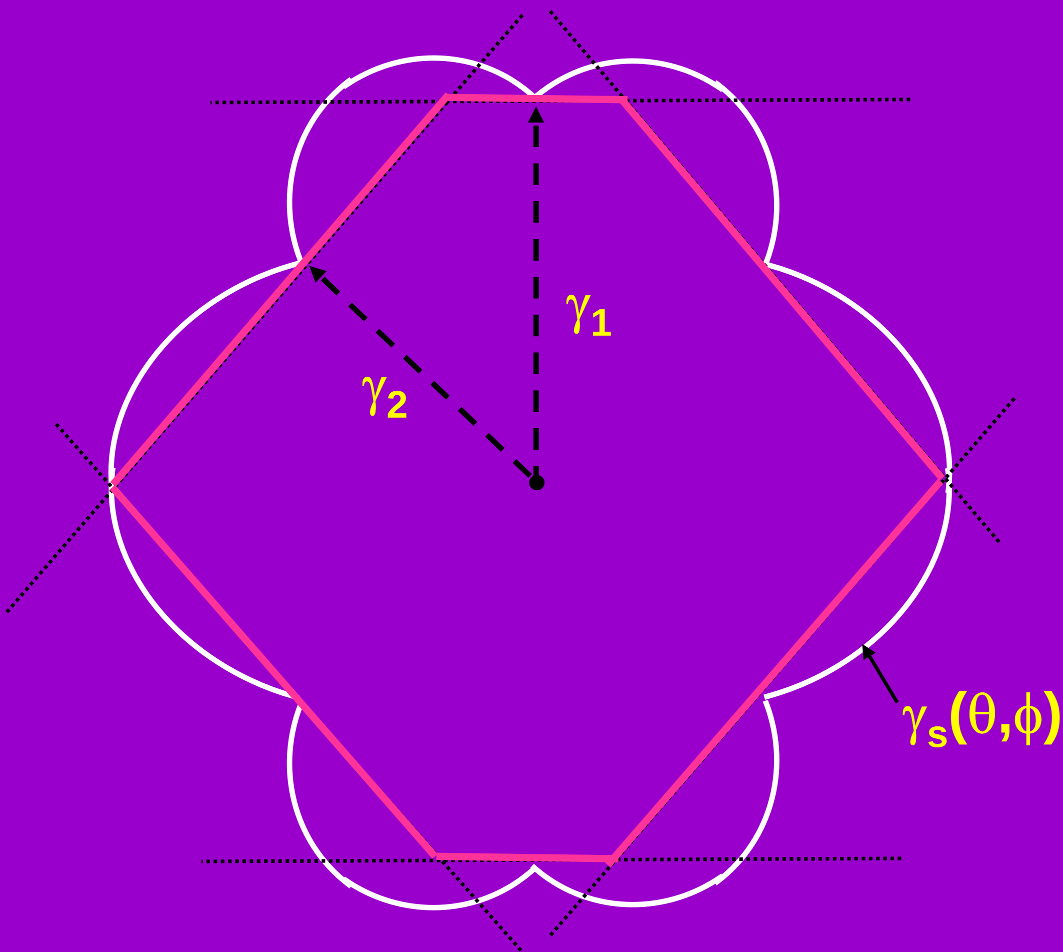
Boundary effect



Ag cluster density vs deposition time

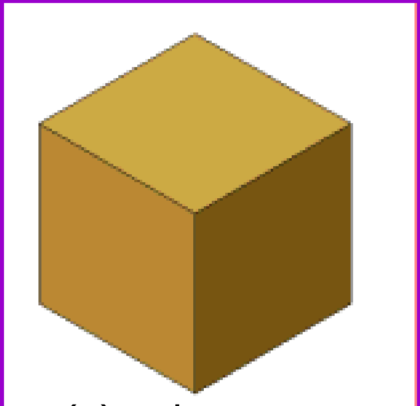


Wulff construction

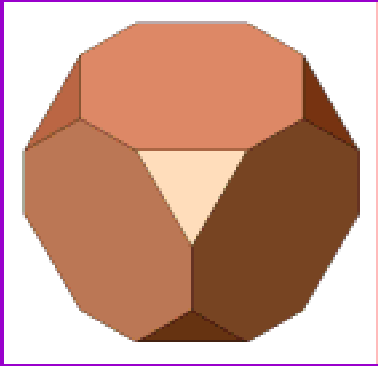


$$G = \int \gamma_s(\theta,\phi)\, dA$$

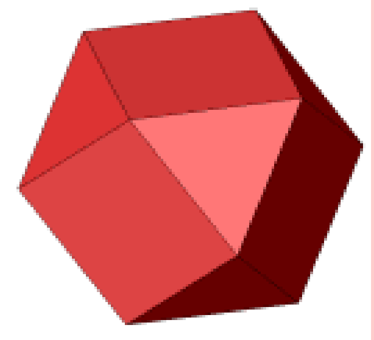
Single crystalline structures



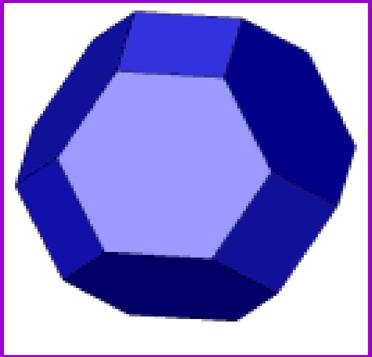
(a) cube



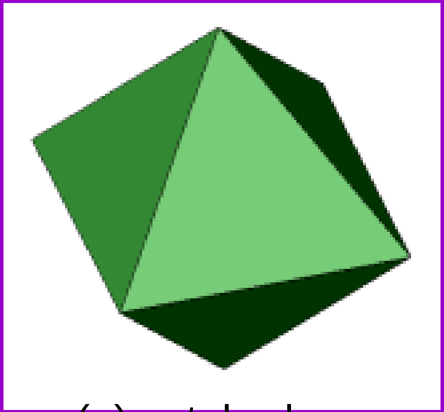
(b) truncated cube



(c) cuboctahedron

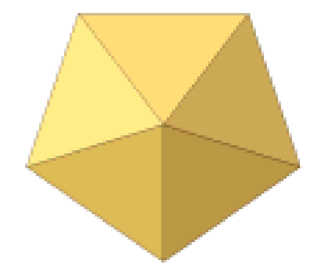


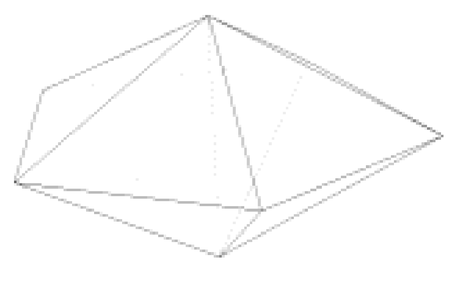
(d) truncated octahedron



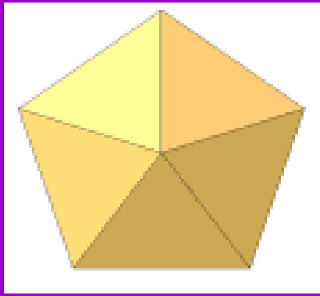
(e) octahedron

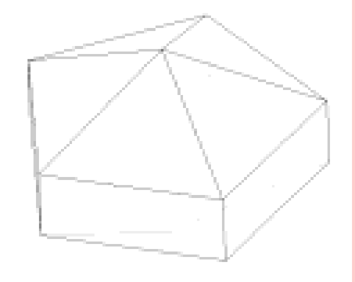
Decahedra



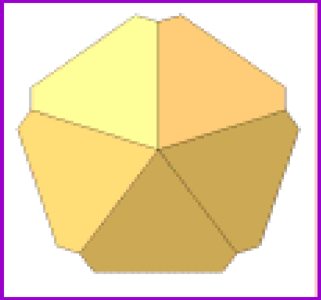


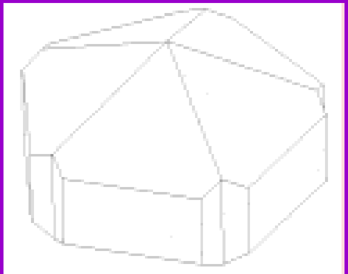
Classic





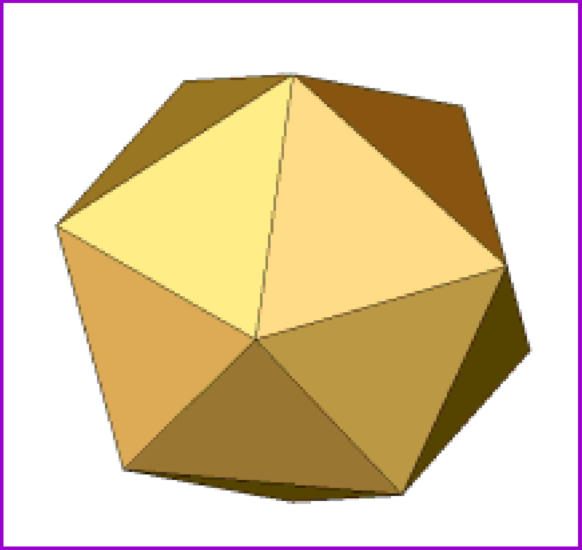
Ino’s

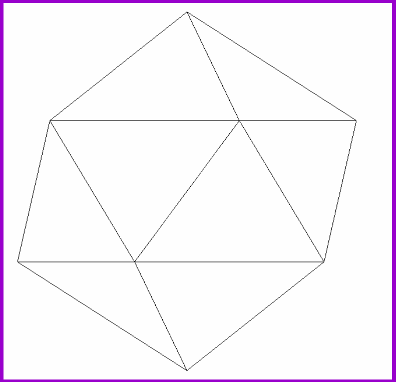




Marks’

Icosahedra





Size-dependent structures calculated for Ni clusters:

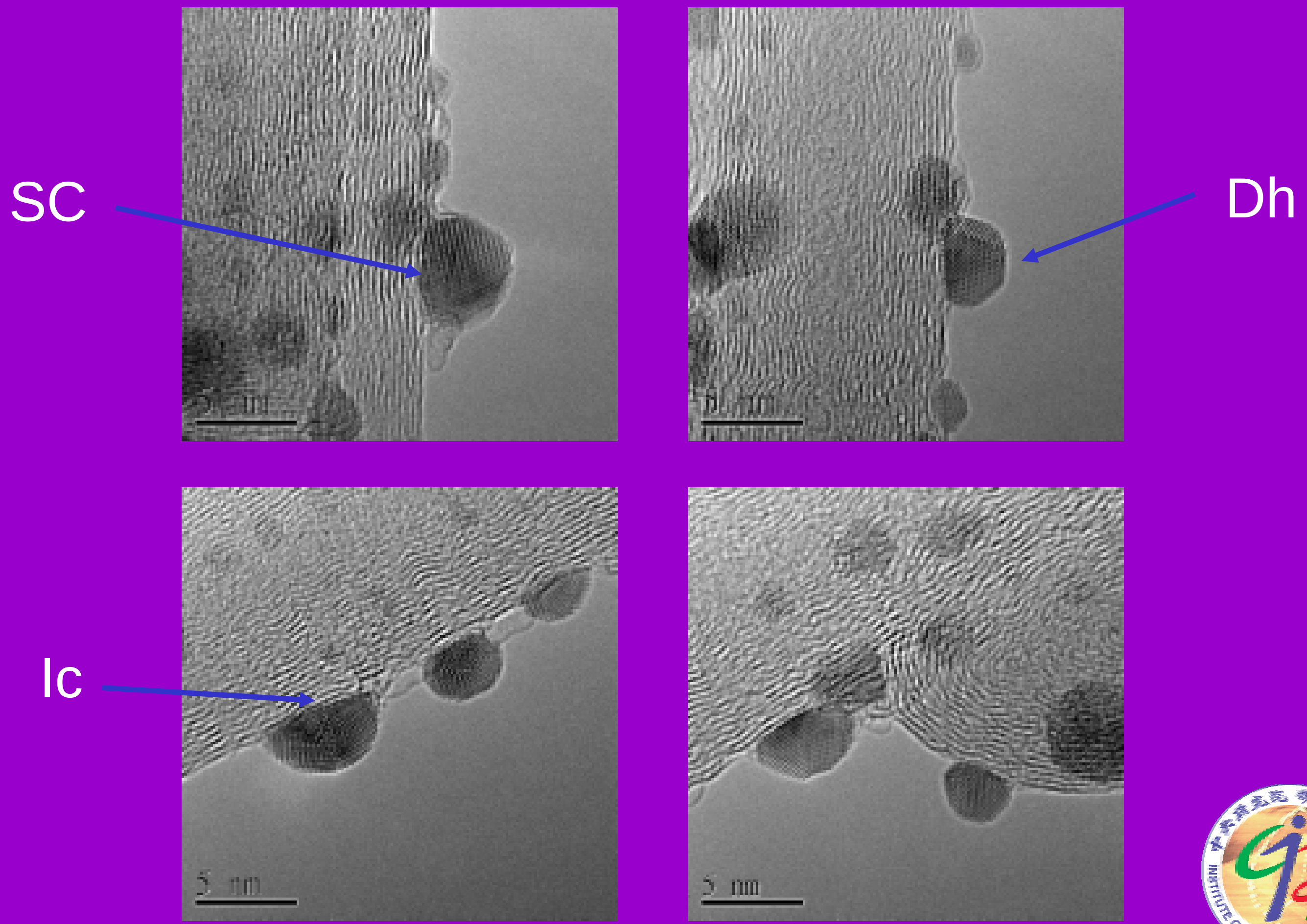
Icosahedra for 142 – 2300 atoms;

Marks' decahedra for 2300 – 17000 atoms;

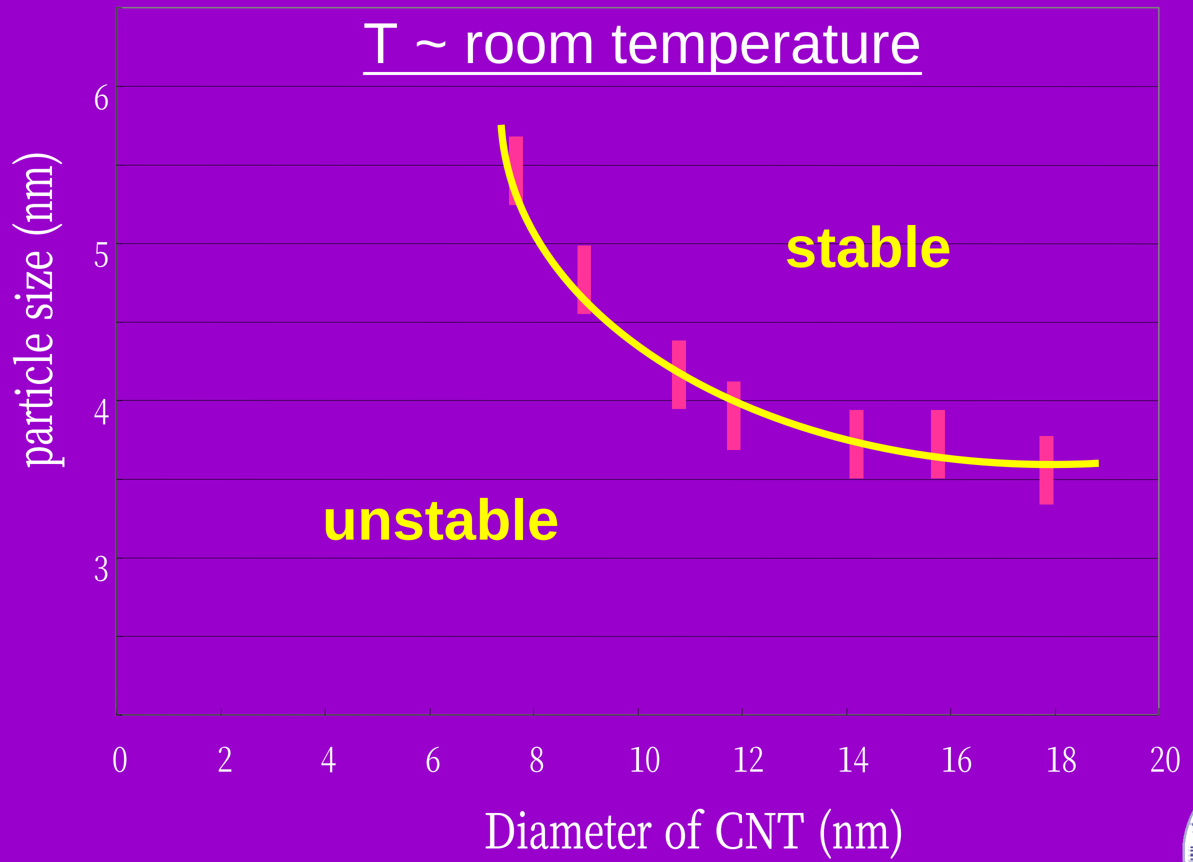
Single crystal for > 17000 atoms.

C.L. Cleveland and Uzi Landman, J. Chem. Phys. 94, 7376 (1991).

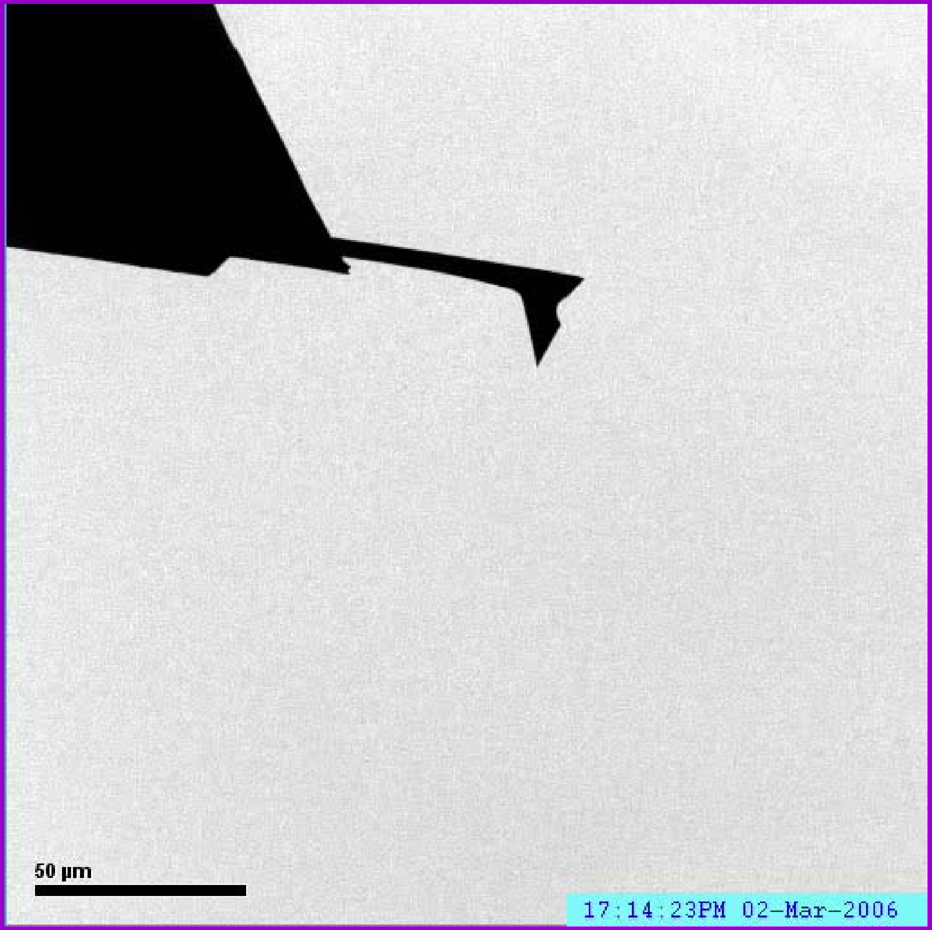
Varying structures of Ag clusters



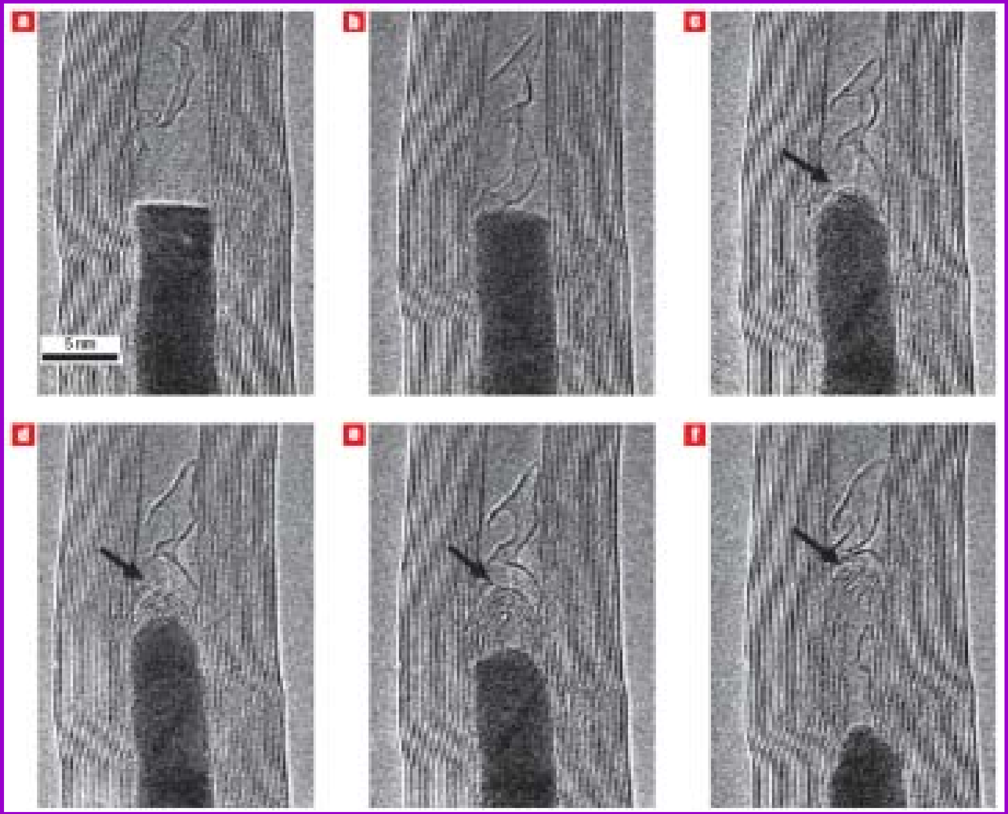
Stability of crystalline phases



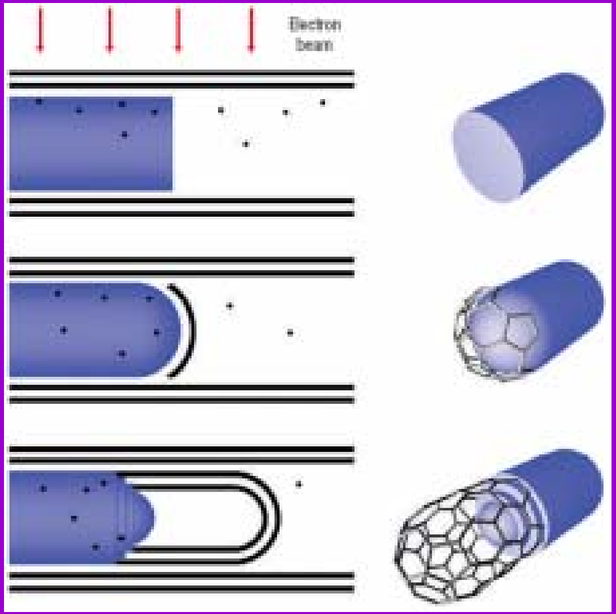
Approaching of two nano tips



Catalytic growth of inner CNT

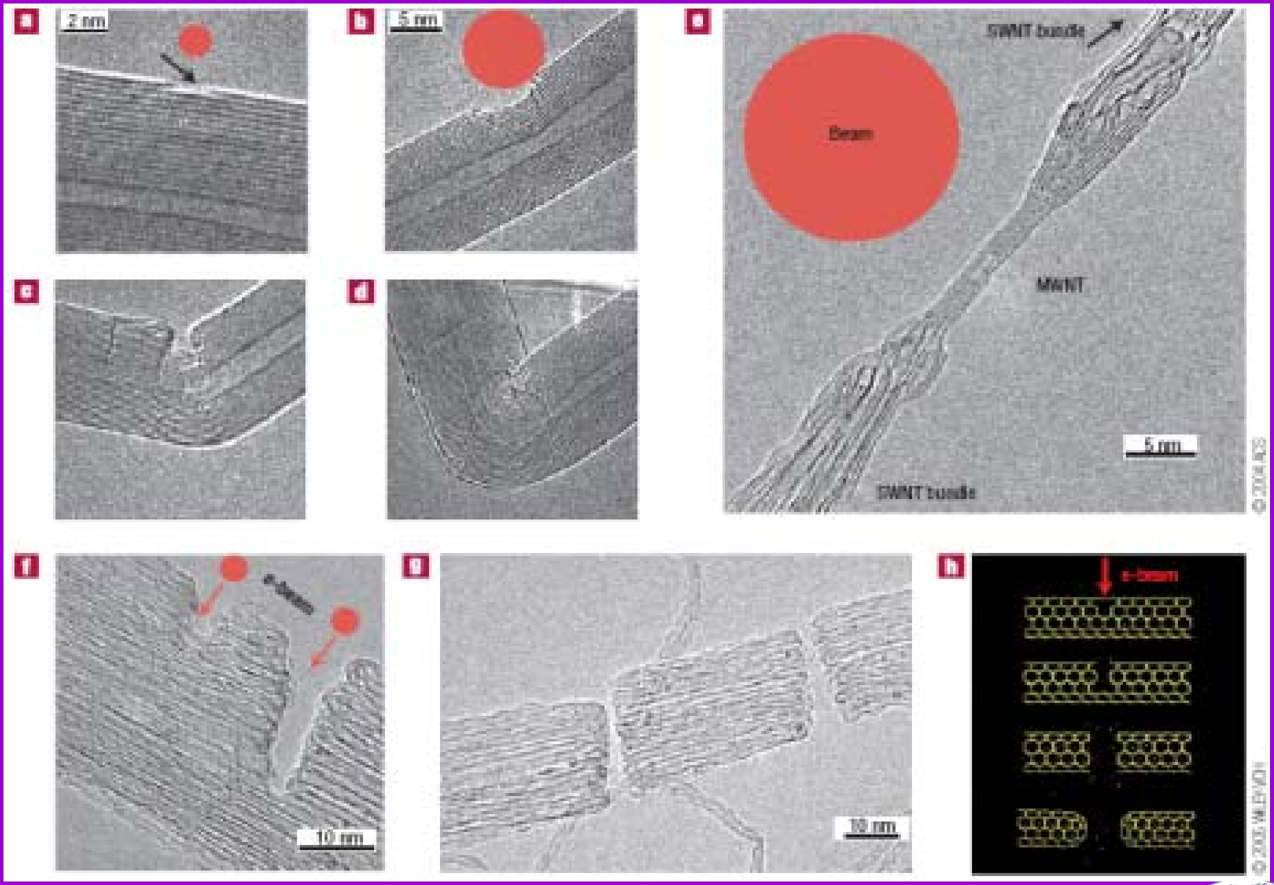


Bulk or surface diffusion?



J. A. Rodríguez-Manzo, M. Terrones, H. Terrones, H. W. Kroto, L. Sun & F. Banhart, *Nature Nanotechnology* **2**, 307 - 311 (2006)

Engineering CNT with energetic e-beam

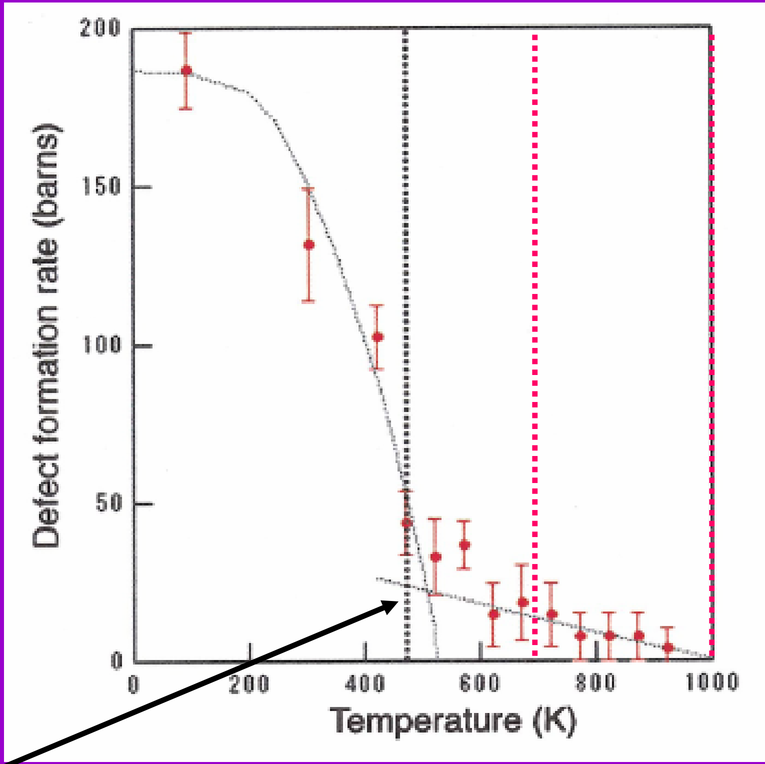


A.V. Krasheninnikov and F. Banhart
Nature Materials **6**, 723 (2007)

Wigner - energy releasing T

E = 120 keV

I = 1 A/cm^2



E = 200 keV

I = 10-50 A/cm^2

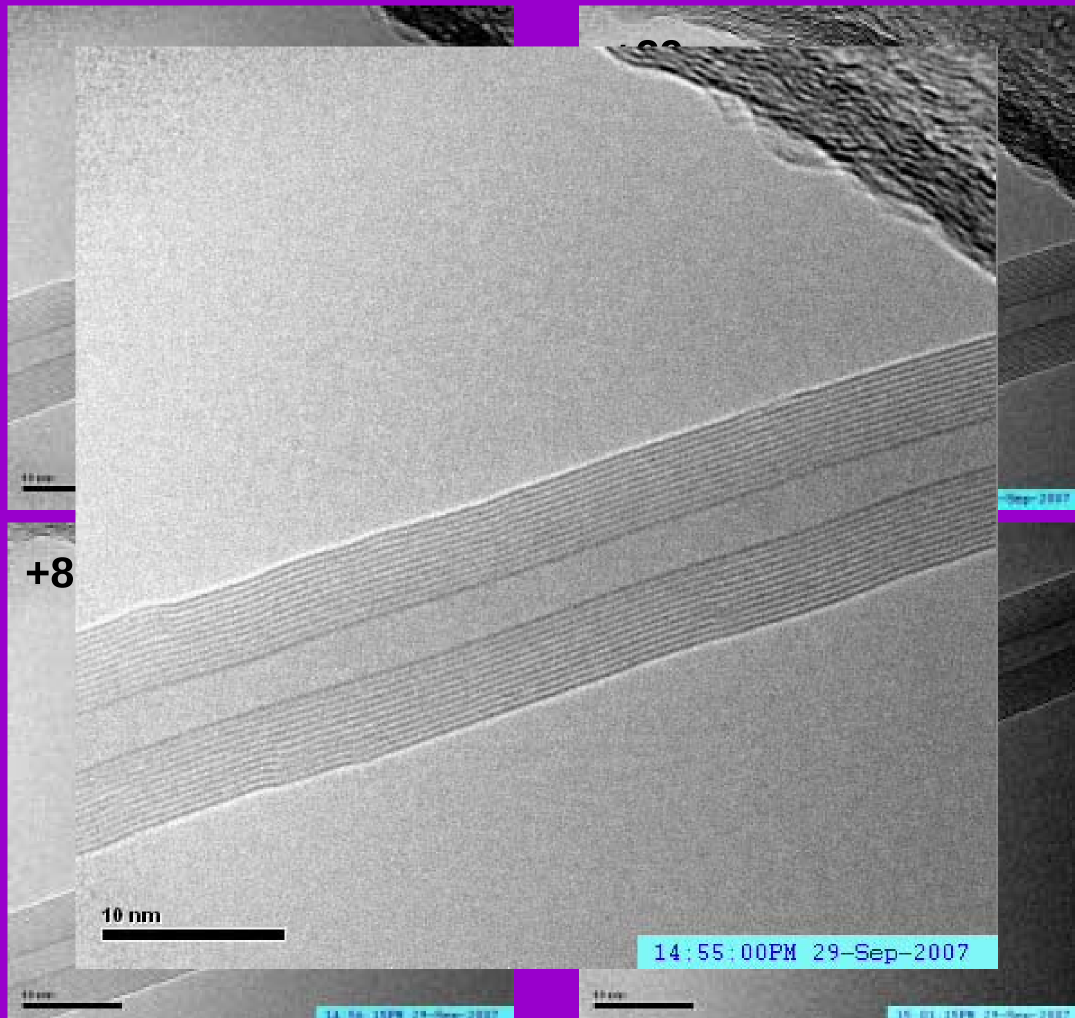
"Wigner-energy releasing T" signifies the I-V recombination barrier

K. Urita *et al*., Phys. Rev. Lett. **94** (2005) 155502

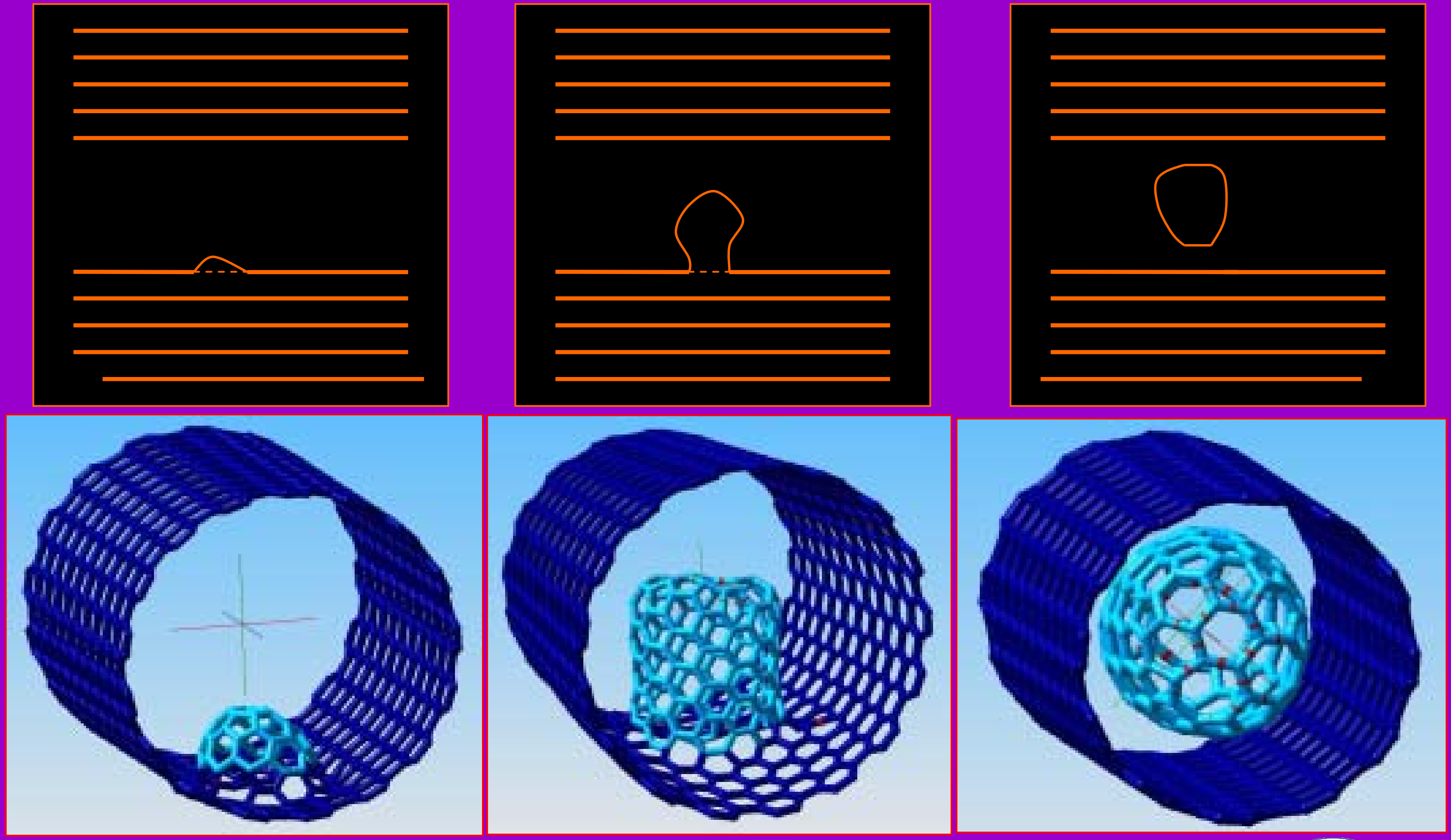
Growth of inner CNT without catalyst

566 °C

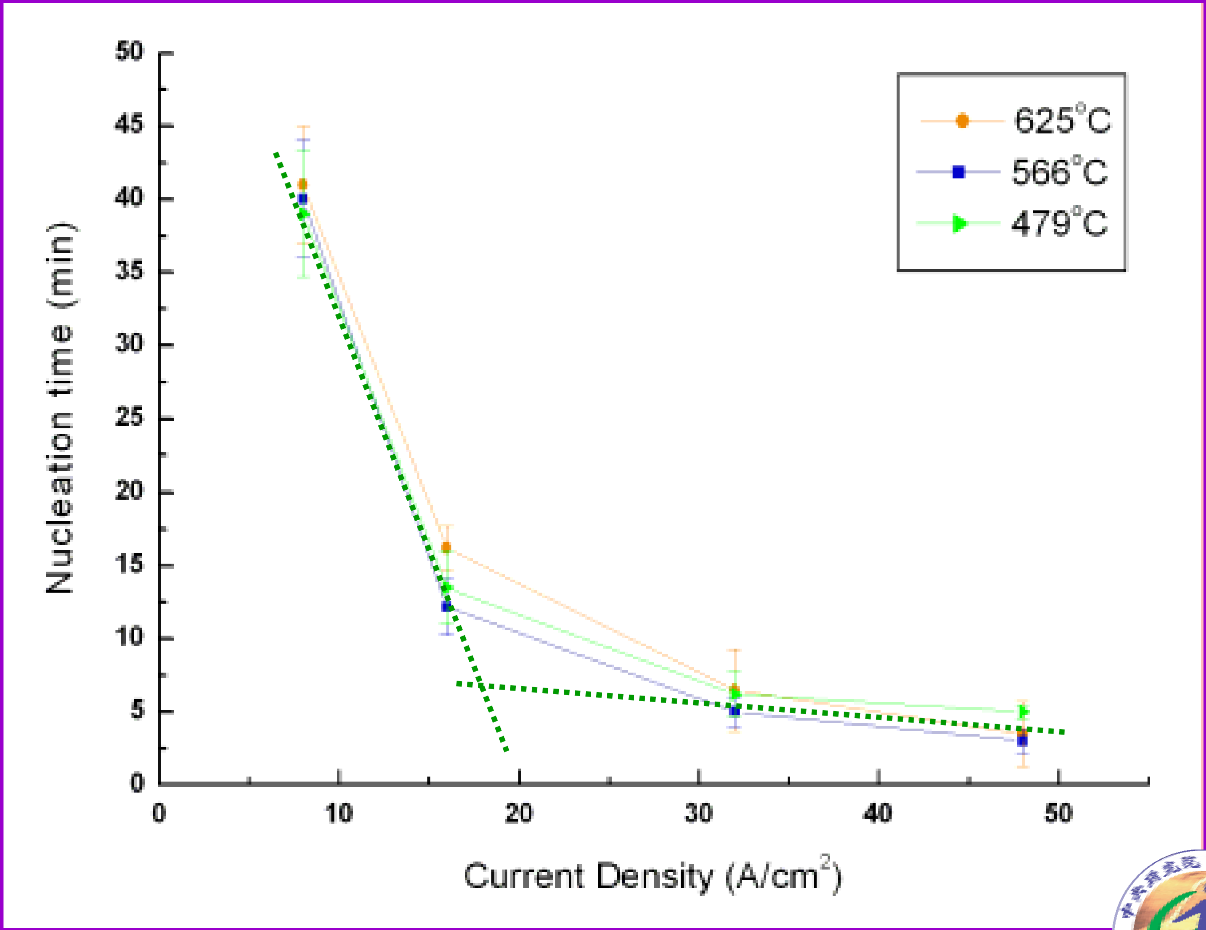
Irradiation current 16 A/cm^2



Schematic model for nucleation

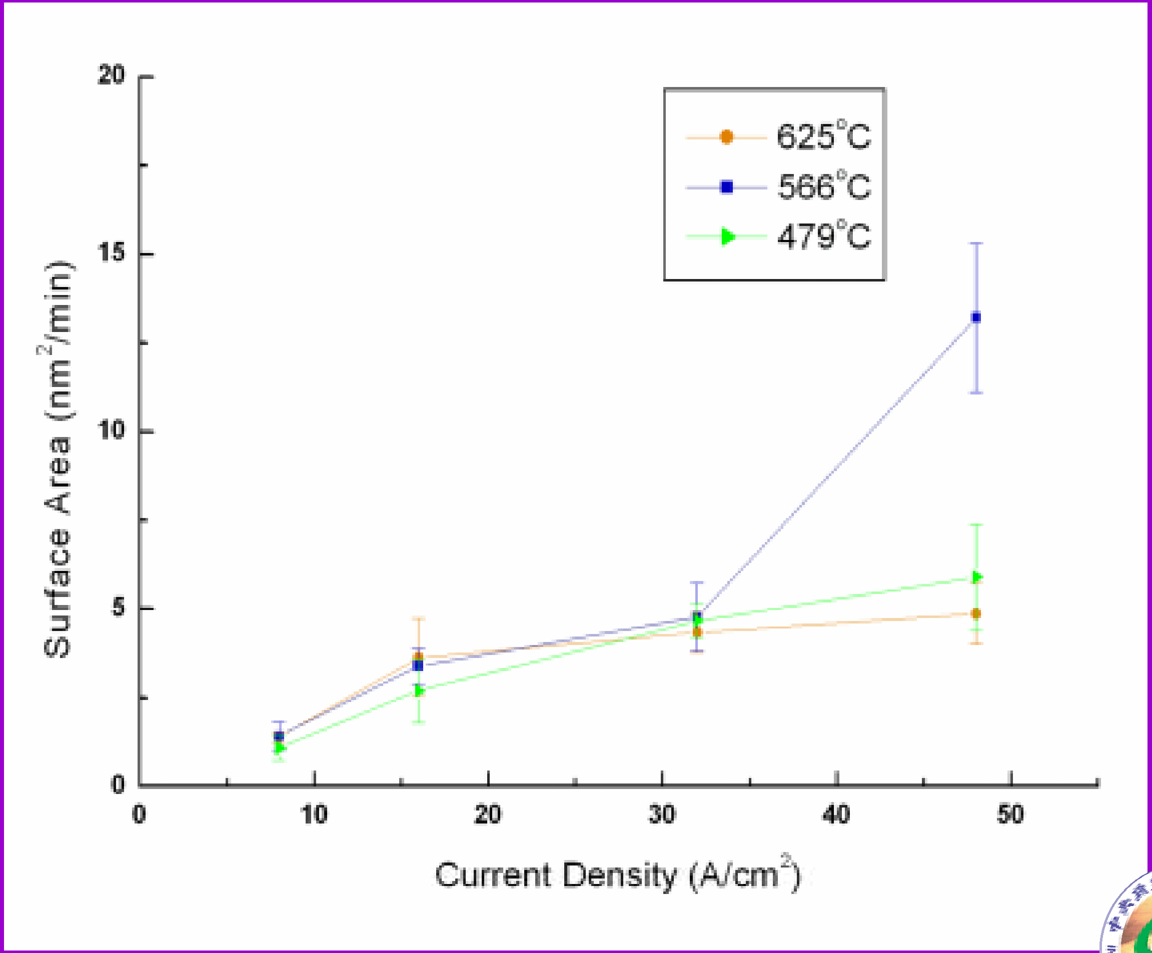


Nucleation time vs e-beam intensity

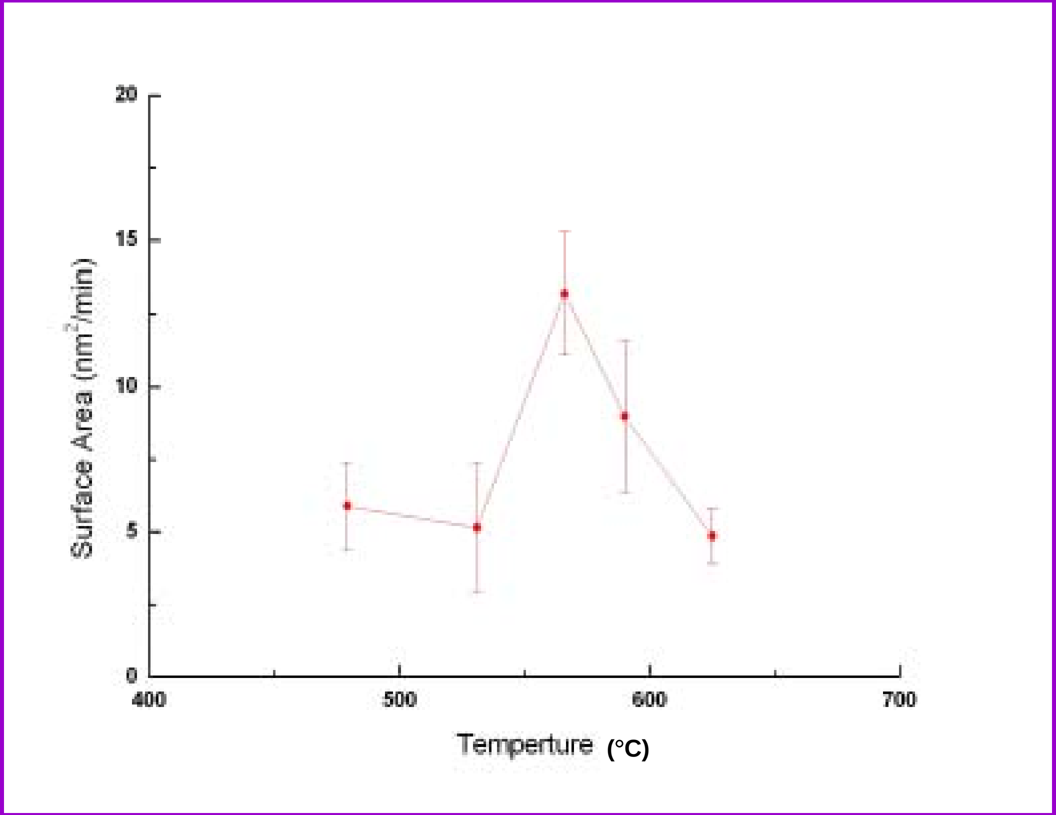


NanoSci Lab

Growth of surface area vs e-beam intensity



Growth of surface area vs sample temperature

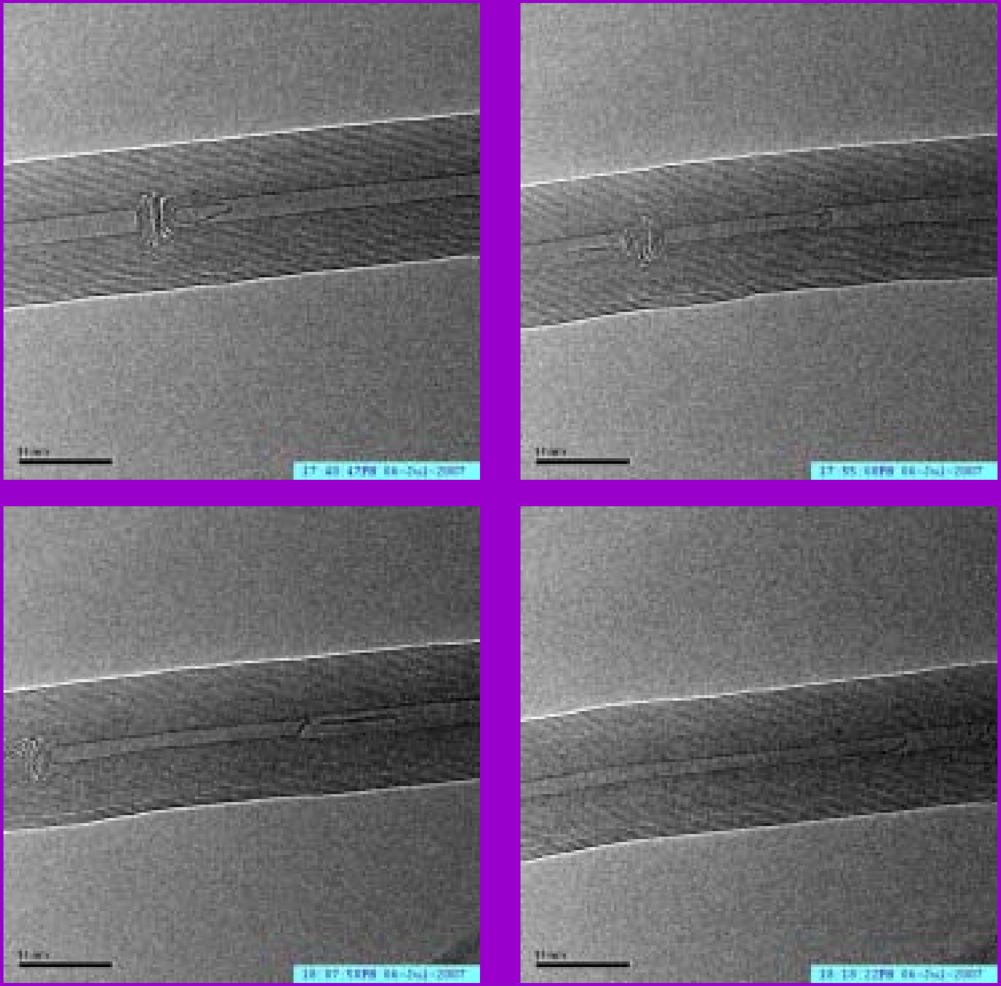


I = 48 A/cm^2

One side growth

625 °C

Irradiation current 32 A/cm^2

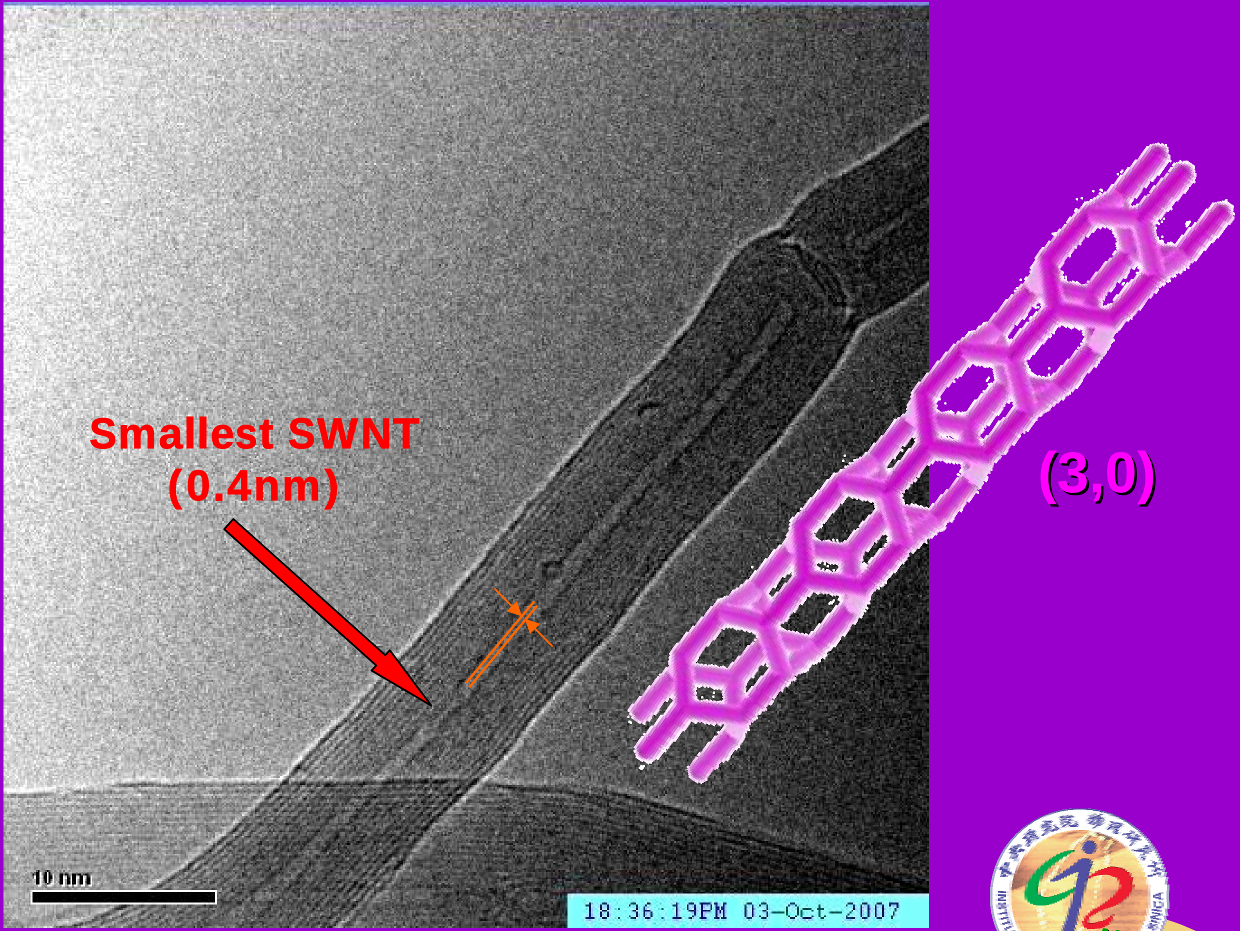


Growth of successive layers

Growth of smallest SWNT

600 °C

Irradiation current 48 A/cm^2

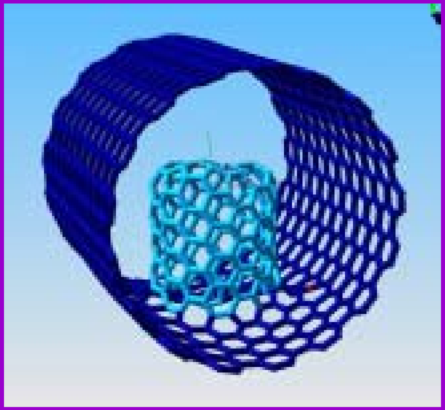


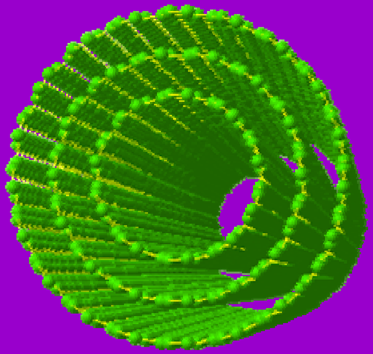
Nucleation and growth of CNT with e-beam

1. Nucleation of CNT growth under e-beam irradiation mainly depends on the beam intensity, which implies the less mobile vacancies created play a key role.
2. Incorporation of carbon atoms in the growth of CNT under e-beam irradiation is also assisted by the e-beam.
3. The growth rate of CNT under e-beam irradiation can be tuned because it is a self-sustaining system.

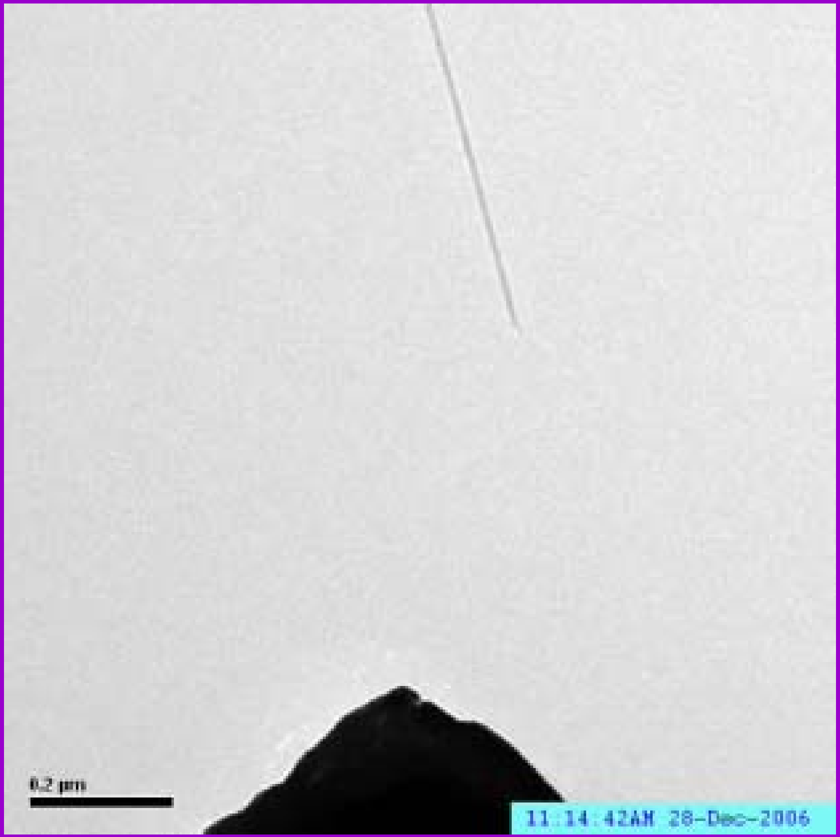
Outline

- Growth of carbon nanotubes
- **Extraction of inner layers**
- Conductance of carbon nanotube

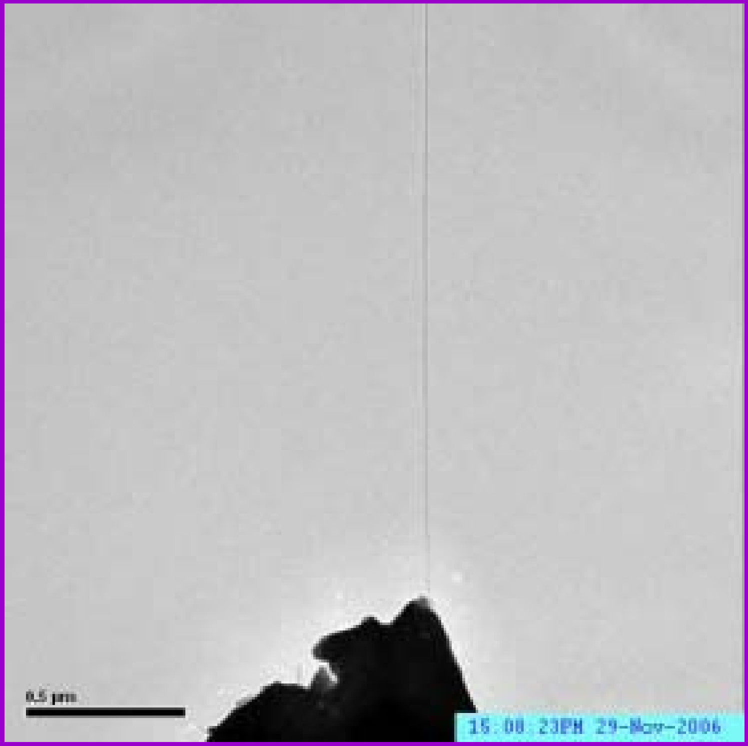


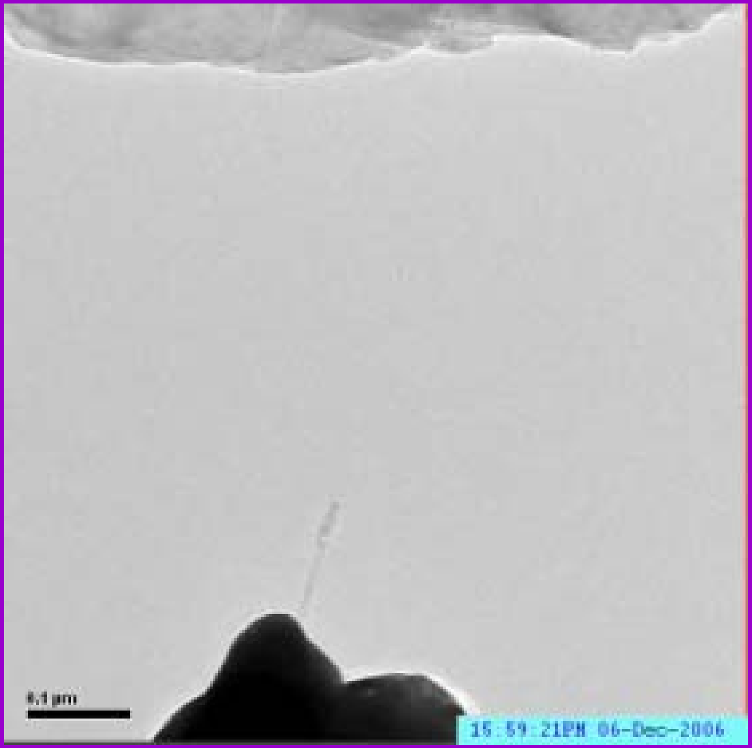


Making CNT tip by STM@TEM

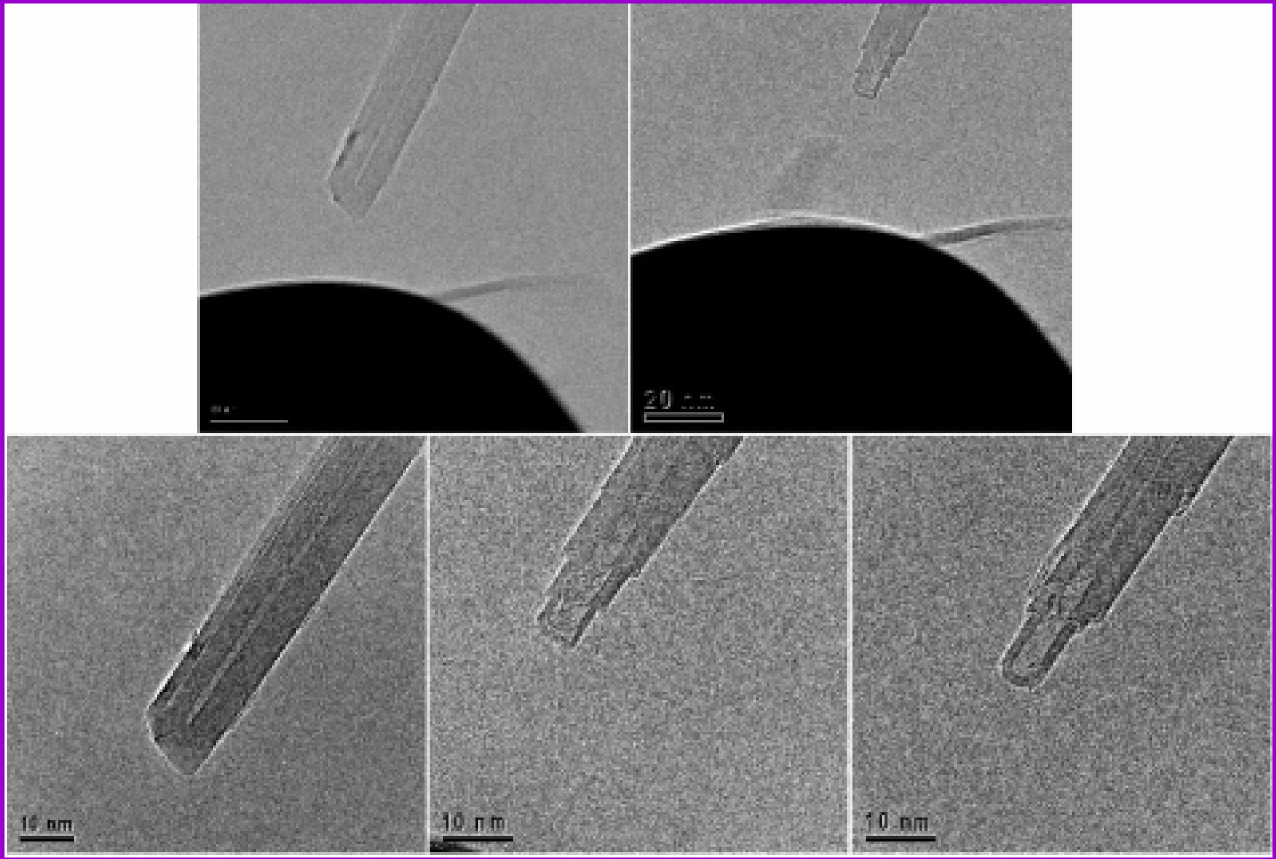


Shortening and removal of CNT



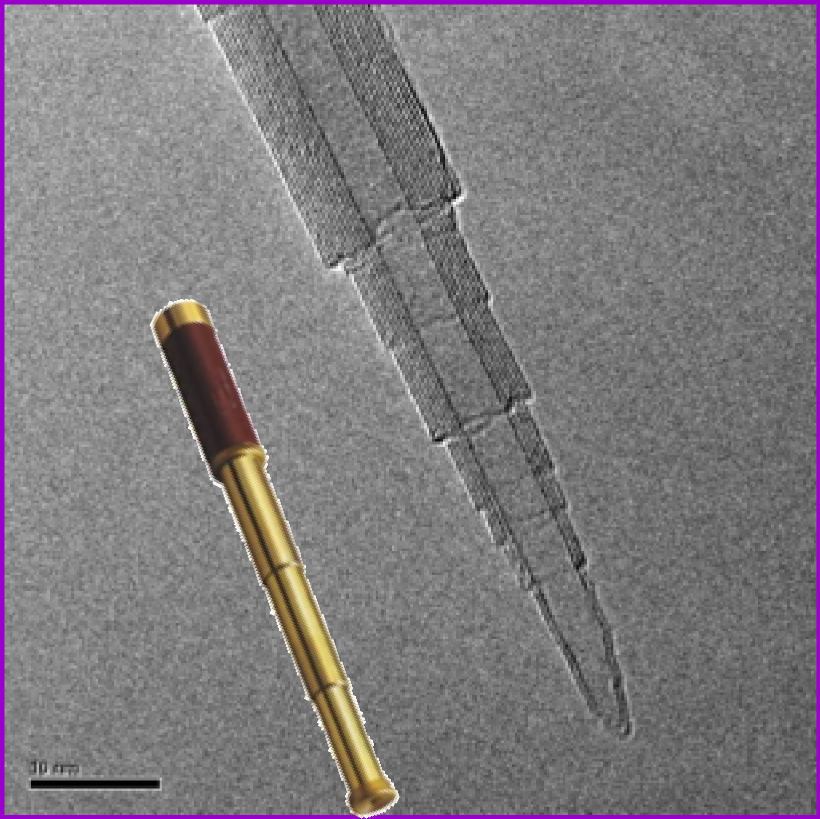


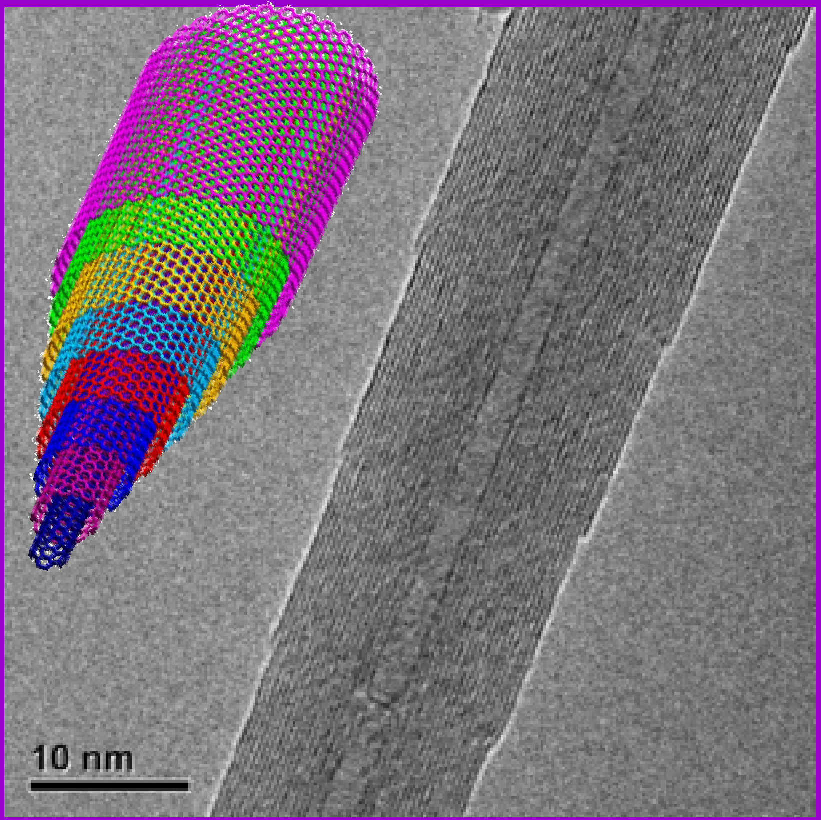
Peeling and sharpening multiwall nanotubes



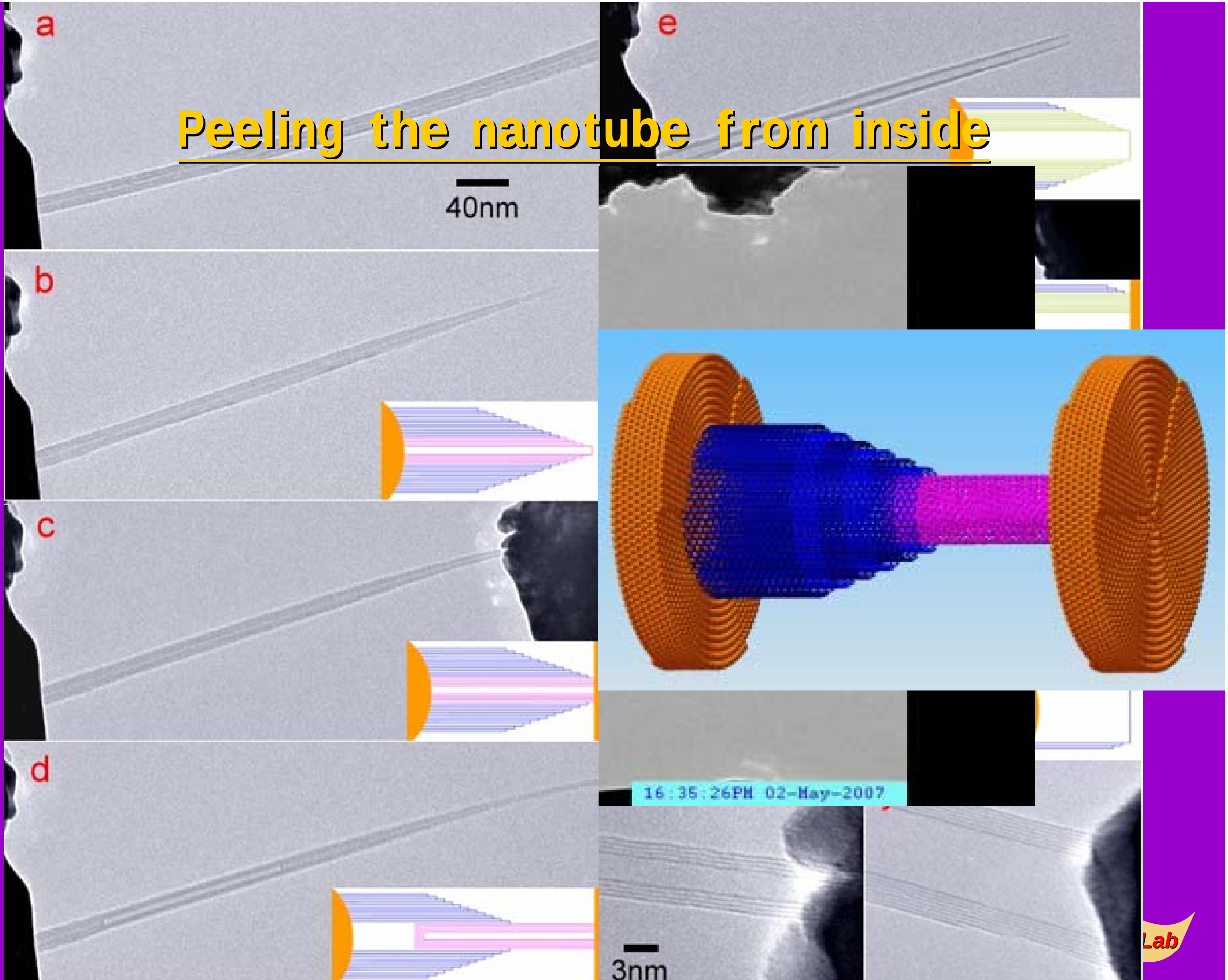
John Cumings, Philip G. Collins, A. Zettl
Nature **406**, 586 (2000)

Telescopic structure

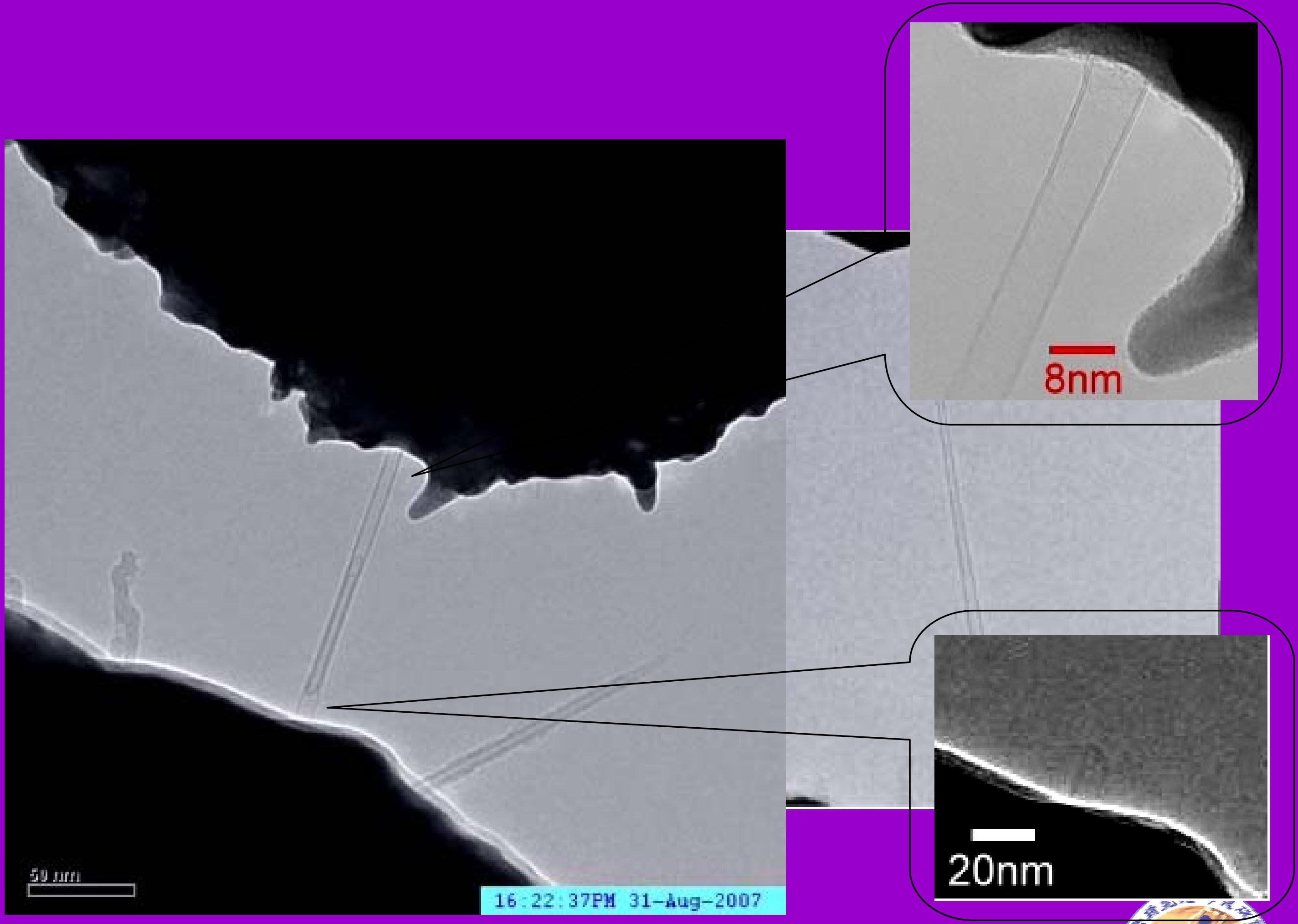




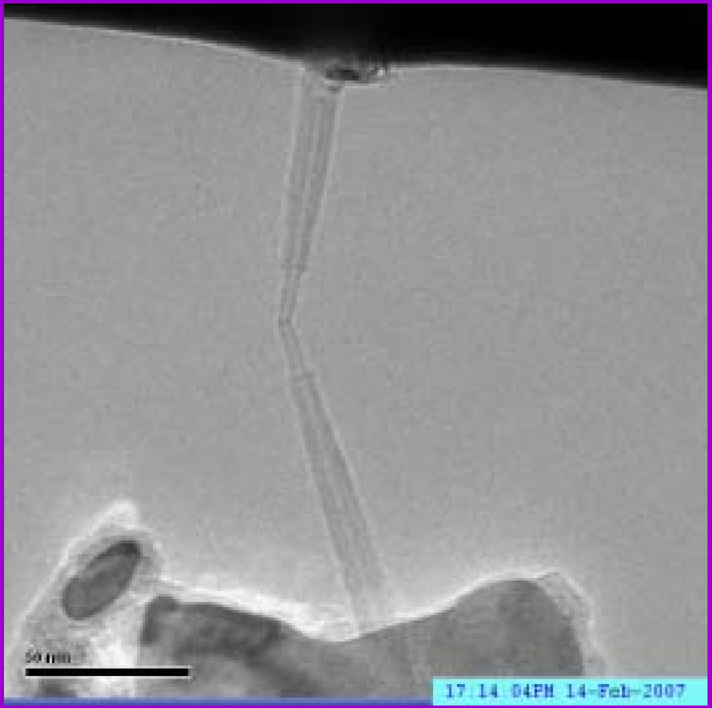
Peeling the nanotube from inside



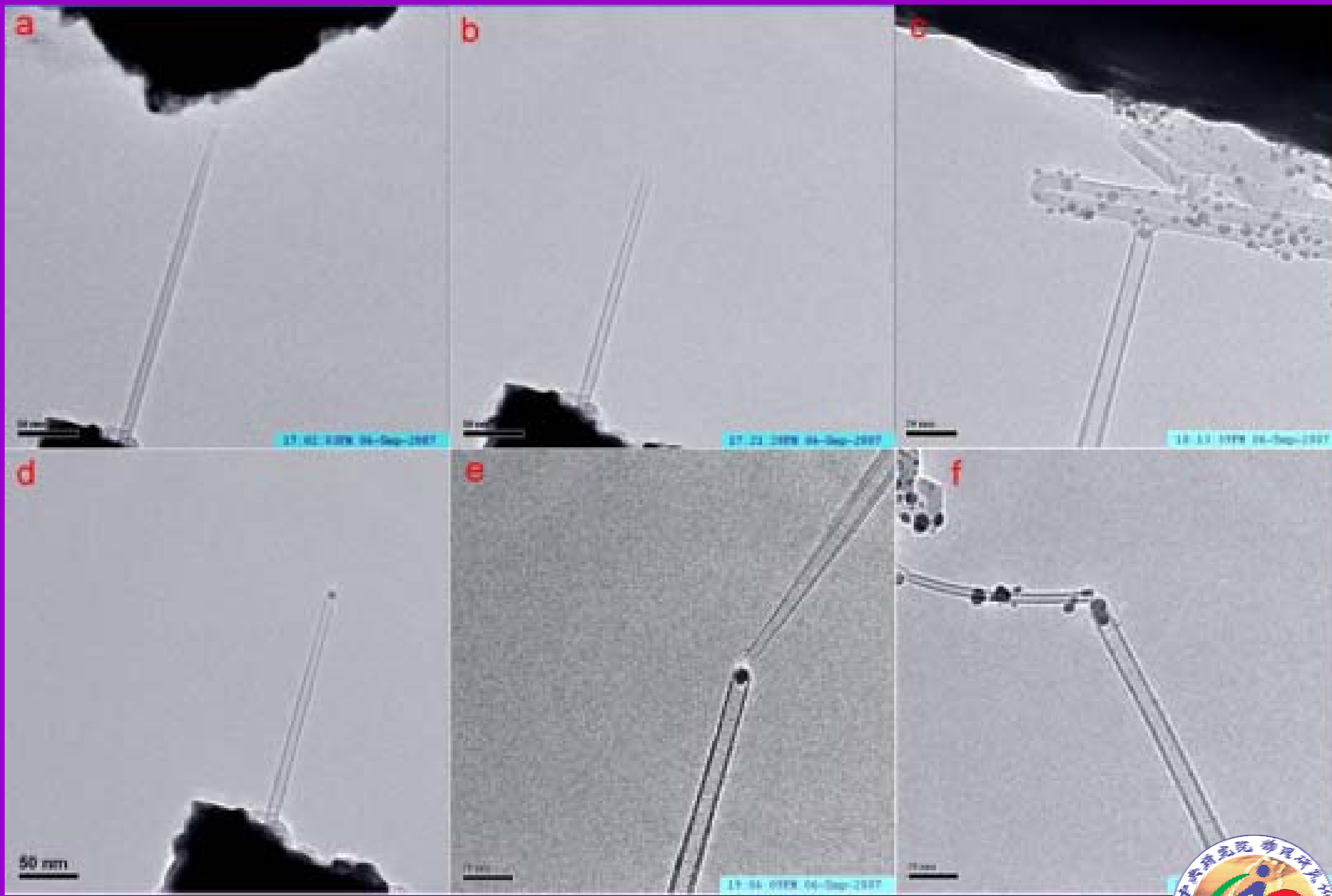
Fabrication of the largest SWNT



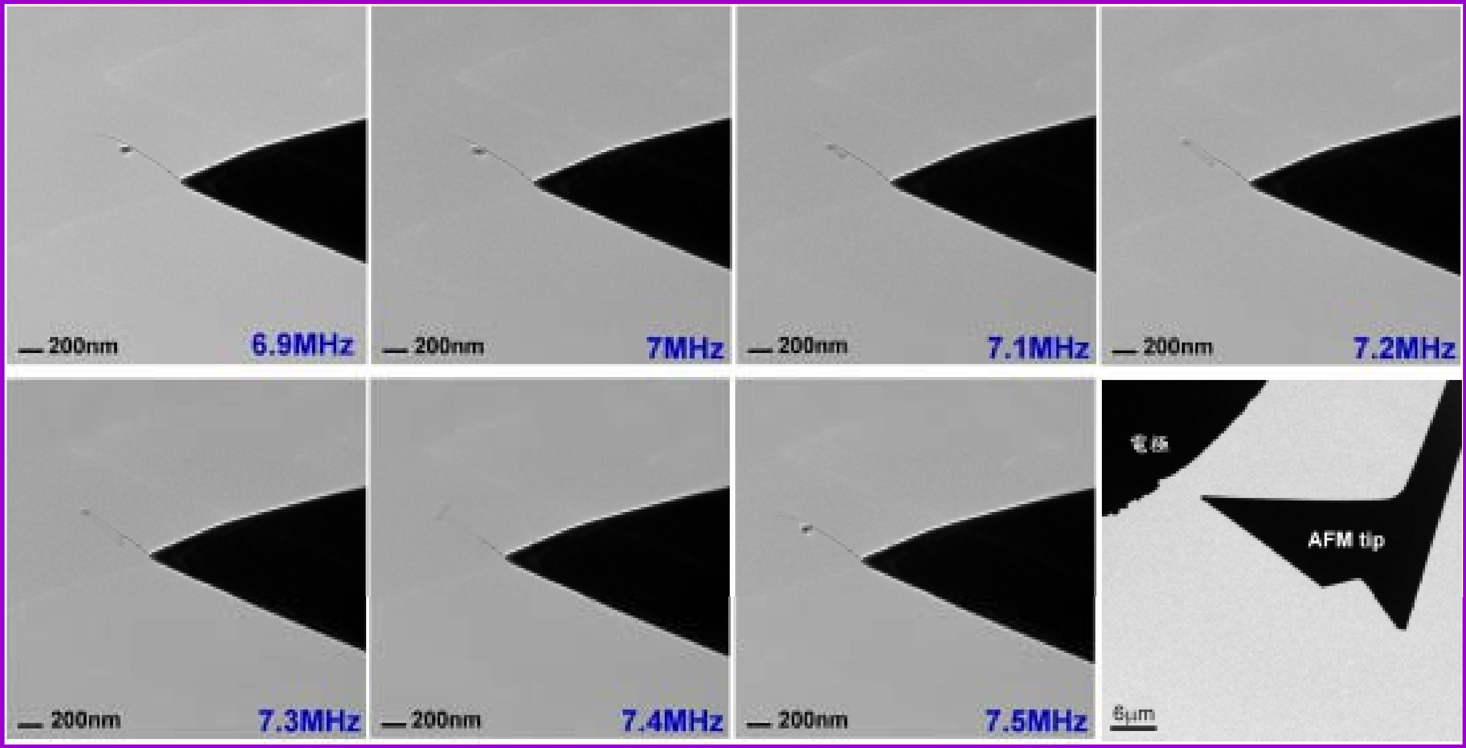
Other manipulation techniques



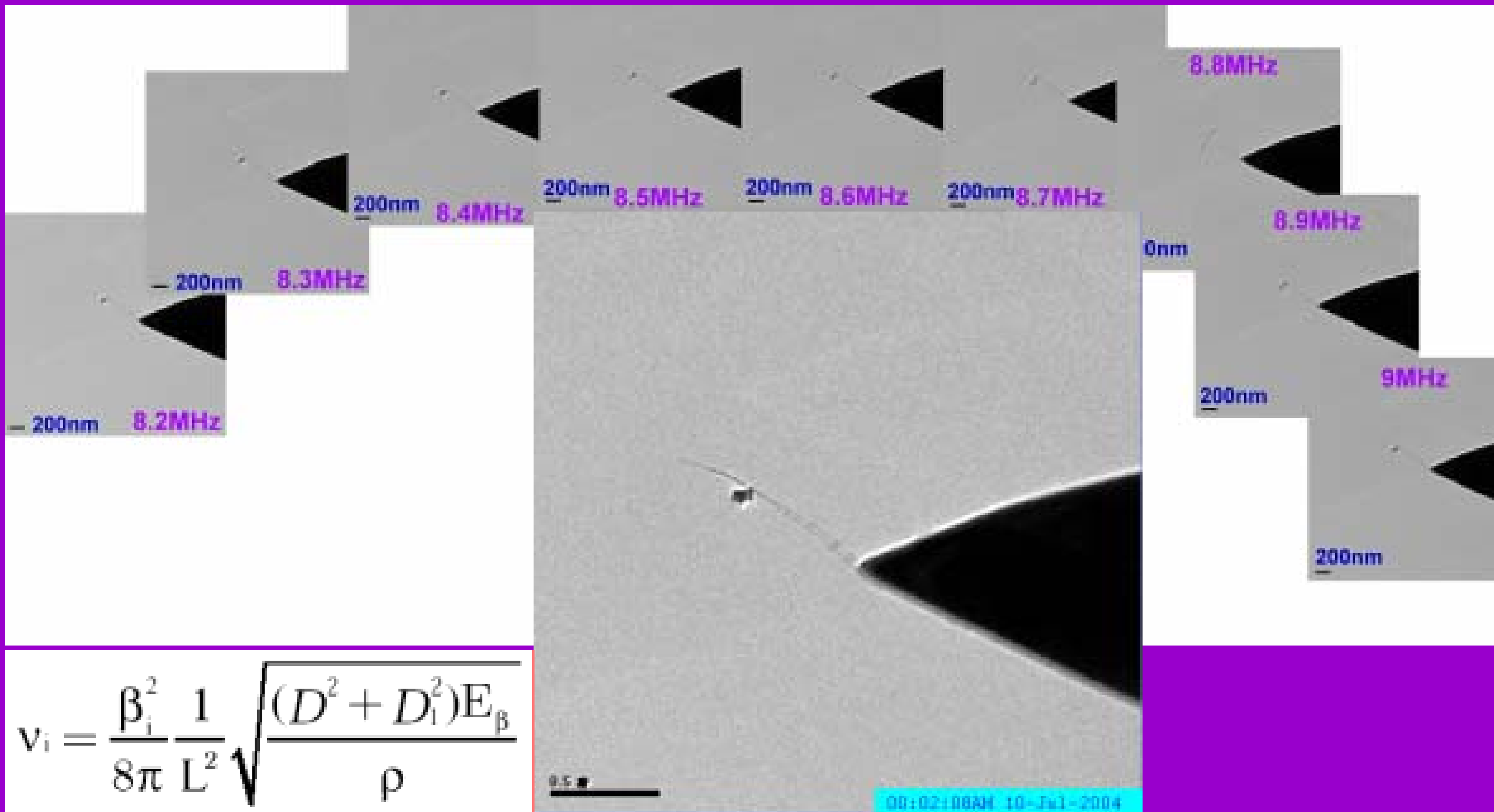
Insertion of extra particles



Nano electromechanical oscillator



Nano electromechanical oscillator

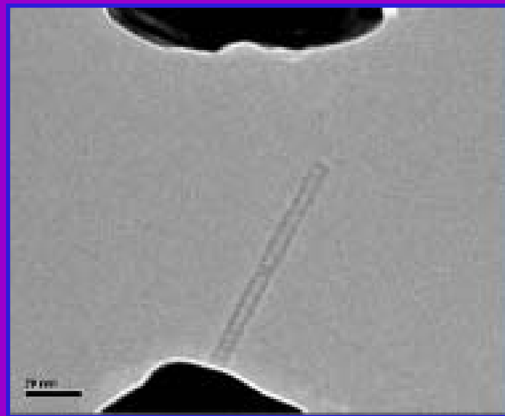


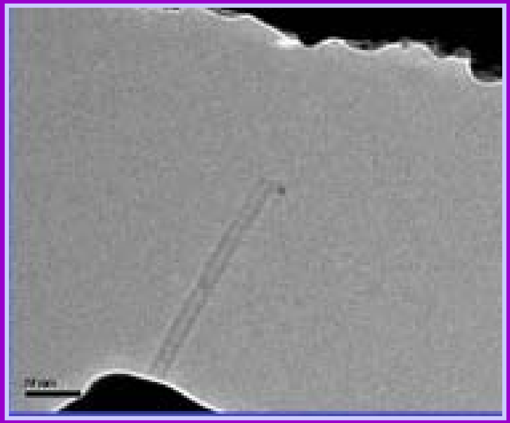
$$\nu_i = \frac{\beta_i^2}{8\pi}\frac{1}{L^2}\sqrt{\frac{(D^2 + D_1^2)E_\beta}{\rho}}$$

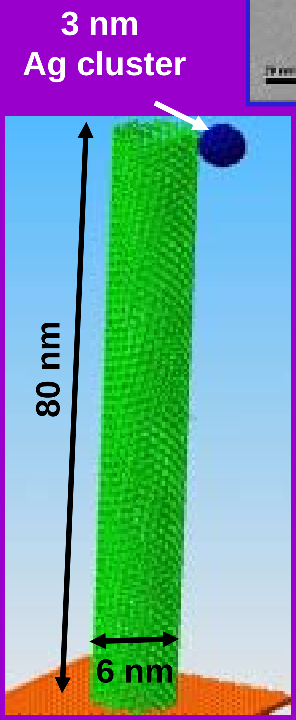
outer diameter (D), inner diameter (D_1), the length (L), the density (ρ)

$\beta_1 = 1.875$ and $\beta_1 = 4.694$ for the first and the second harmonics

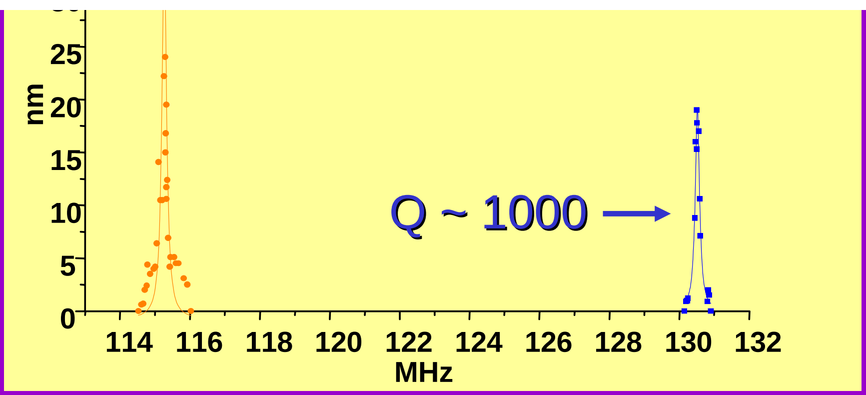
"Atom" balance





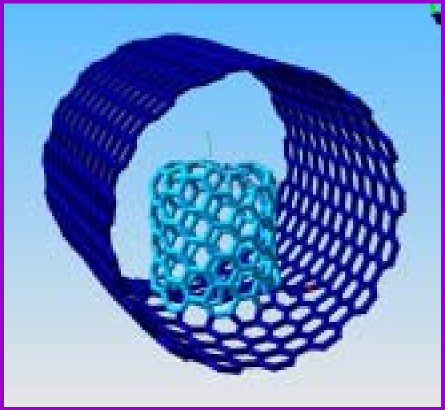


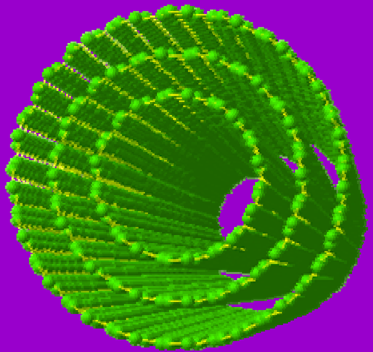
$m \sim m_0(\Delta f/2f_0) \sim 1.8\times10^{-19}$ g (mass of 1000 Ag atoms)



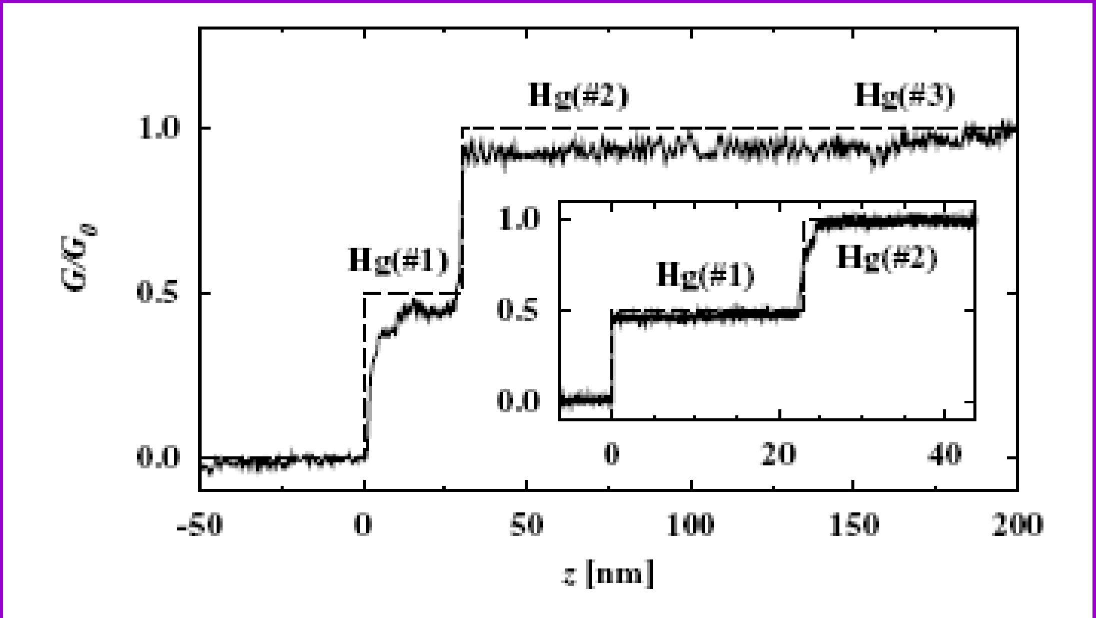
Outline

- Growth of carbon nanotubes
- Extraction of inner layers
- **Conductance of carbon nanotube**





Fractional Quantum Conductance in MWNT



Stefan Frank *et al., Science* **280**, 1744 (1998)

Stefano Sanvito *et al*., *Phys. Rev. Lett.* **84**, 1974 (2000)

Electrowetting in Carbon Nanotubes

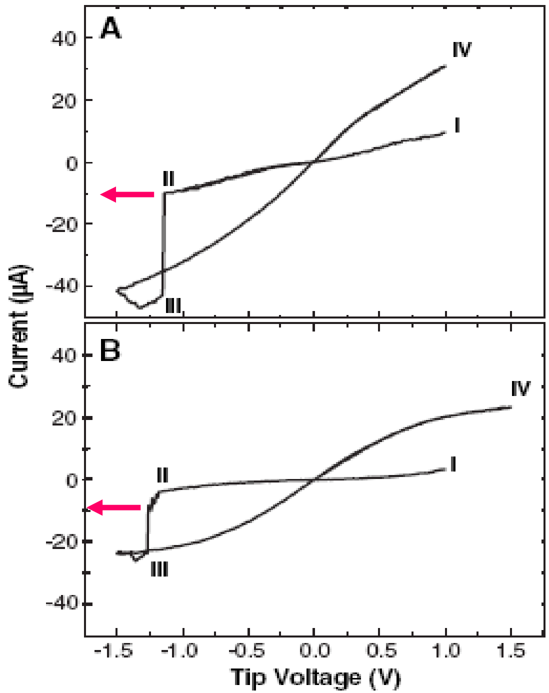
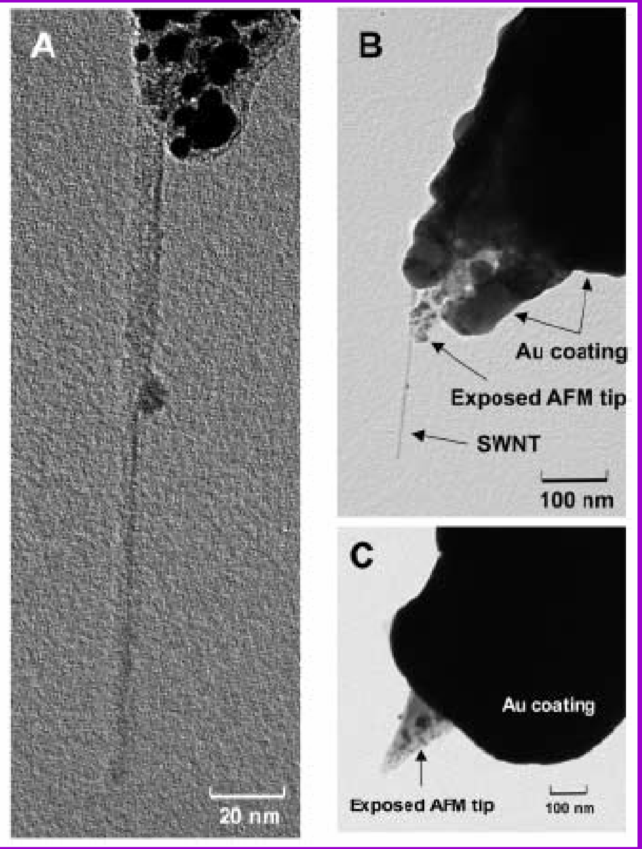
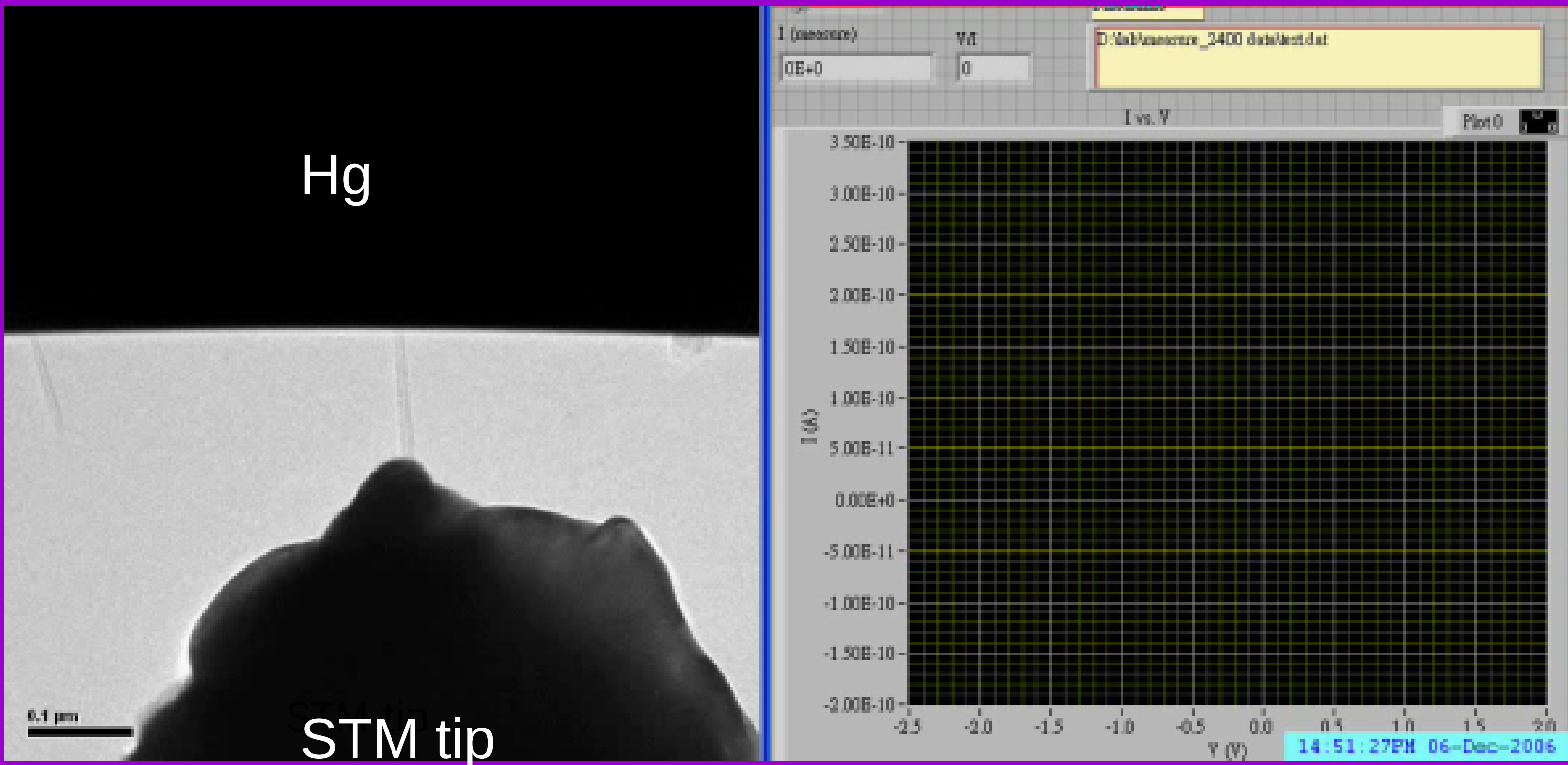


Fig. 1. Probe current as a function of applied tip voltage for (A) an 80-nm-long metallic SWNT and (B) a 130-nm-long semiconducting SWNT. Both nanotubes are immersed by 17 ± 2 nm into a mercury droplet. Curve I to II corresponds to the low-conductivity state. Curve II to III indicates the abrupt transition to the high-conductivity state, which is described by curve III to IV.

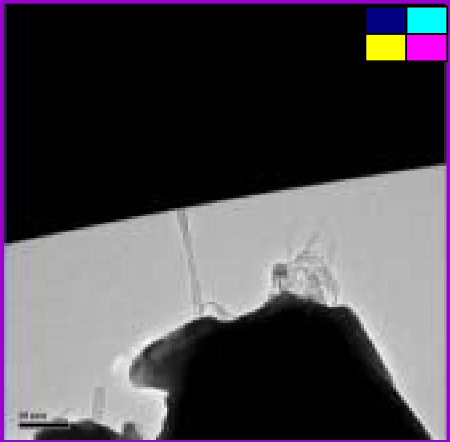


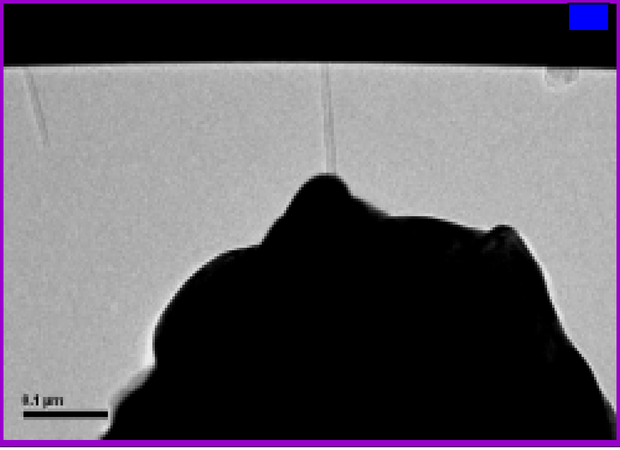
J. Y. Chen, *et al*. ***Science* 310**, 1480 (2005)

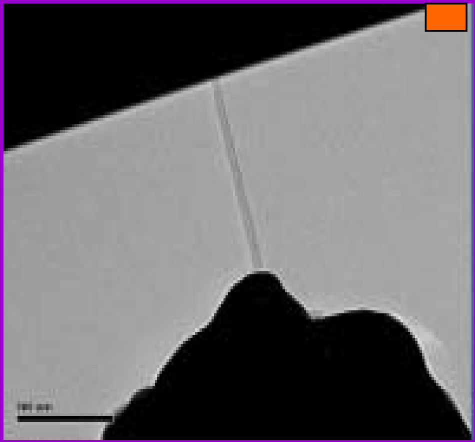
In situ measurement of MWNT conductance

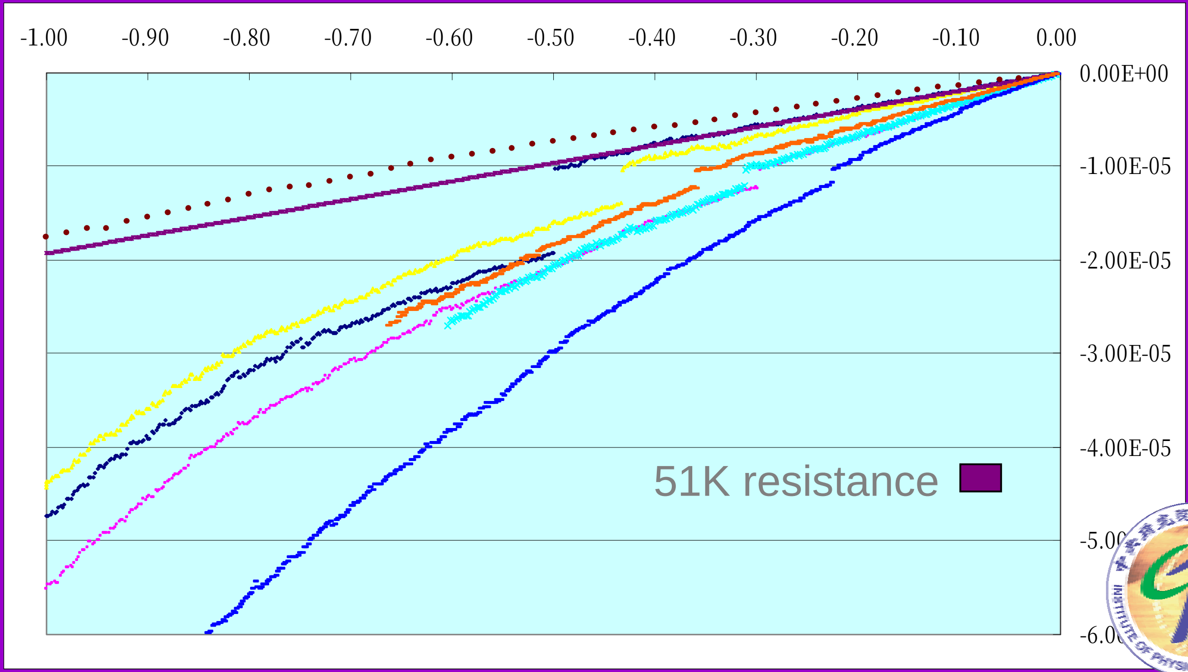


Conductance measurements on diff. samples

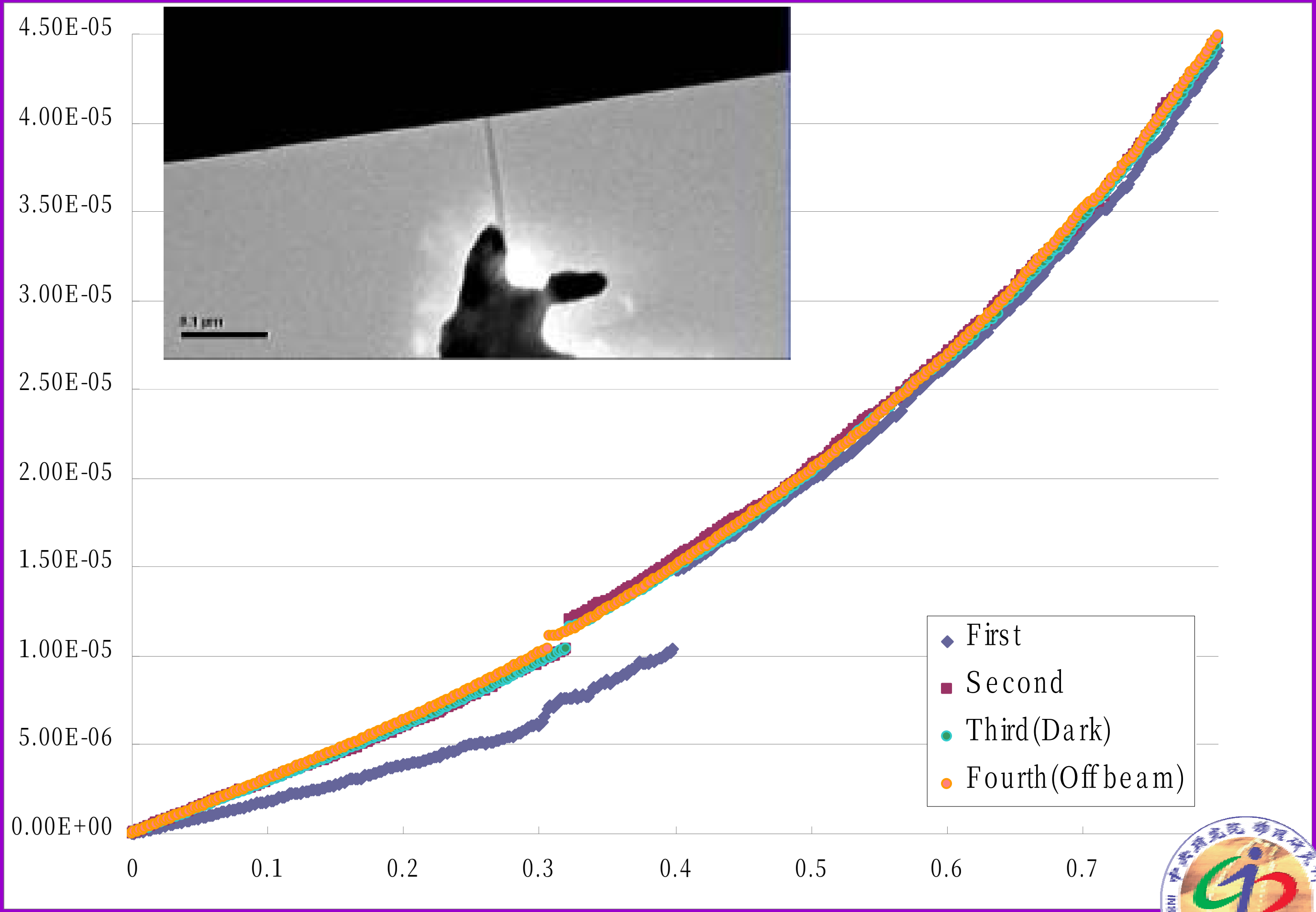




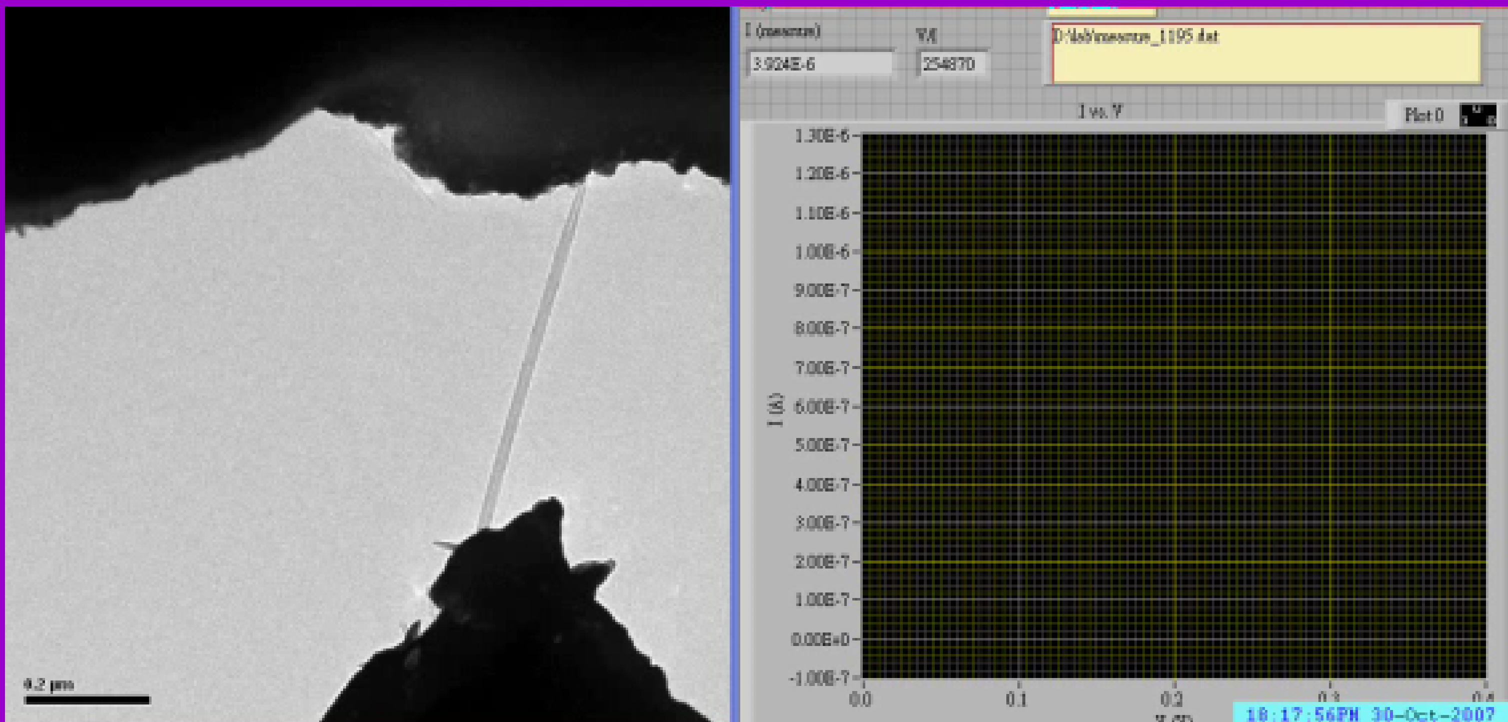




Conductance measurements with positive bias



Conductance measurements with Au electrodes



Summary

- Carbon nanotubes are fascinating materials for nanoscience research.
- We have shown our ability in observing the *in situ* growth of carbon nanotubes and performing real-time manipulation and measurements with the UHV TEM/STM combining system.
- Many questions concerning the nanoscale phenomena remain unanswered. We are seeking the inputs of theoretical calculations and simulations for clarifying these issues.

NanoSci Lab