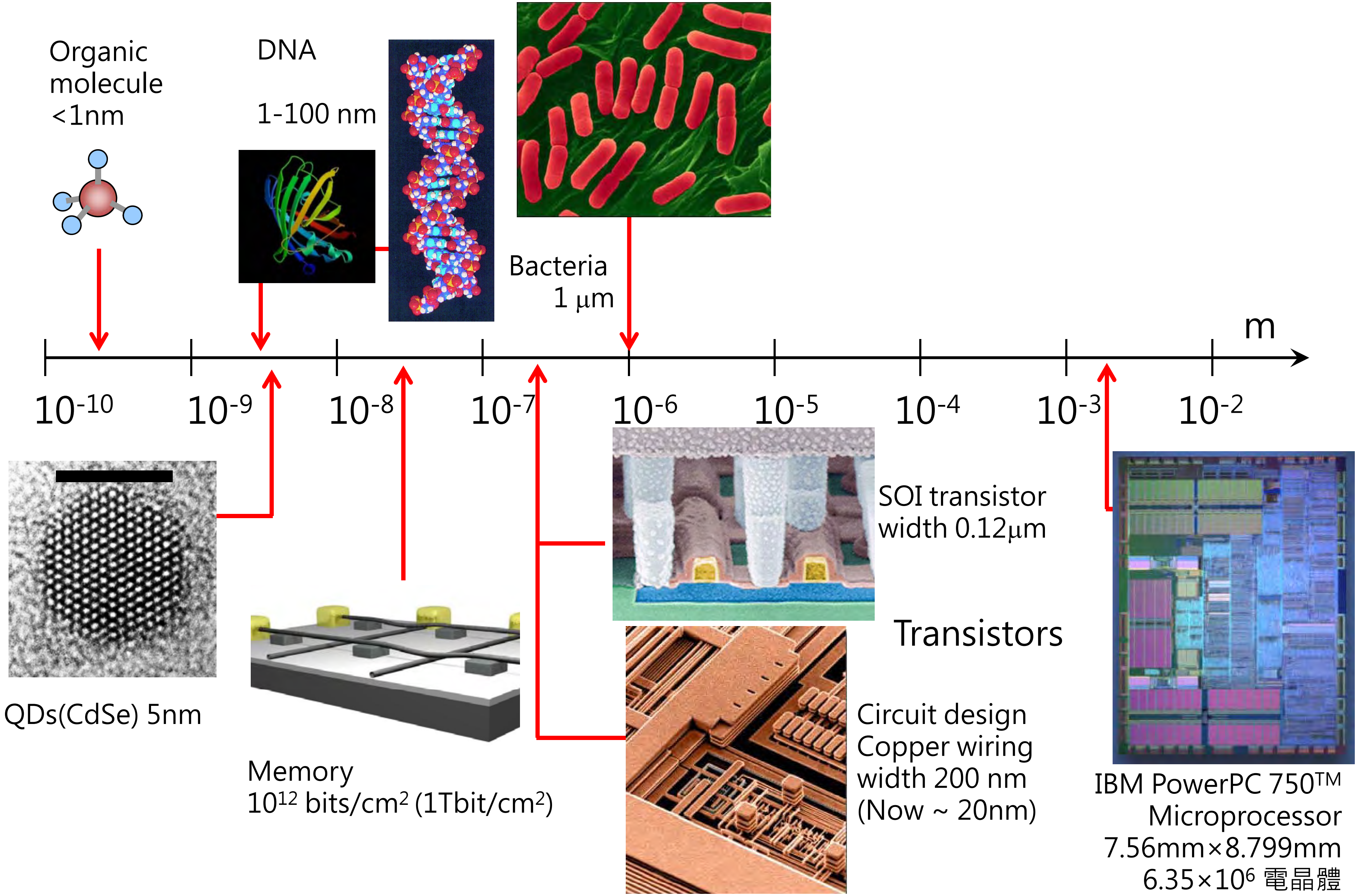
Quantum Nature of the Nano-world

Size of Nano??


Organic molecule <1nm
DNA
1-100 nm
Bacteria 1 μm
m
10-10
10-9
10-8
10-7
10-6
10-5
10-4
10-3
10-2
QDs(CdSe) 5nm
Memory
1012 bits/cm2 (1Tbit/cm2)
SOI transistor width 0.12μm
Transistors
Circuit design Copper wiring width 200 nm (Now ~ 20nm)
IBM PowerPC 750TM Microprocessor
7.56mm×8.799mm
6.35×106 電晶體

Definition of Nanomaterial

Original： "quantum size effect" where the electronic properties of solids are altered with great reductions in particle size

。

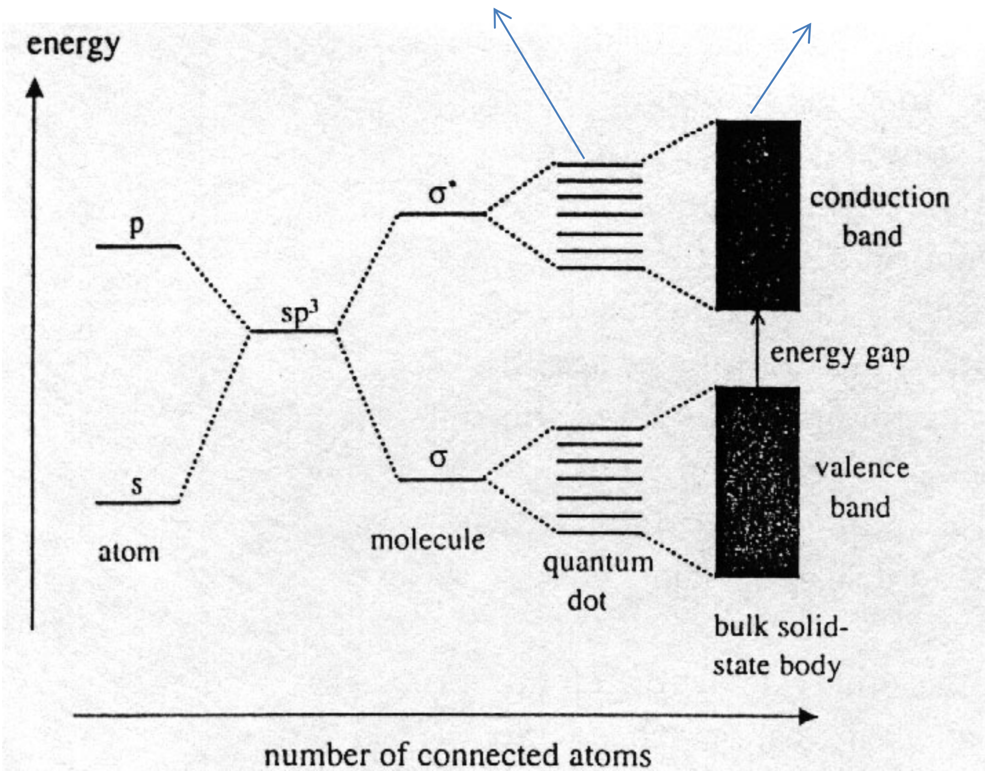
（New）

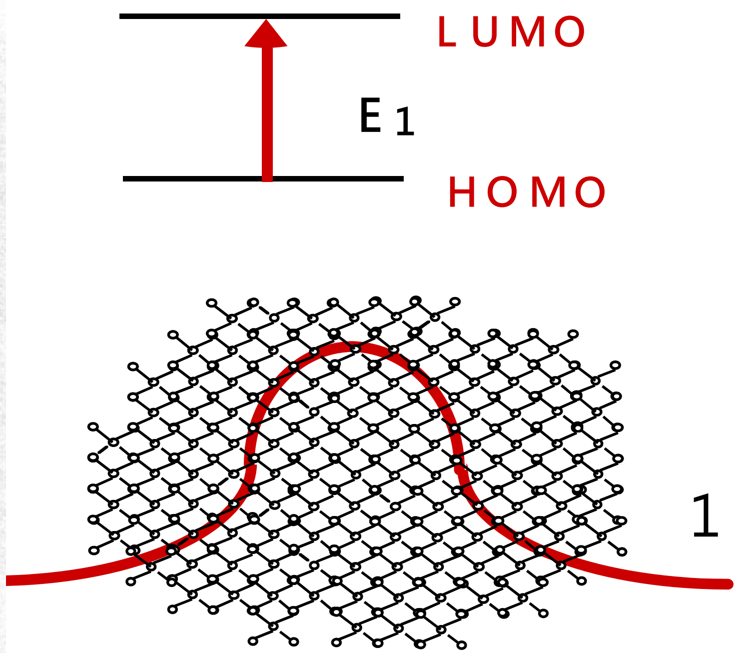
On 18 October 2011, the European Commission adopted the following definition of a nanomaterial:[2]

A natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range *1 nm – 100 nm*.

"

Quantum confinement effect



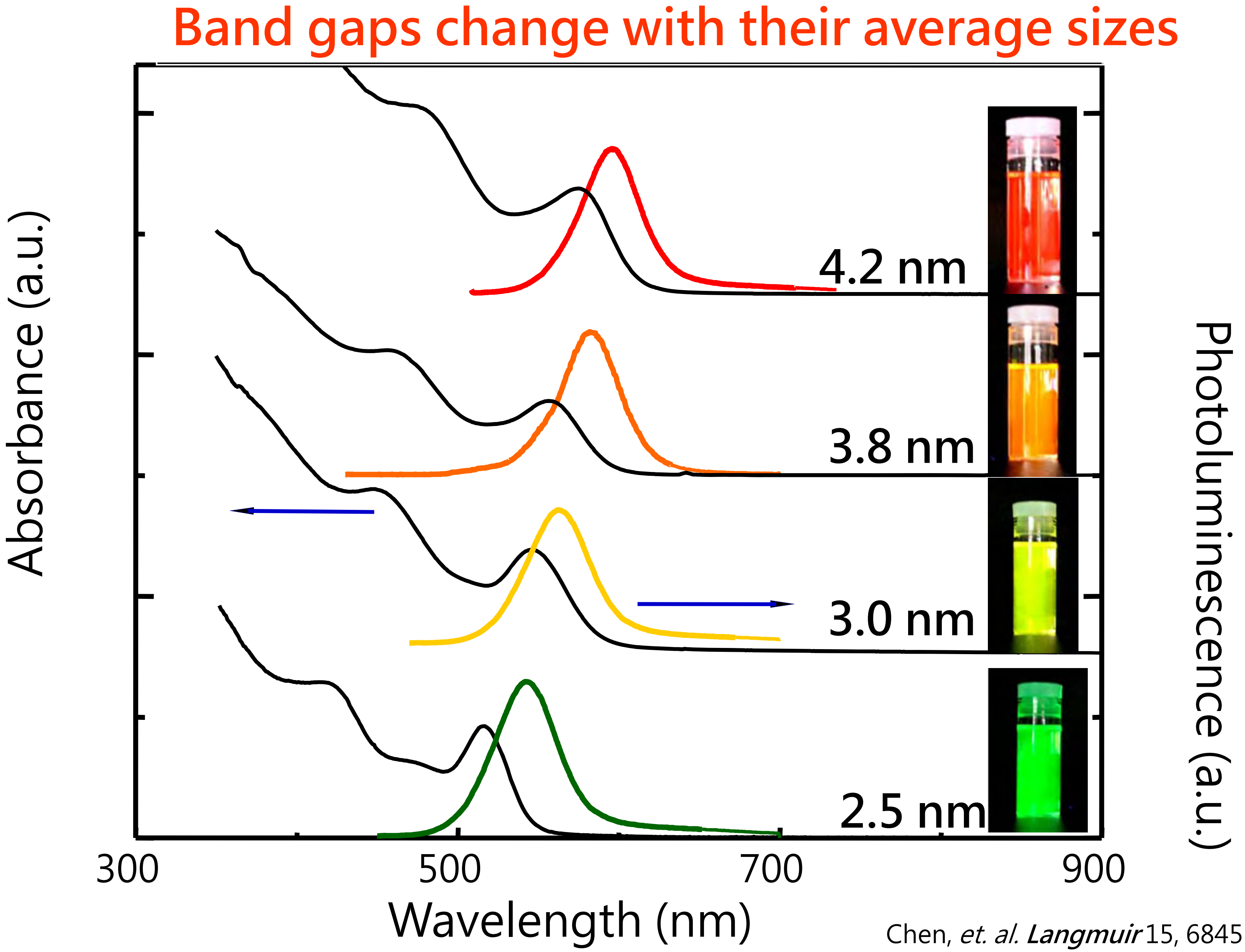


$$E(R) = Eg + \frac{\hbar^2 \pi^2}{2R^2}\left[\frac{1}{m_e} + \frac{1}{m_h}\right] - \frac{1.8e^2}{\varepsilon R}$$

m_e and m_h : effective masses

e : bulk optical dielectric coefficient

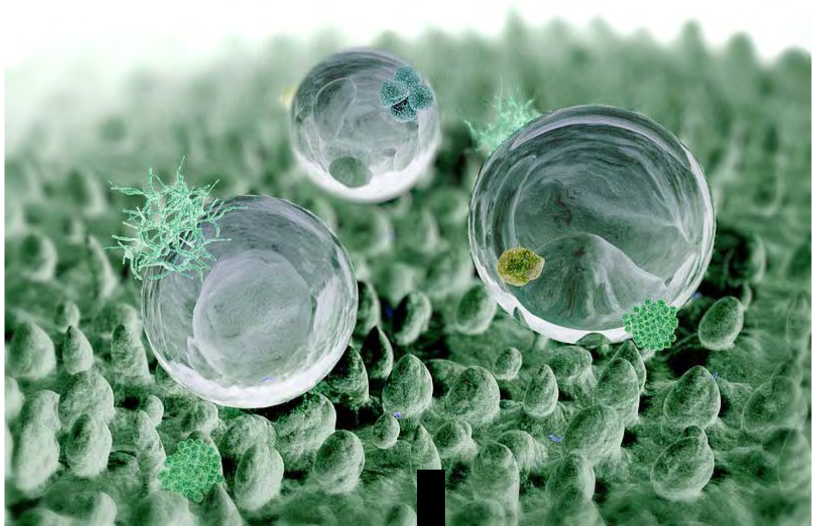
Size-dependent optical properties of CdSe QDs



Chen, *et. al.* ***Langmuir*** 15, 6845 (1999)

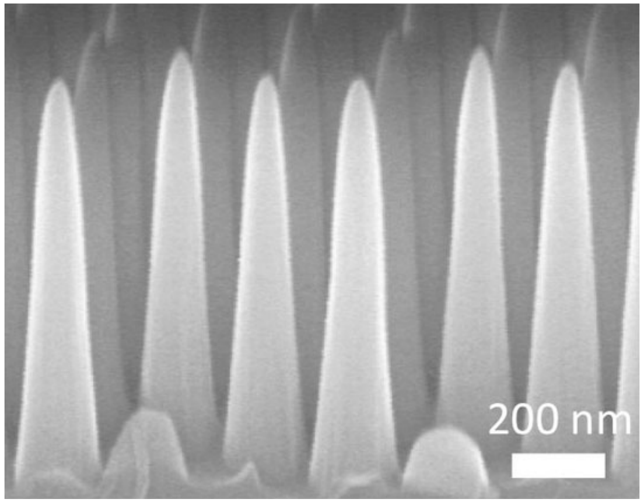
Lotus Effect

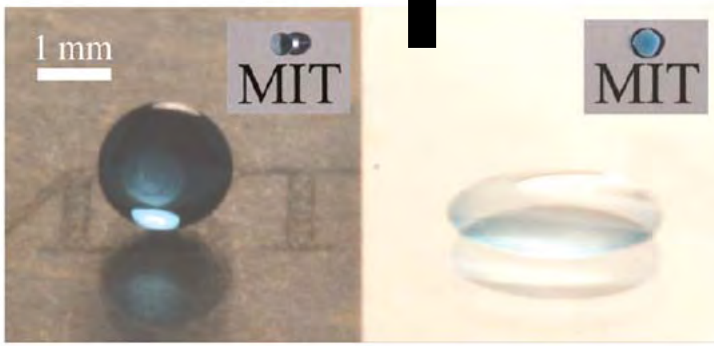
Lotus



Self-cleaning

Nano array on glass substrate





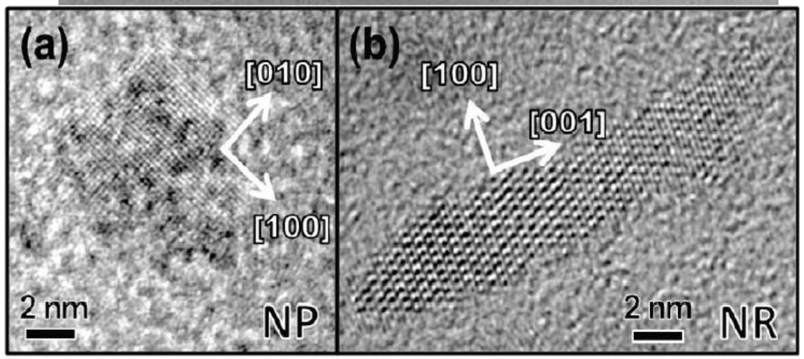
Park, K. C. et. al., *ACS Nano* **2012**, *in ASAP.*

Photocatylysts using Nanomaterials

- Bulk TiO_2 V.S. TiO_2 nanorods/nanoparticles

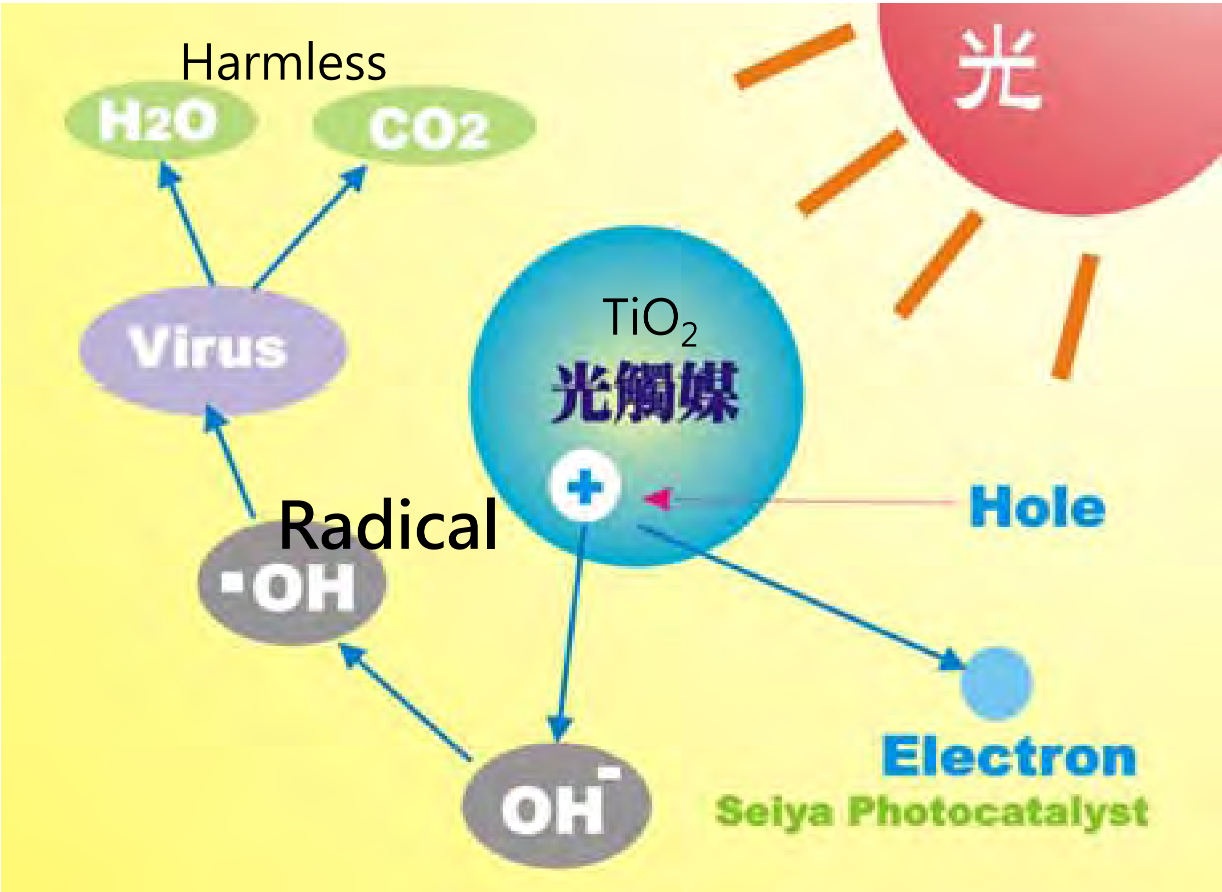
http://www.35664.net/new/public/tag.php?name=%E4%B8%93%E9%A2%98&page=14

http://www.hiwtc.com/products/tio2-ultra-fine-and-high-purity-333573-22847.htm



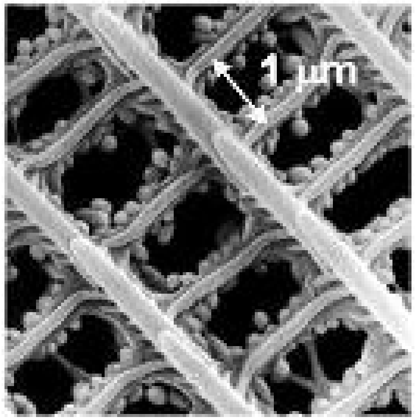
Journal of American Chemical Society, 133,11614, (2011)

Photocatalytic effect

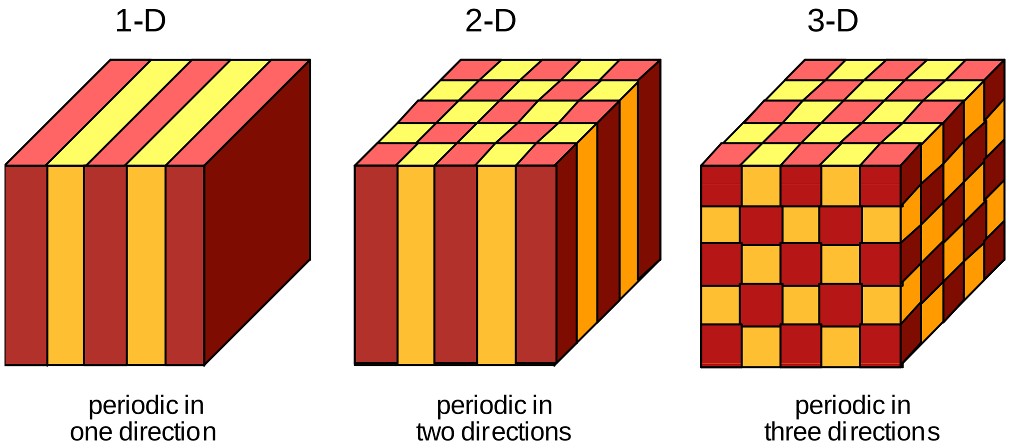


http://proj3.moeaidb.gov.tw/nanomark/Licens

Photonic crystals



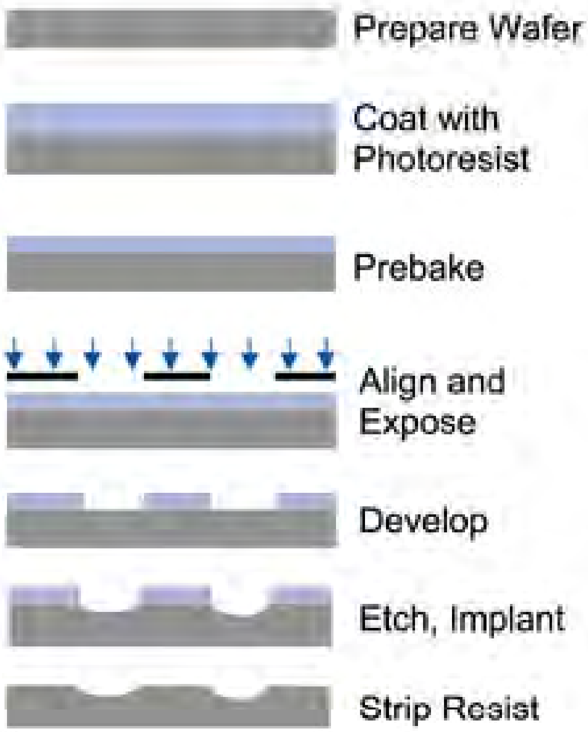
From 《奈米科學網》

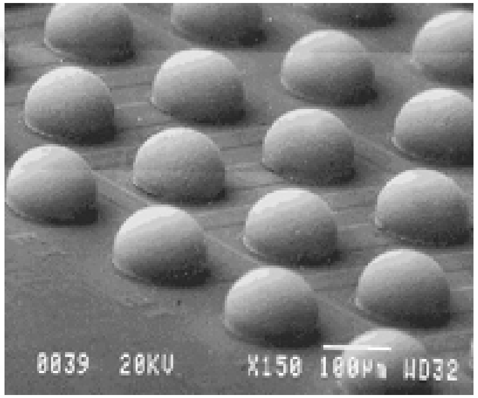


periodic electromagnetic media

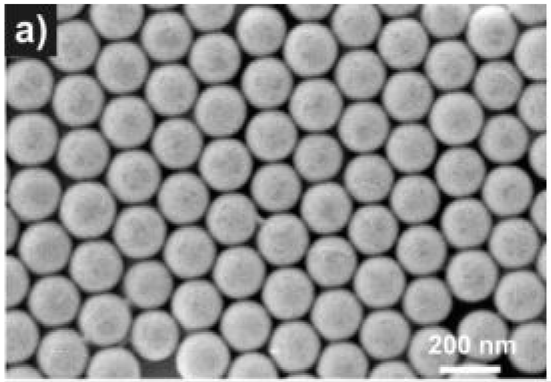
How to make Nanomaterials ??

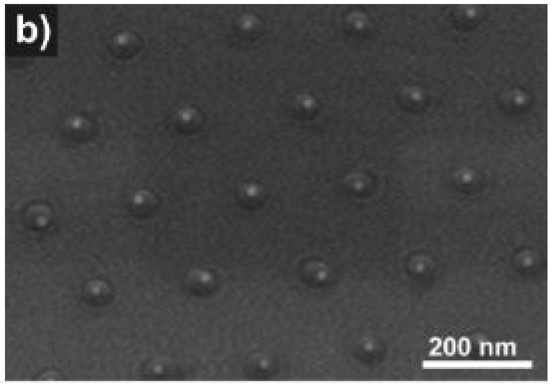
- Top－down (Physical method): lithography
- Advantage: Easily controlled
- Disadvantage: Expensive





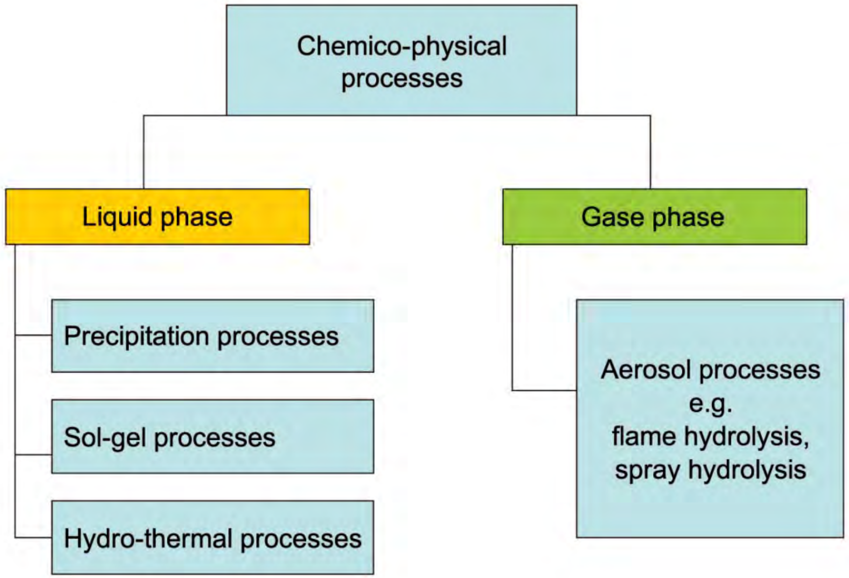
http://www.beilstein-journals.org/bjnano/single/articleFullText.htm?publicId=2190-4286-2-50

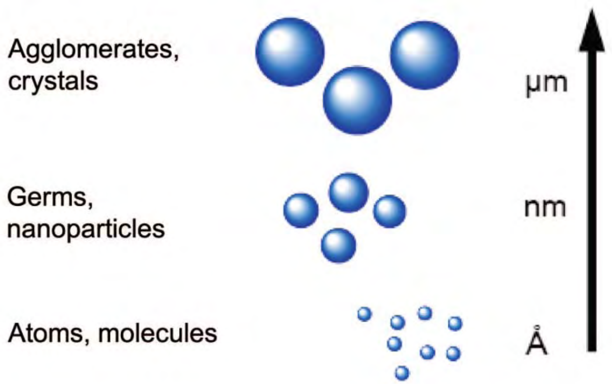


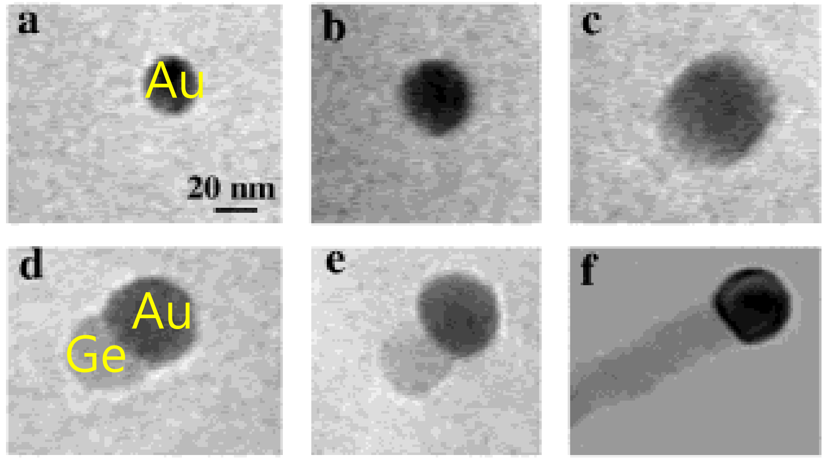


http://spie.org/x32391.xml

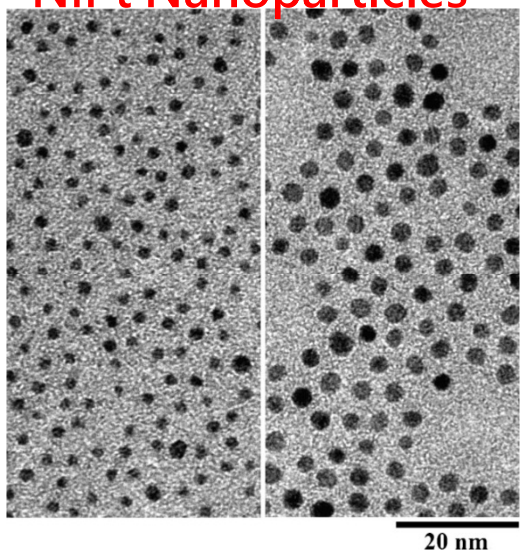
Bottom up (Chemical Method)

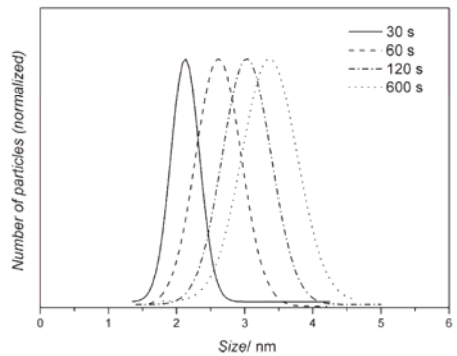






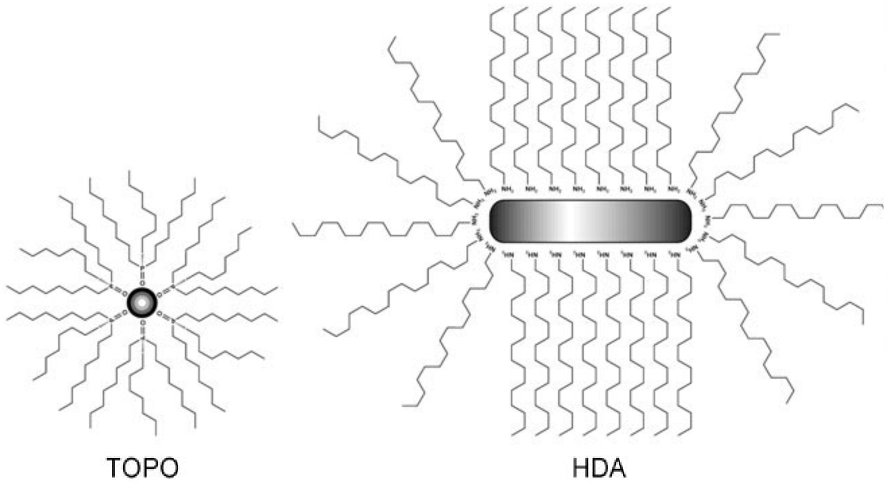
NiPt Nanoparticles



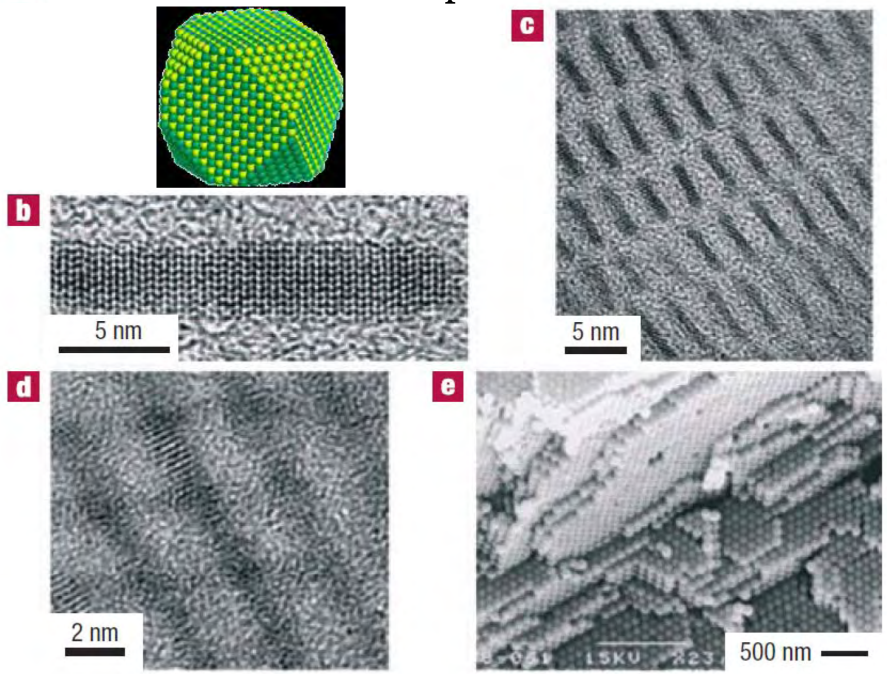


Ahrenstorf, K. et. al., Adv. Funct. Mater. 2008, 18, 3850–3856

Atomic Foundry

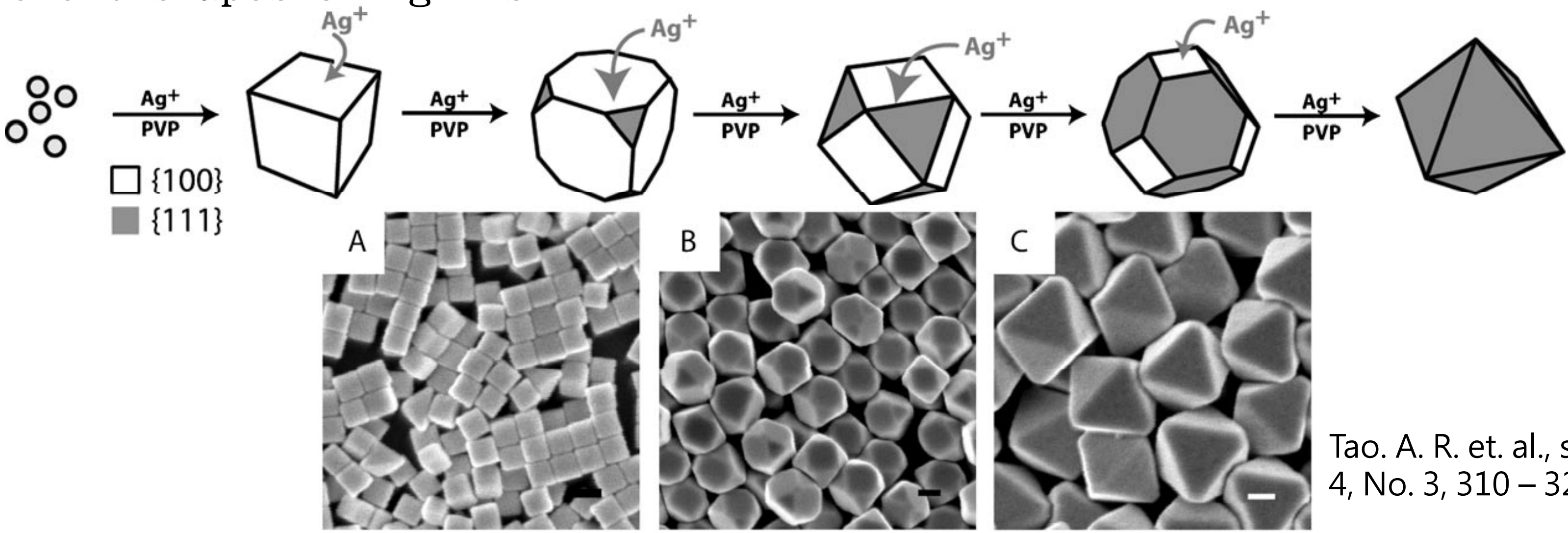


Different shapes of CdSe



Min, Y. et. al., Nature Materials 7, 527 - 538 (2008)

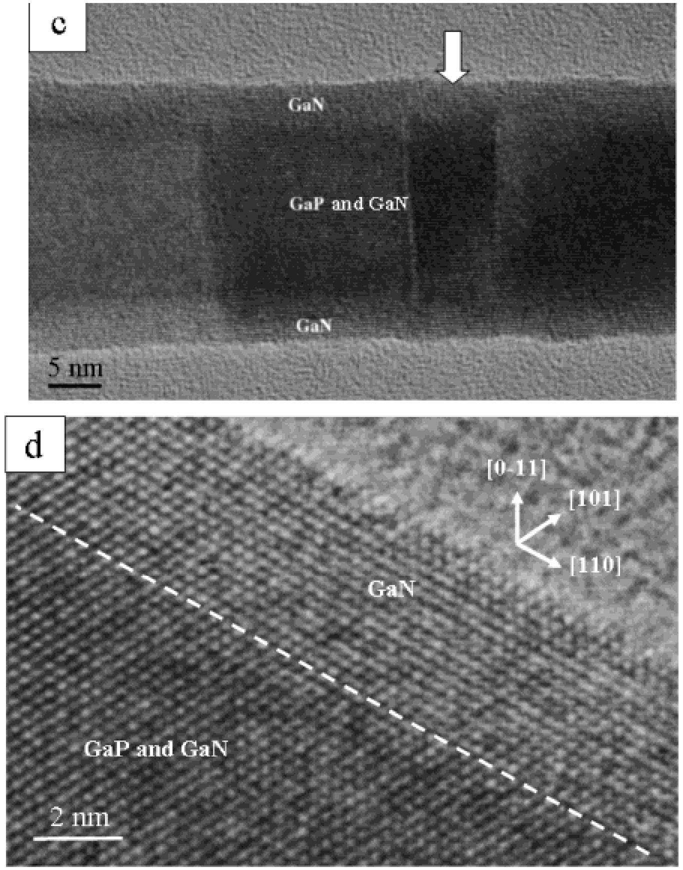
Different shapes of Ag NPs



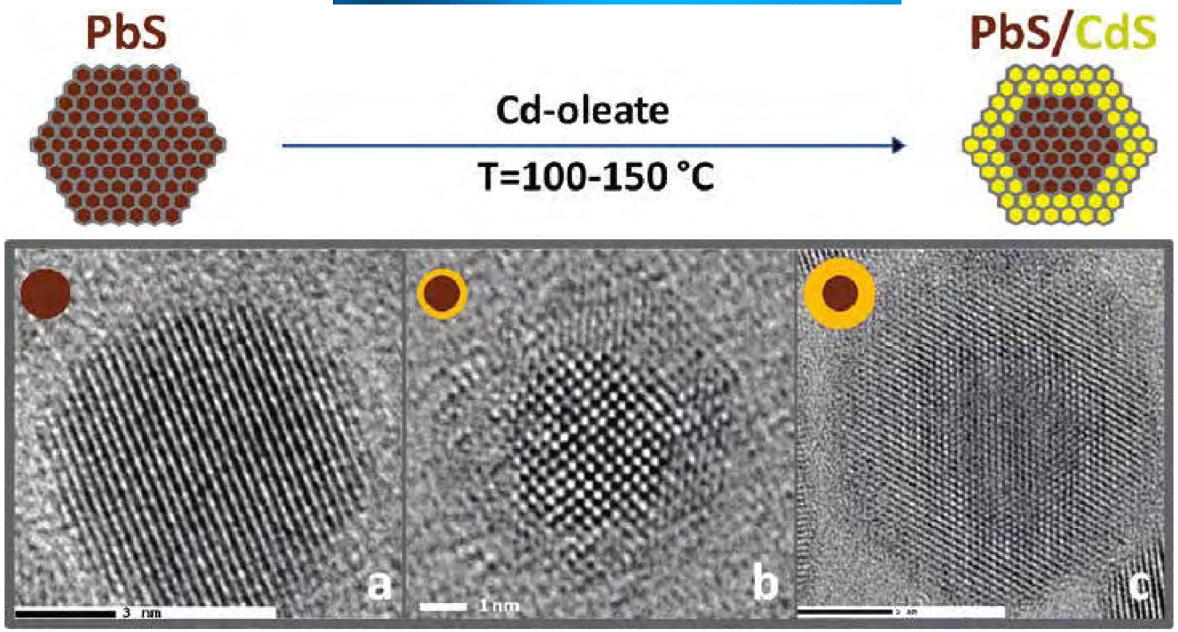
Tao. A. R. et. al., small 2008, 4, No. 3, 310 – 325

How to observe Nanomaterials??

Transmission electron microscopy(TEM)

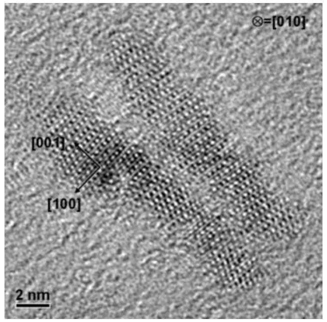


Lin, H. M. et. al., Nano Lett., Vol. 3, No. 4, **2003**



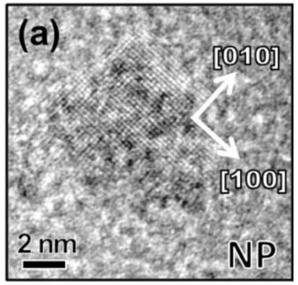
Kinder, E. et. al., *J. Am. Chem. Soc.* 2011, 133, 20488–20499

3D STEM Tomography images of P3HT/TiO_2 hybrids

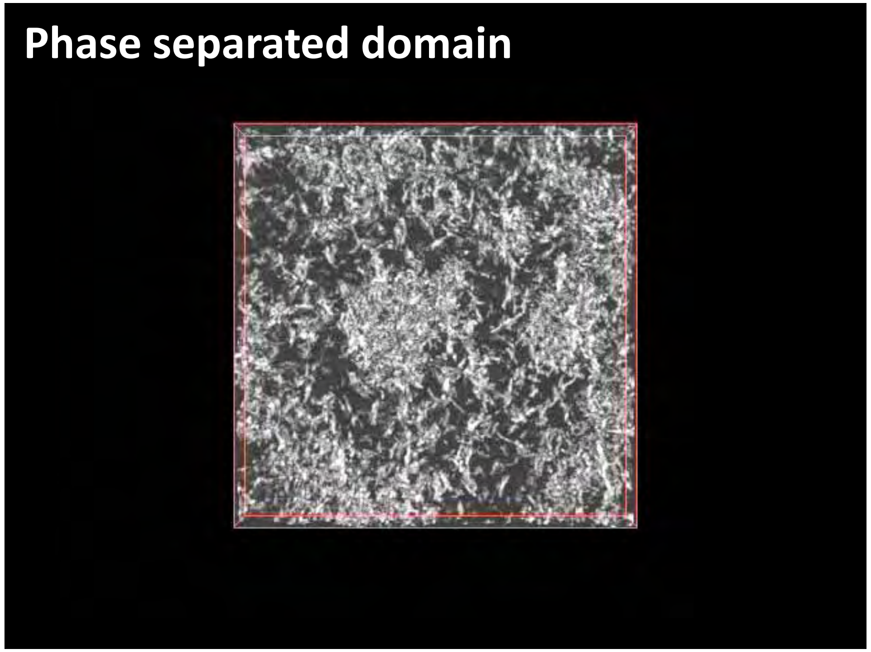


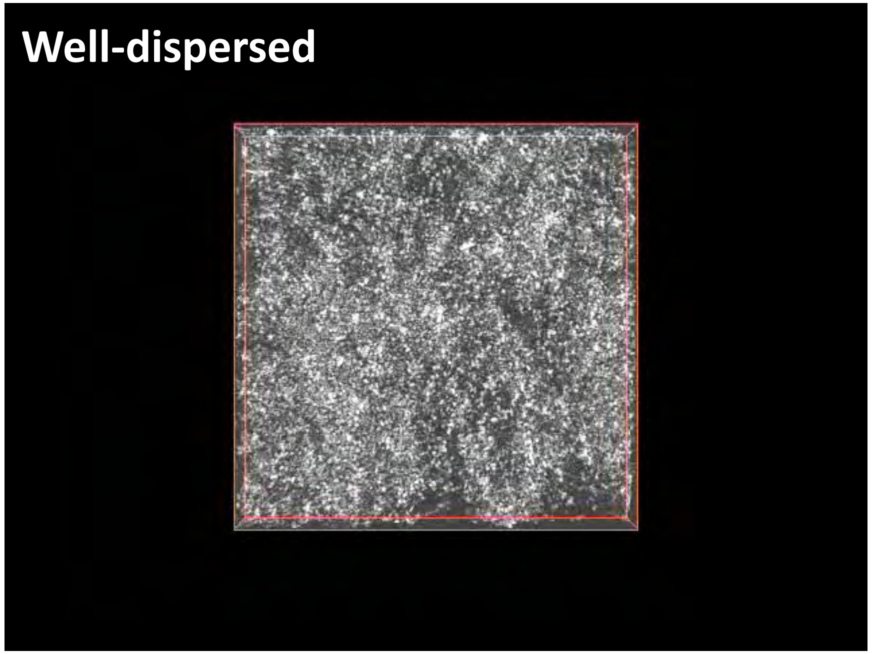
TiO_2 nano rod
(NR)
4nm x 20nm

TiO_2 nano particle
(NP)
5nm x 5nm

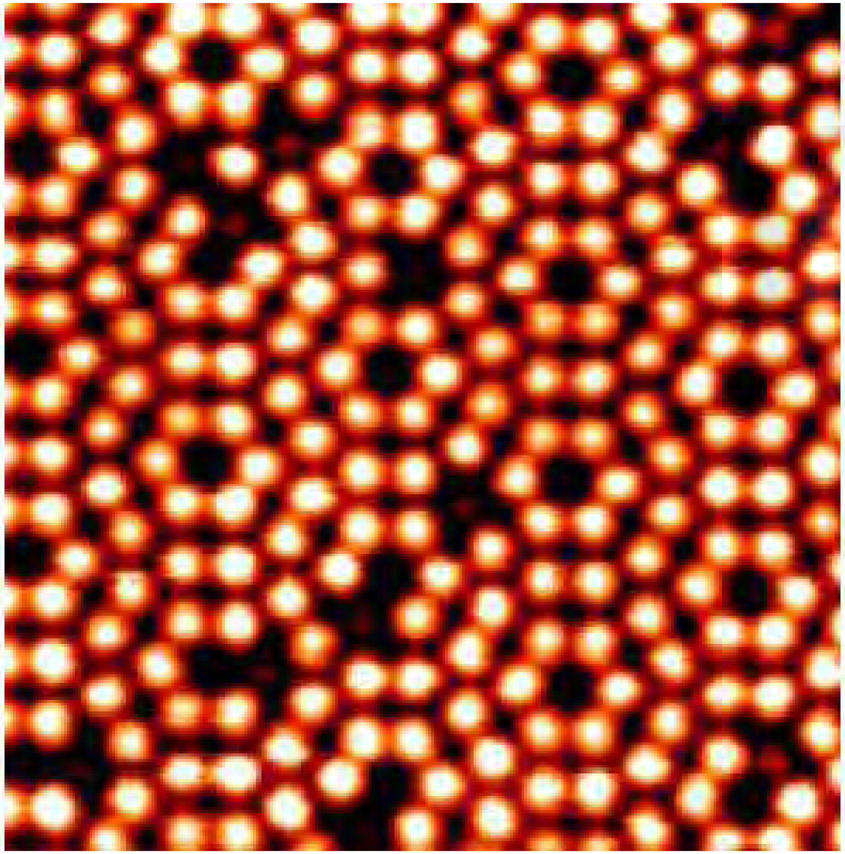


STEM-HAADF electron tomography (2 Å resolution)





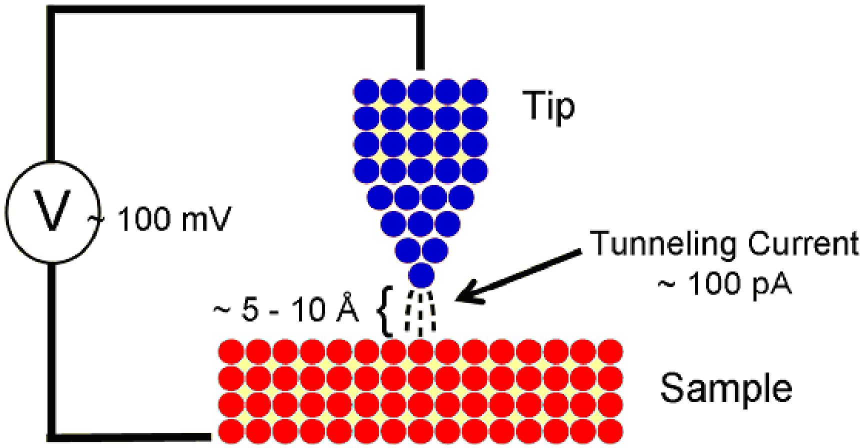
Scanning electron microscopy(STM)



Silicon atoms on a surface

http://www.exo.net/~pauld/workshops/Atoms.html

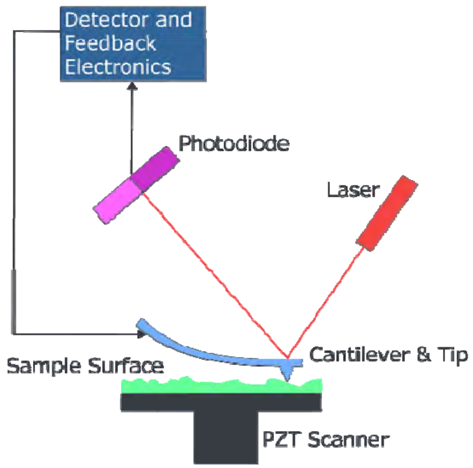
(Quantum tunneling effct)

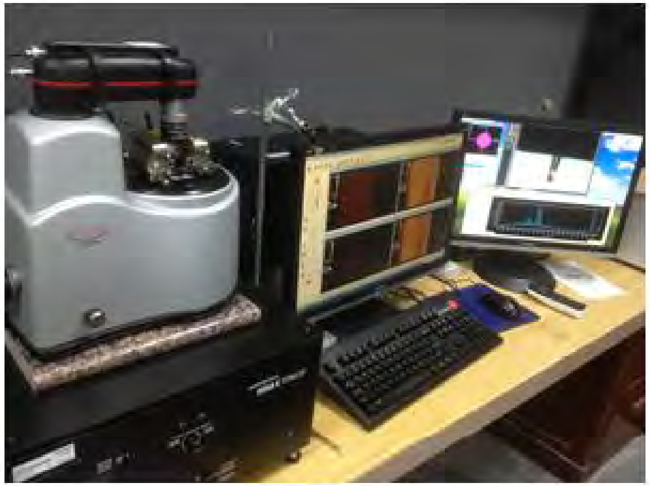


http://www.personal.psu.edu/ewh10/ResearchBackground.ht
m

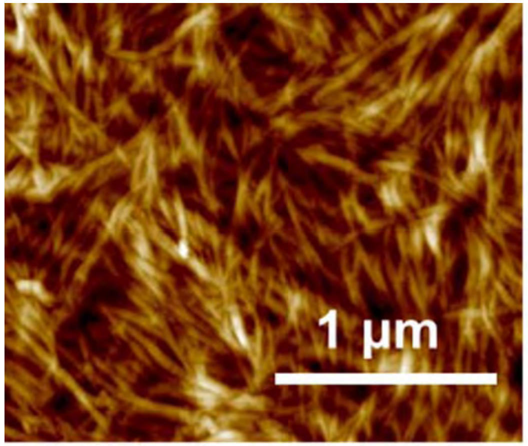
Atomic Force Microscopy (AFM)

Atomic Force Microscopy (AFM)

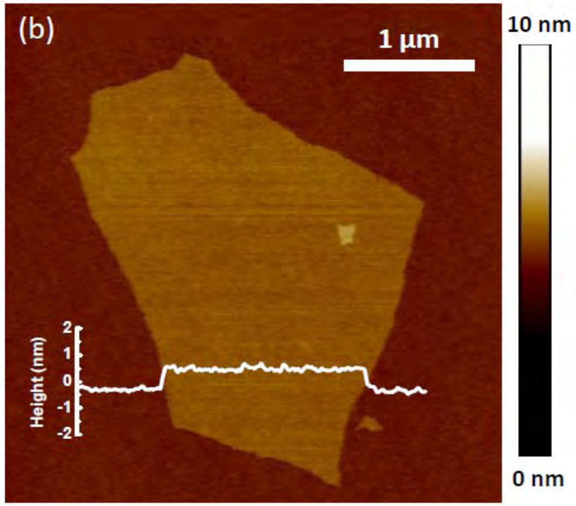




single wall carbon nanotube



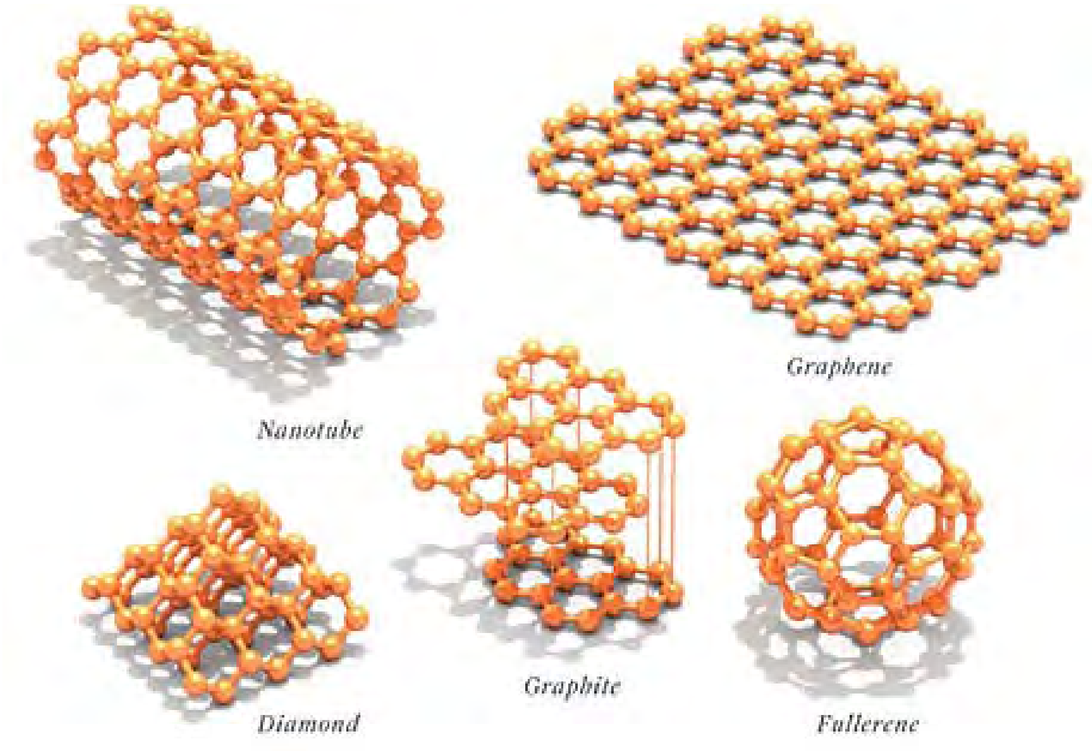
(Graphene oxide)



Nanomaterials--
Carbon nanotubes (CNTs) and Graphene

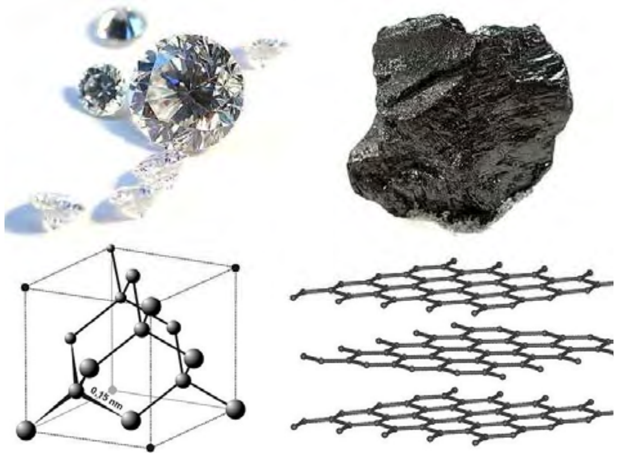
Carbon Nanomaterials

- 3D
  - Graphite
  - Diamond
- 2D
  - **Graphene**
- 1D
  - **Carbon nanotube**
- 0D
  - Fullerene

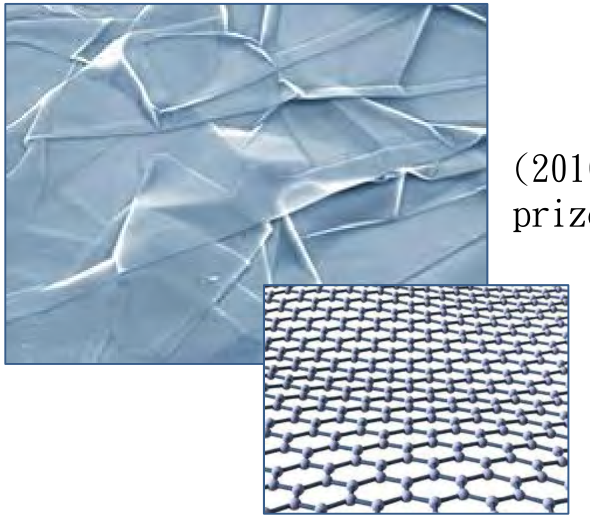


Cabon-related materials

3D Diamond and Graphite

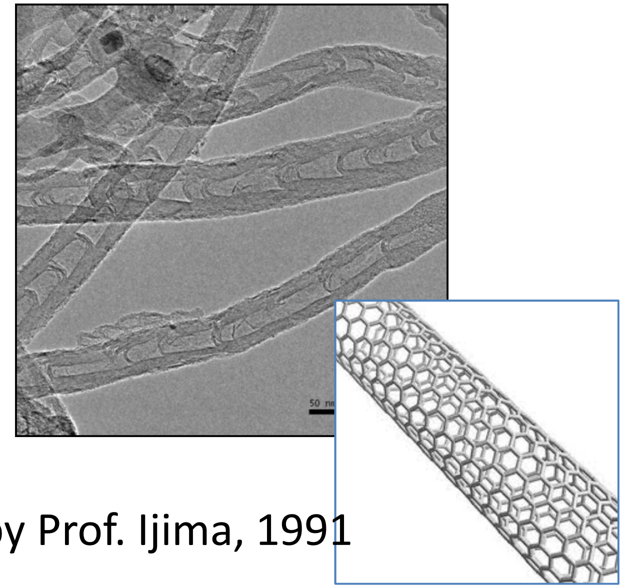


2D Graphene



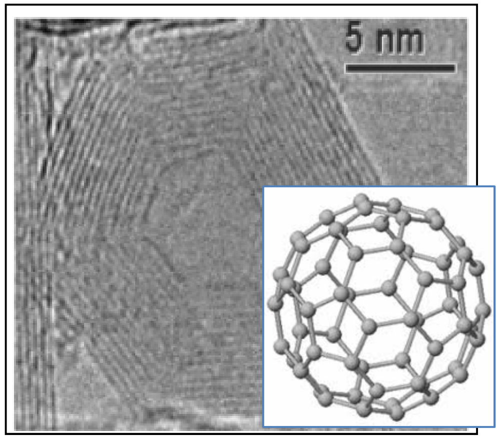
(2010 Nobel prize in physics)

1D Carbon nanotube



discovered by Prof. Ijima, 1991

0D Bulkyball(C_{60})



(1996 Nobel prize in Chemistry)

CNT History

- 1952: Radushkevich and Lukyanovich found nano-sized carbon fibers (Russian)
- 1991: CNTs were discovered by Prof. Ijima and named
- 1992: Theoretical predictions of the electronic properties of SWCNT
- 1997: First CNT transistor
-

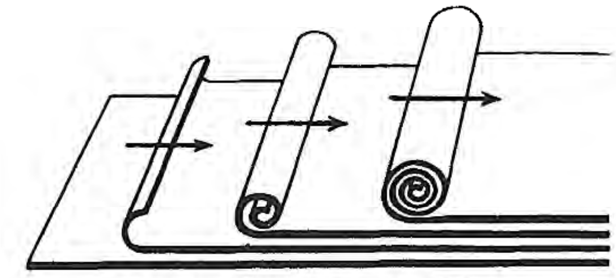
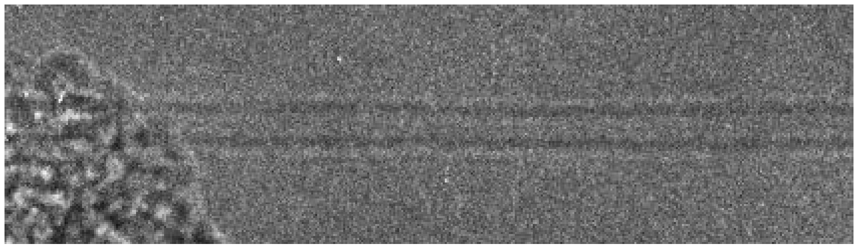
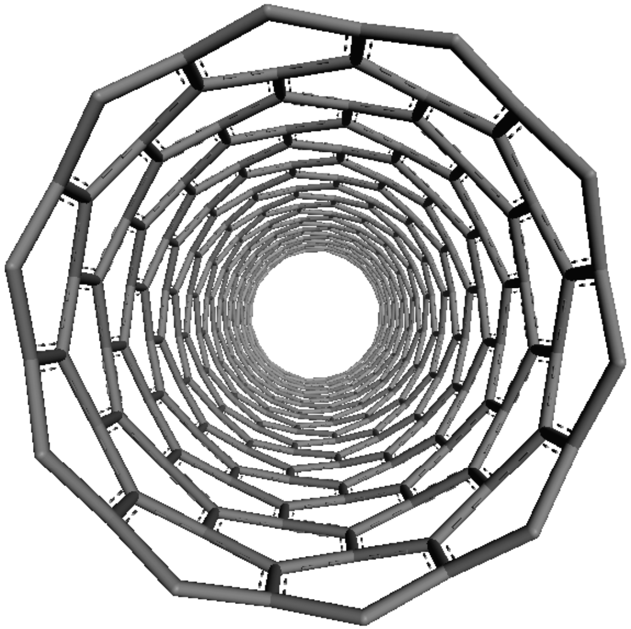


Fig. 3. Schematic illustration of rollers



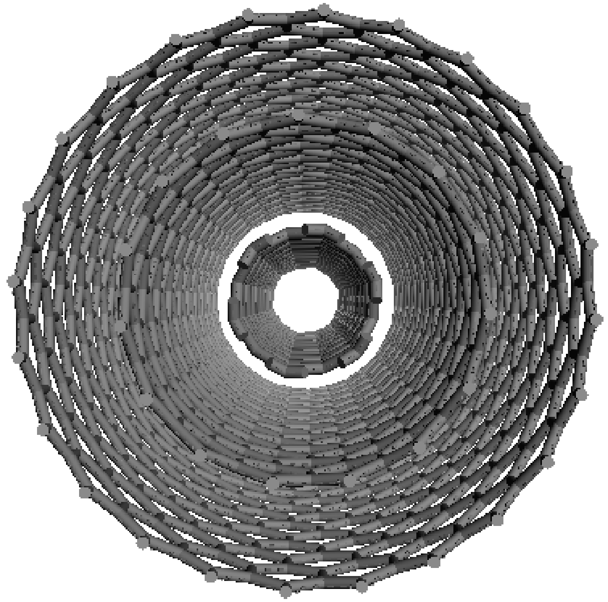
Structure of CNT

Single-Walled CNT (SWCNT)



(10,0)

Multi-Walled CNT (MWCNT)

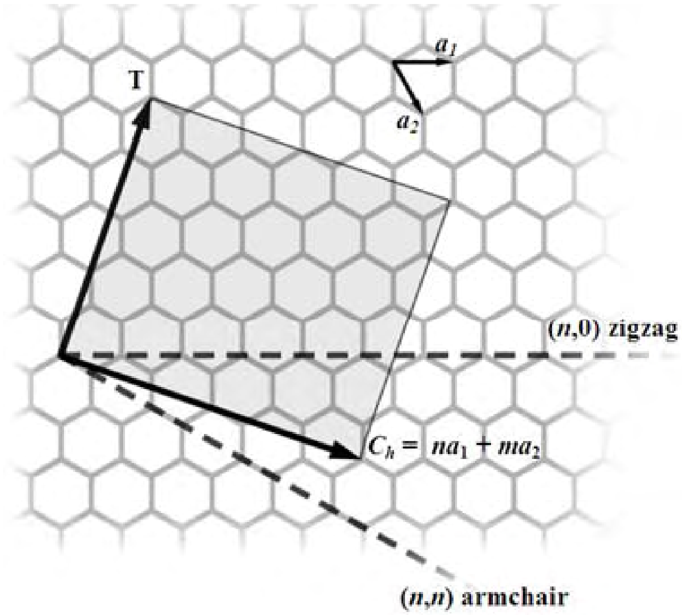


(6,0)+(15,0)+(24,0)

The interlayer distance in multi-walled nanotubes is close to the distance between graphene layers in graphite, approximately **3.4 Å**.

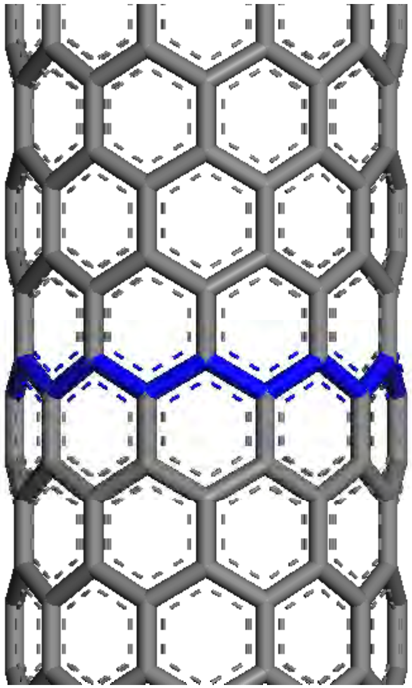
Structure of CNT

- Similar to GNRs, we should take the chirality of CNTs into account

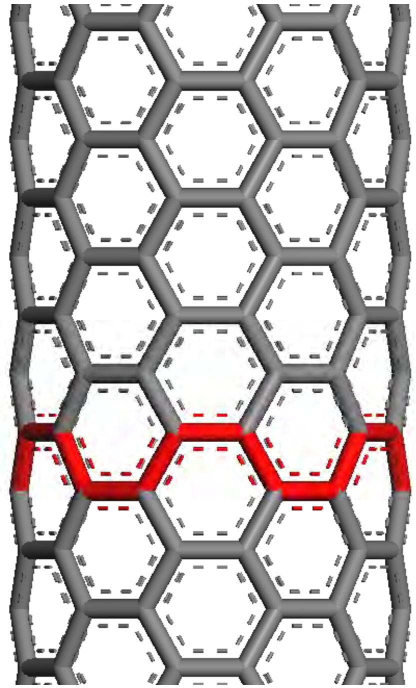


The diameter of [n,m] CNT:

$$d_{CNT} = \frac{a}{\pi}\sqrt{n^2 + nm + m^2}$$



(10,0) Z-CNT

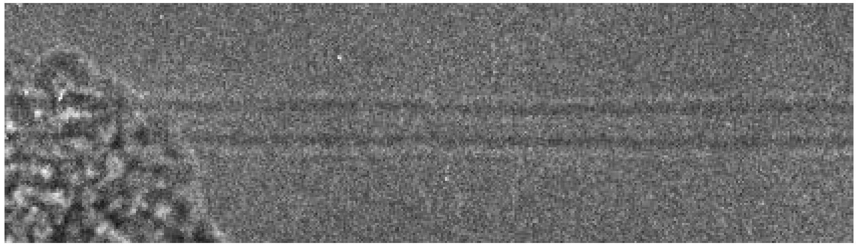


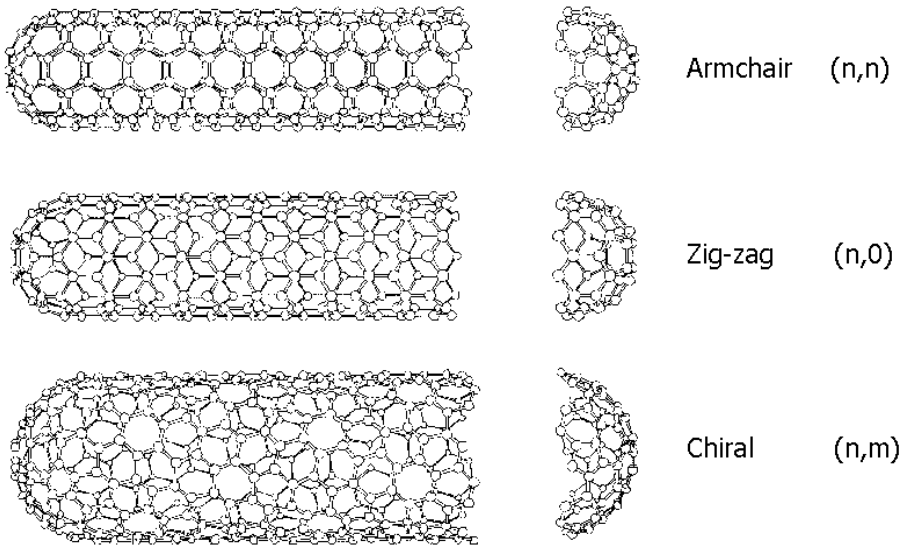
(6,6) A-CNT

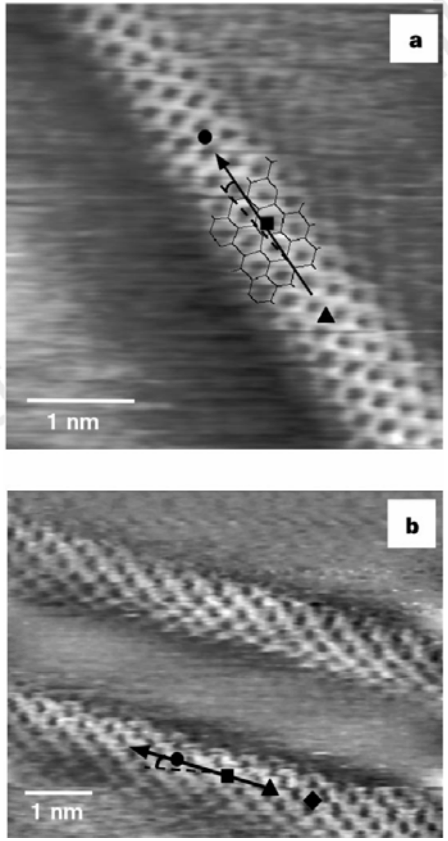
Physical Properties of CNT

- Semiconductor or metal. (depending on the chiral angle)
- Excellent mechanical properties
- Excellent electrical transport (ballistic transport)
- Excellent thermal conductivity
- Difficulty– Control the chiralty

1-D nanomaterials (Carbon nanotube)

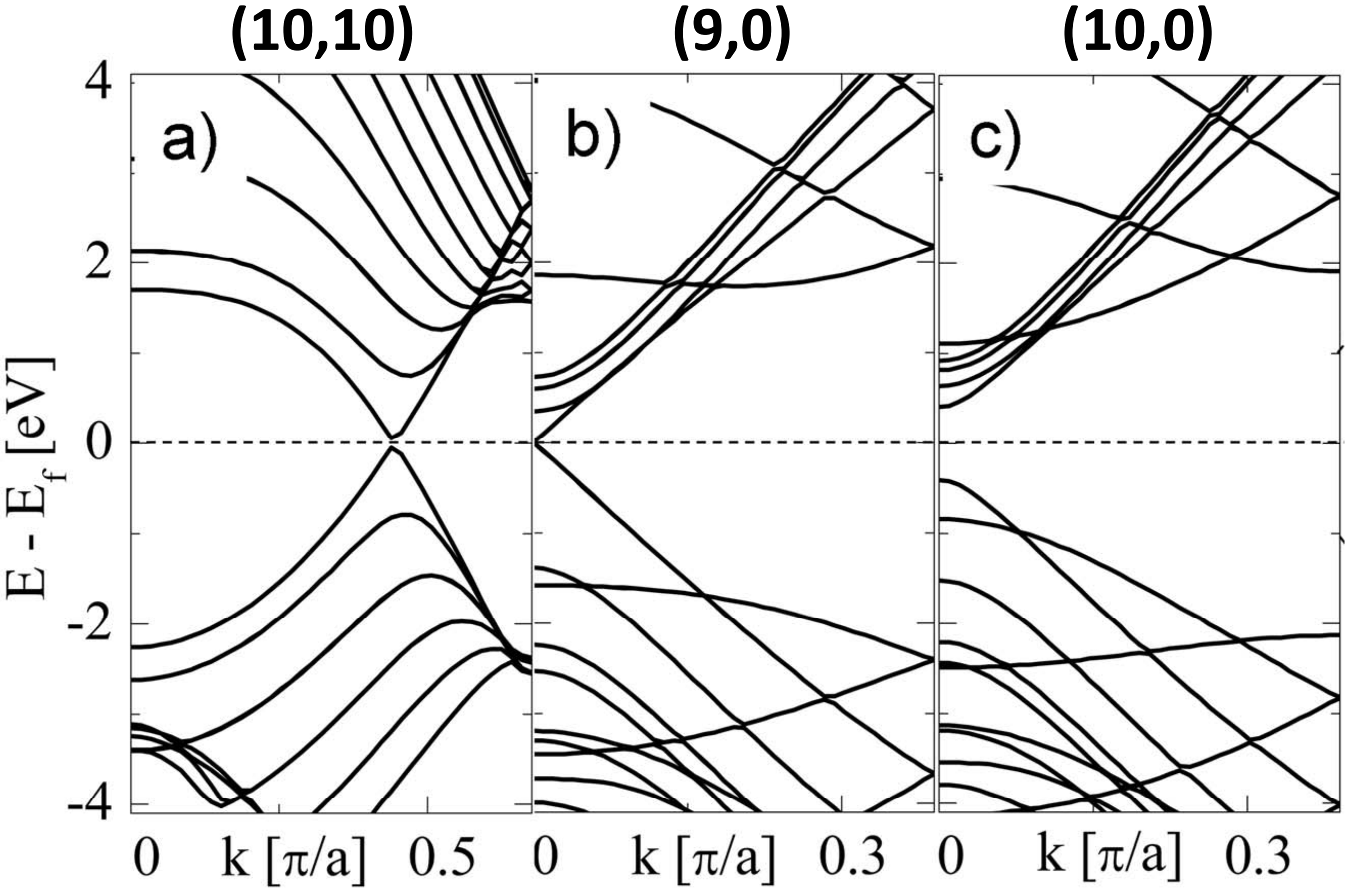






Discovered by Iijima (1991)

Band Structures of CNT



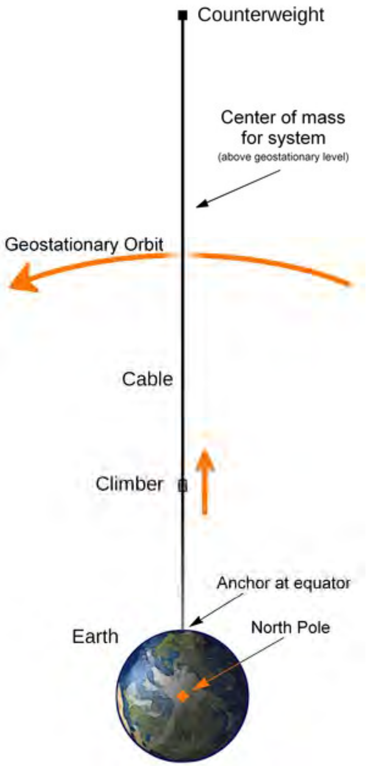
Band structures of (a) (10,10) (b) (9,0) (c) (10,0) CNTs

A. Baskin et al., *Scientific Reports* **1**, 36 (2011)

Structural Materials

- Due to the outstanding mechanical properties and light-weighted, CNT is a potential material for some special usages

Space elevator



Bulletproof cloth, shield, glass

Bicycle components

Mechanical Properties

- CNT is one of the strongest materials in nature
  - Very strong in the axial direction

	Young's modulus (GPa)	Tensile strength (GPa)	Elongation at break (%)
SWCNT	>1000	13-53	16
Steel	186-214	0.38-1.55	15-50
Diamond	1220	2.8	-

  - Very hard; even harder than the diamond

	Bulk modulus (GPa)
SWCNT	462-546
Steel	160
Diamond	442

Belluci, S. et al., *Phys. Status Solidi C* **2** (1), 34 (2005)
Sinnott, S.B. et al., *Crit. Rev. Solid State* **26** (3), 145 (2001)

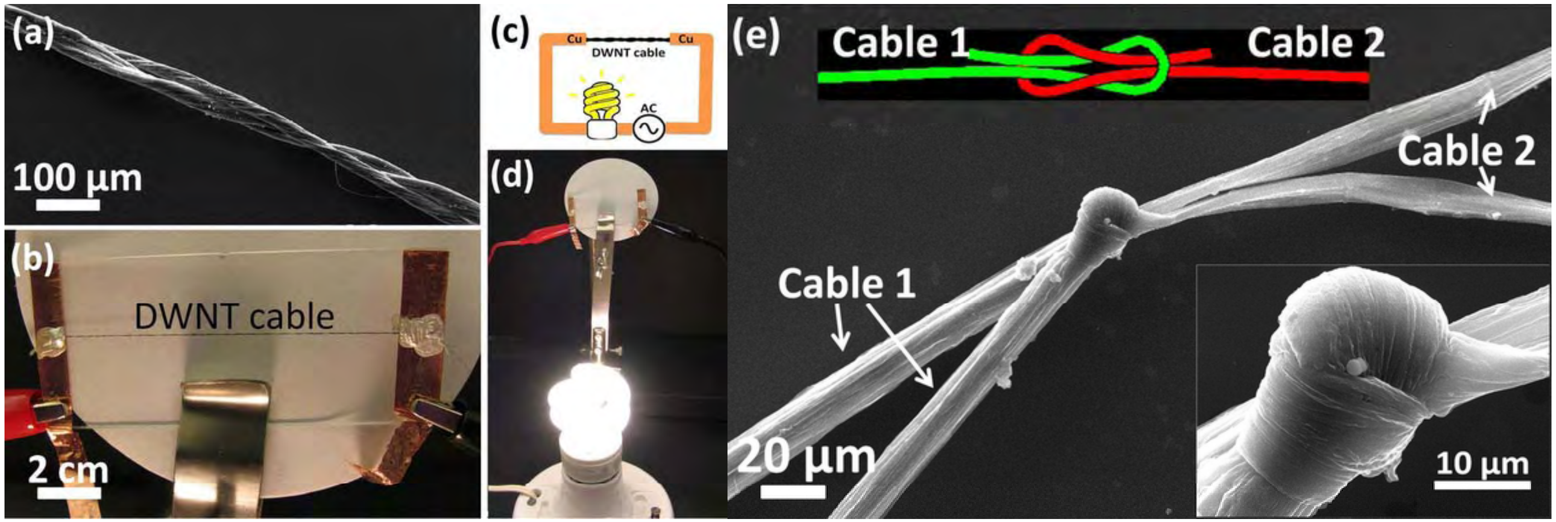
Electronic Properties

- CNTs are semiconducting or metallic, depending on the chirality
- High mobility (100,000 $cm^2/(V \cdot s)$ at room temperature)
- High electric current density of metallic CNT ($4 \times 10^9\ A/cm^2$, which is over 1000 times of Cu)
- Superconductivity (no clear evidence, under debating)

Tang, Z. K. et al., Science 292 (5526), 2462 (2001)

Interconnects

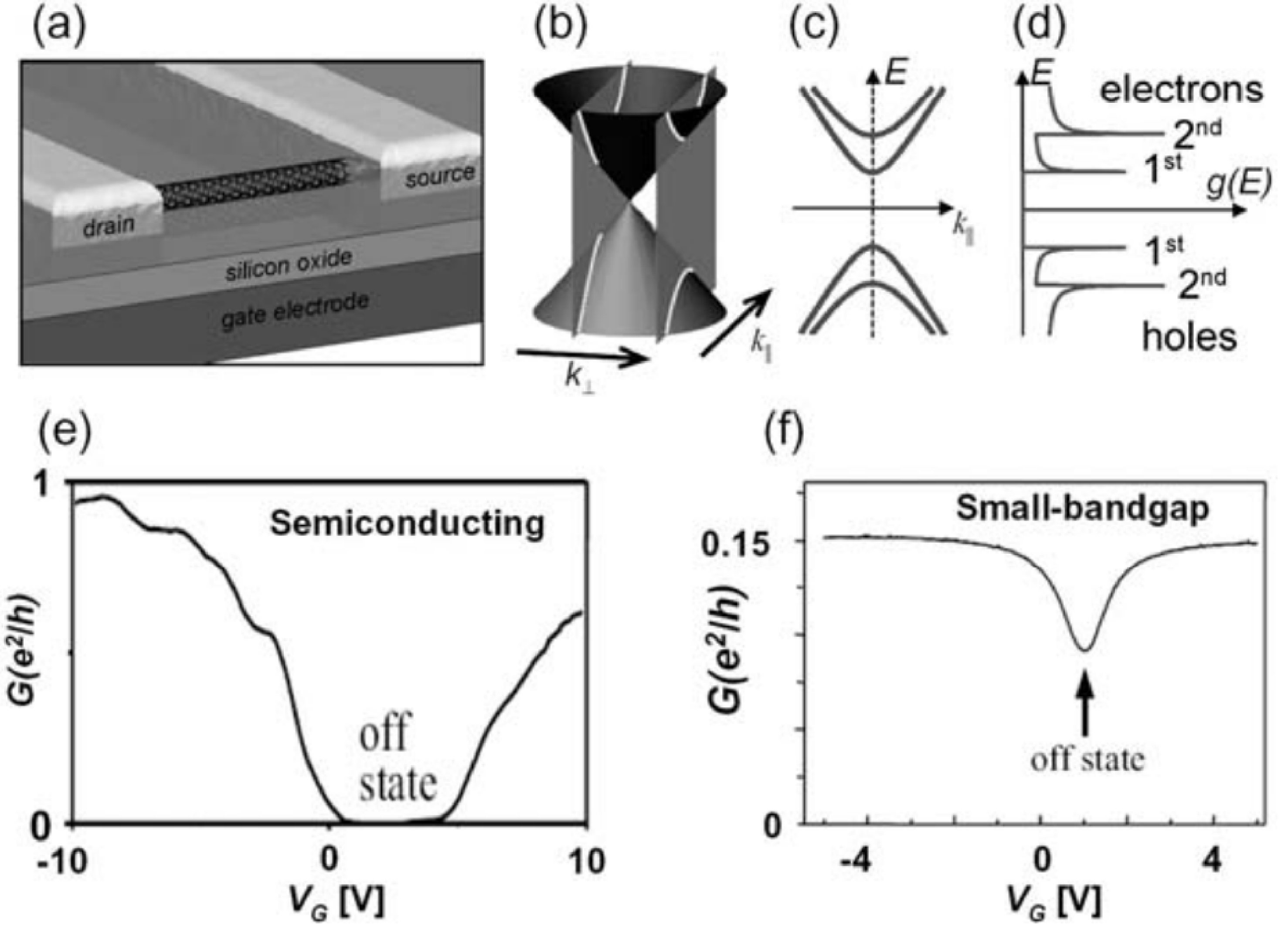
- Similar to GNRs, CNTs are potential materials to replace metal (such that Cu, Au) as non-metal high-conductivity interconnects in the integrated circuits



Y. Zhao et al., *Scientific Reports* **1**, 83 (2011)

Transport of CNT

Nanotube field-effect transistor



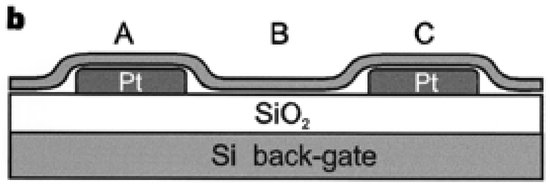
Ambipolar Electrical Transport in Semiconducting Single-Wall Carbon Nanotubes

A. Jorio, et. al. Topics Appl. Physics 111, 455–493

CNT Transistor

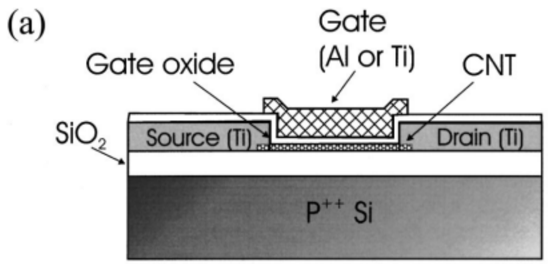
- Various type of CNT transistors had been developed

Back-gated



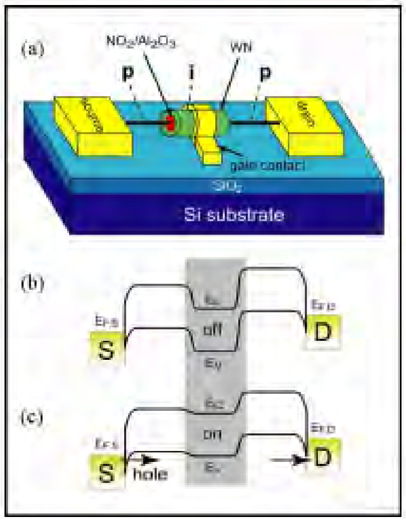
Sander J. Tans, et. al., *Nature* 1998, **393**, 49-52

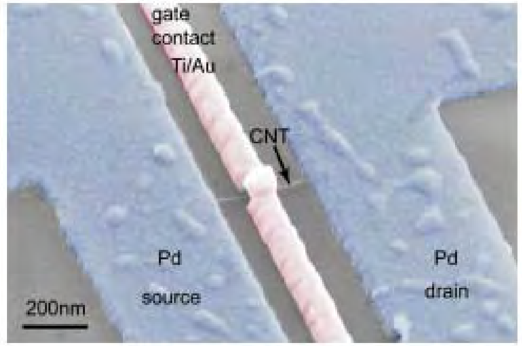
Top-gated



Wind, S. J. et. al., 2002 *Applied Physics Letters* **80** (20): 3817

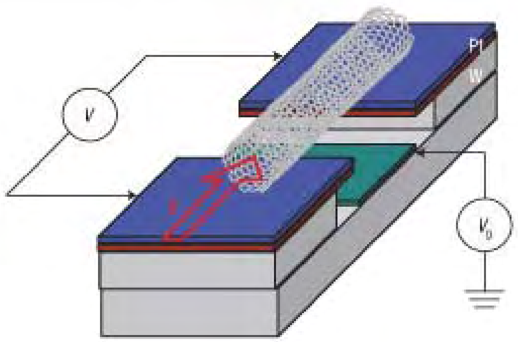
Wrap-around gate

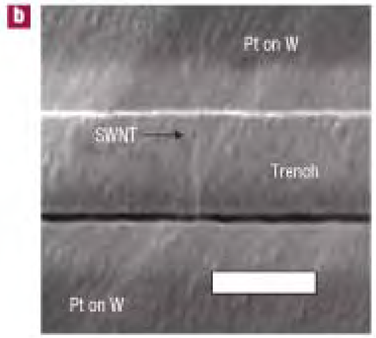




Chen, Z., et. al., IEEE ELECTRON DEVICE LETTERS, VOL. 29, NO. 2, 0741.

Suspended

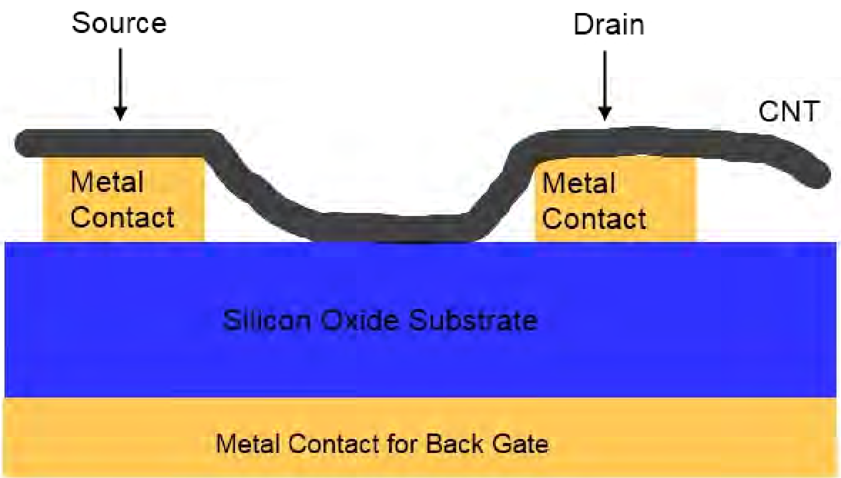




Cao. J., et. al. Nature Materials **4**, 745 - 749 (2005)

Designs of CNT Transistors

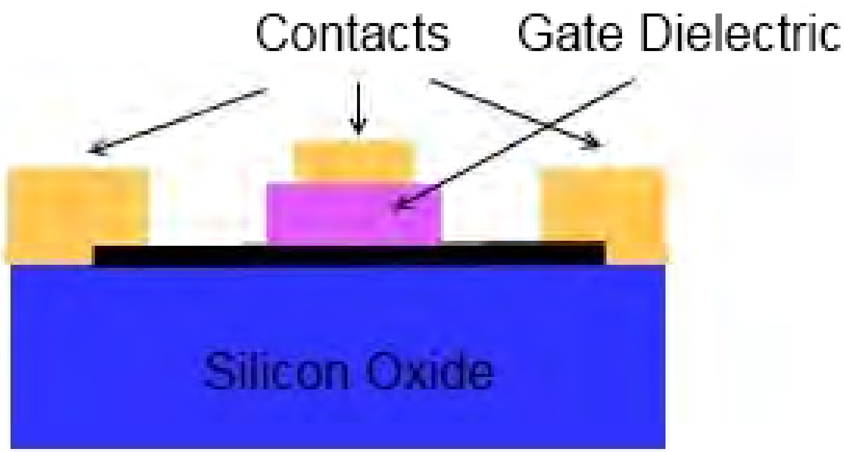
Back-gated



First CNT FET be invented. The process is easy, but there are many drawbacks

1. Contact resistance exists between metal and CNT
2. Hard to switch off using low voltage
3. Poor contact between SiO_2 and CNT

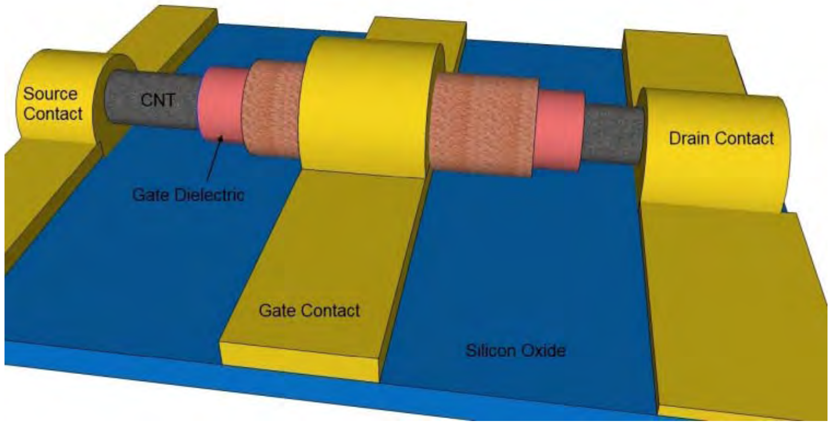
Top-gated



Advanced designs from back-gate FET. The thinner gate dielectric lower the switch-off voltage, which is the main advantage of the top-gate FET.

Designs of CNT Transistors

Wrap-around gate

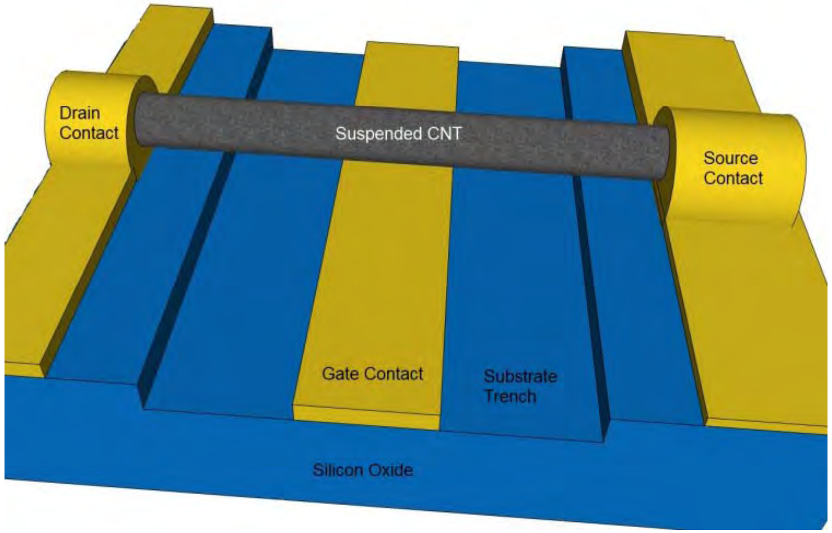


Developed in 2008. This design

1. Improve the on/off ratio and the performance
2. Reduce the leakage current

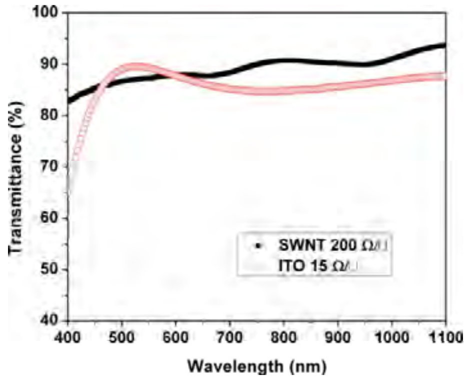
Z. Chen et al., *EDL* **29** (2), 183 (2008)
J. Cao et al., *Nature Materials* **4**, 745 (2005)

Suspended



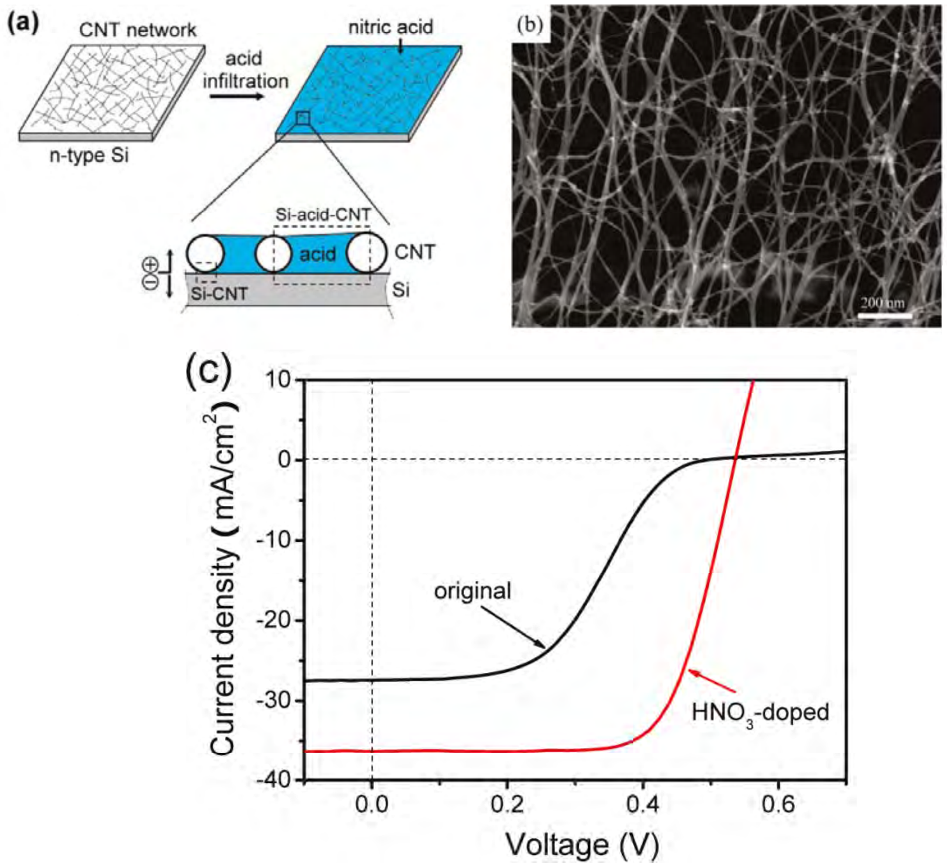
Developed in 2005. This design reduces the scattering at the interface of the CNT-substrate.
However, materials of devices are limited. It is only for studying the properties of clean CNT and cannot be commercialized.

Carbon Nanotube on photovoltaic and LED applications



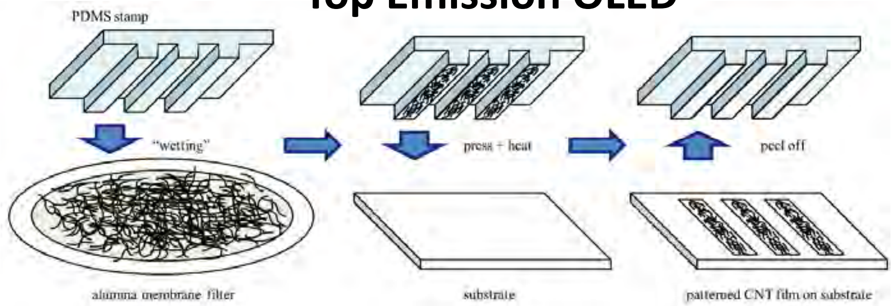
※High transparency on visible and NIR range
※Good conductivity
※Flexible

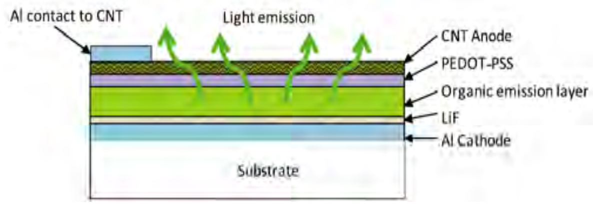
Silicon-CNT heterojunction solar cell

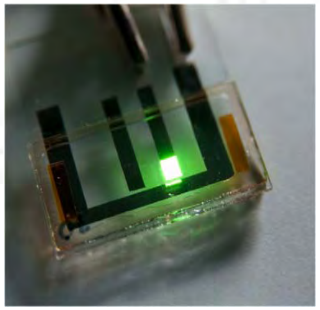


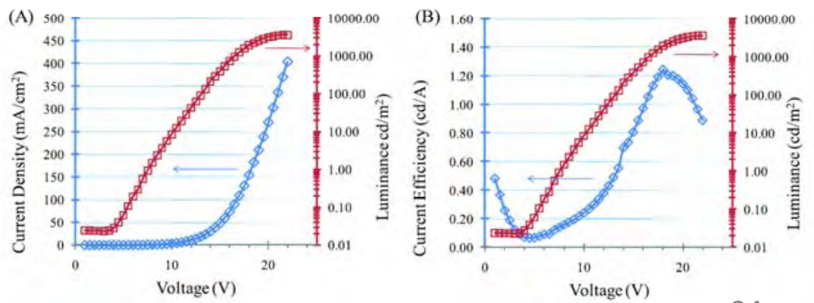
Jia, Y. et. al., *Nano Lett*, **2011**, *11,* 1901.

Top Emission OLED





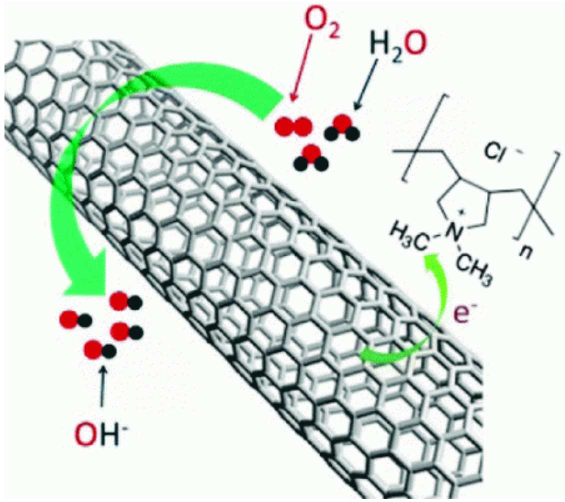




Chien, Y. M. et. al, *Nanotechnology*, **2010**, *21*, 134020

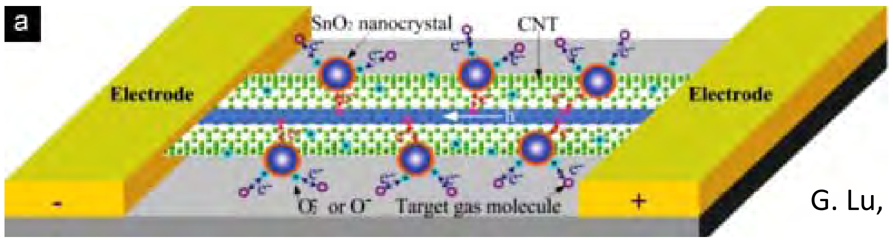
Other Applications

- Fuel cells
  - Store H_2 in CNT



Wang, S. Et. al., J. Am. Chem. Soc., **2011**, *133* (14), 5182

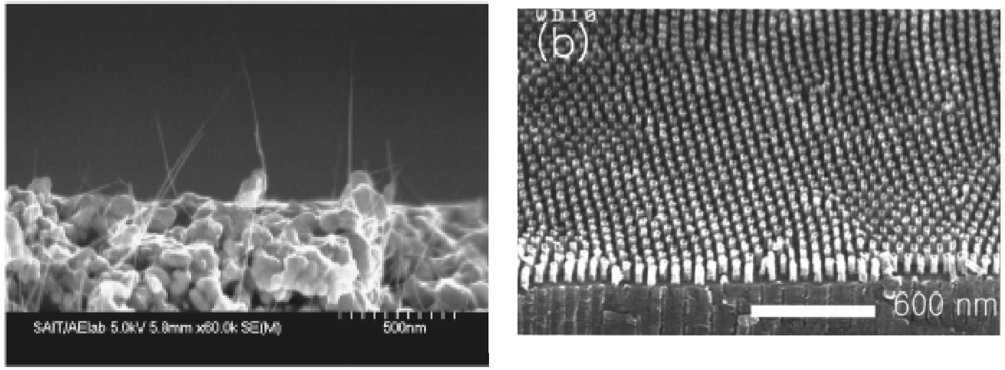
- Gas detector
  - Molecules adsorb on the channel of CNT FET, modifying the electrical properties of CNT



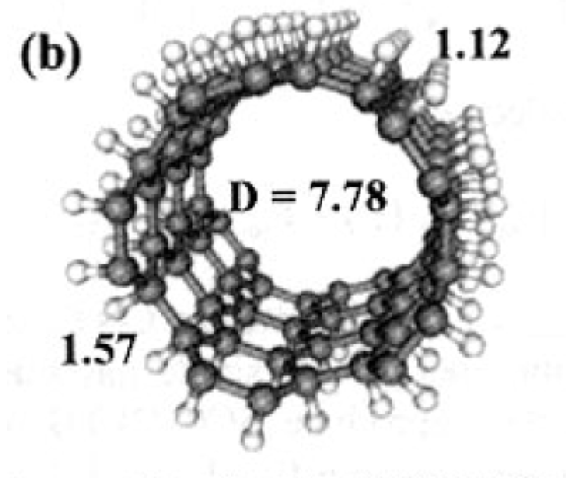
G. Lu, L.E. Ocola J. Chen, Adv. Mater, 2009, 21, 2487

Applications of Carbon Nanotube

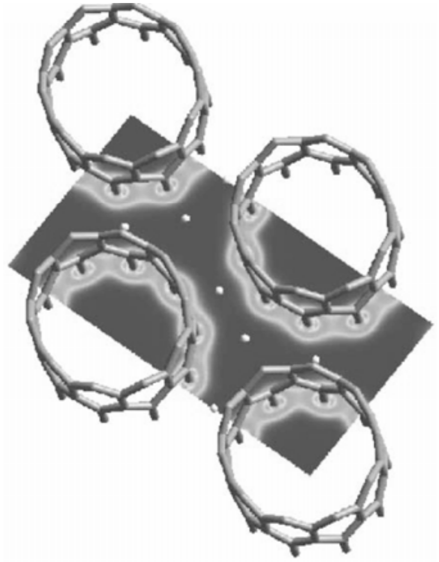
Field Emitter



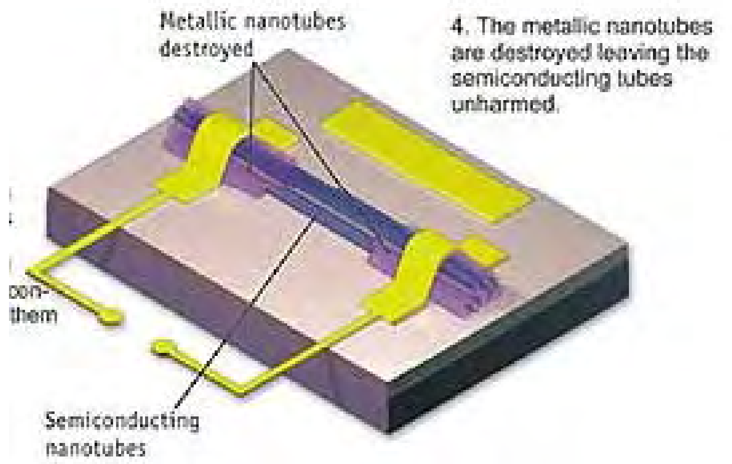
Hydrogen Storage



Li-ion battery anode

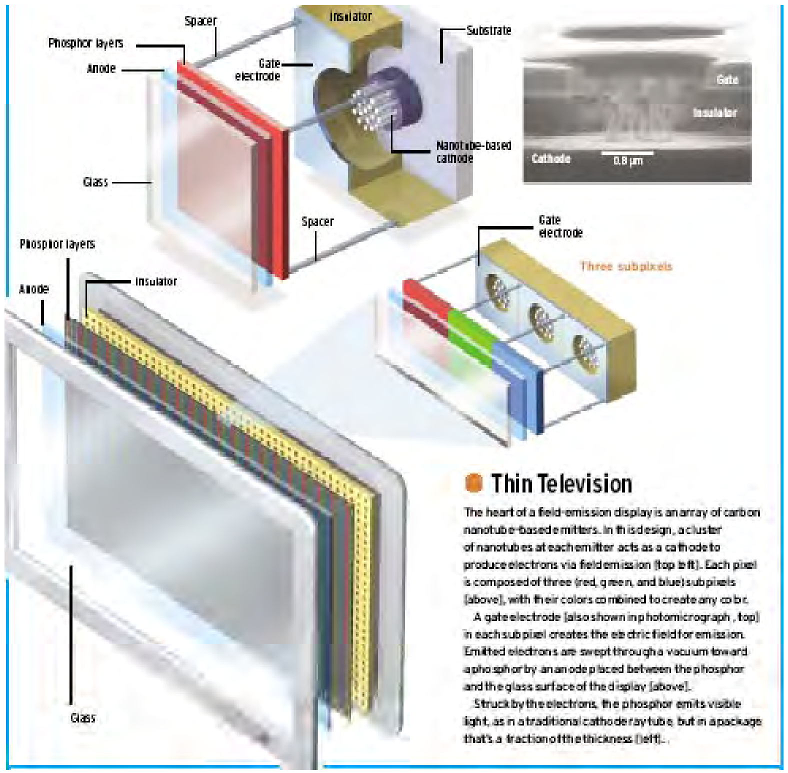


Logic gate by IBM



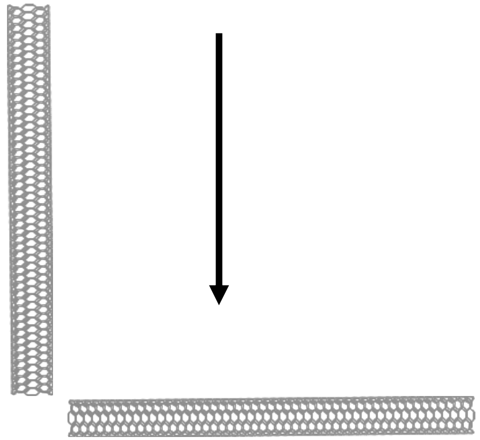
Applications of CNTs in electronic devices

CNT field emission display



From IEEE spectrum 2003

E field

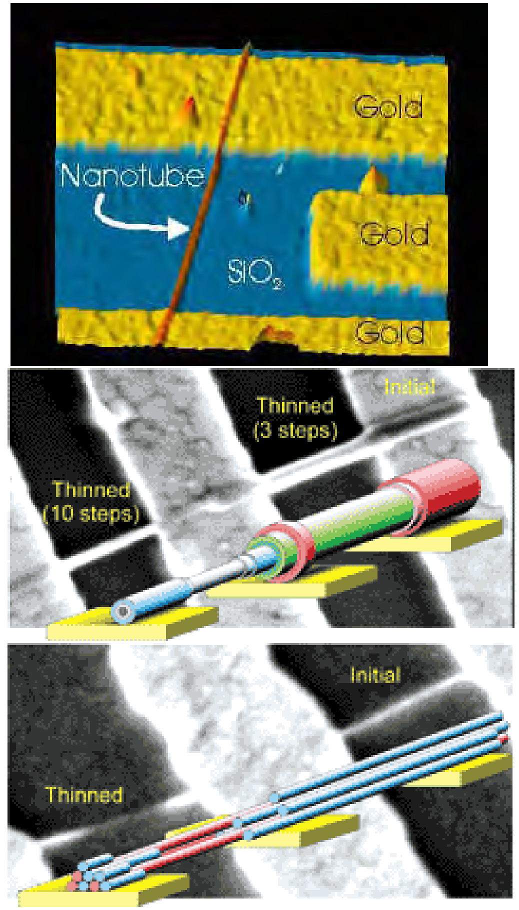


Small dimension

→High local field

→Electronic structure changes

CNT Field effect transistor



From IBM