

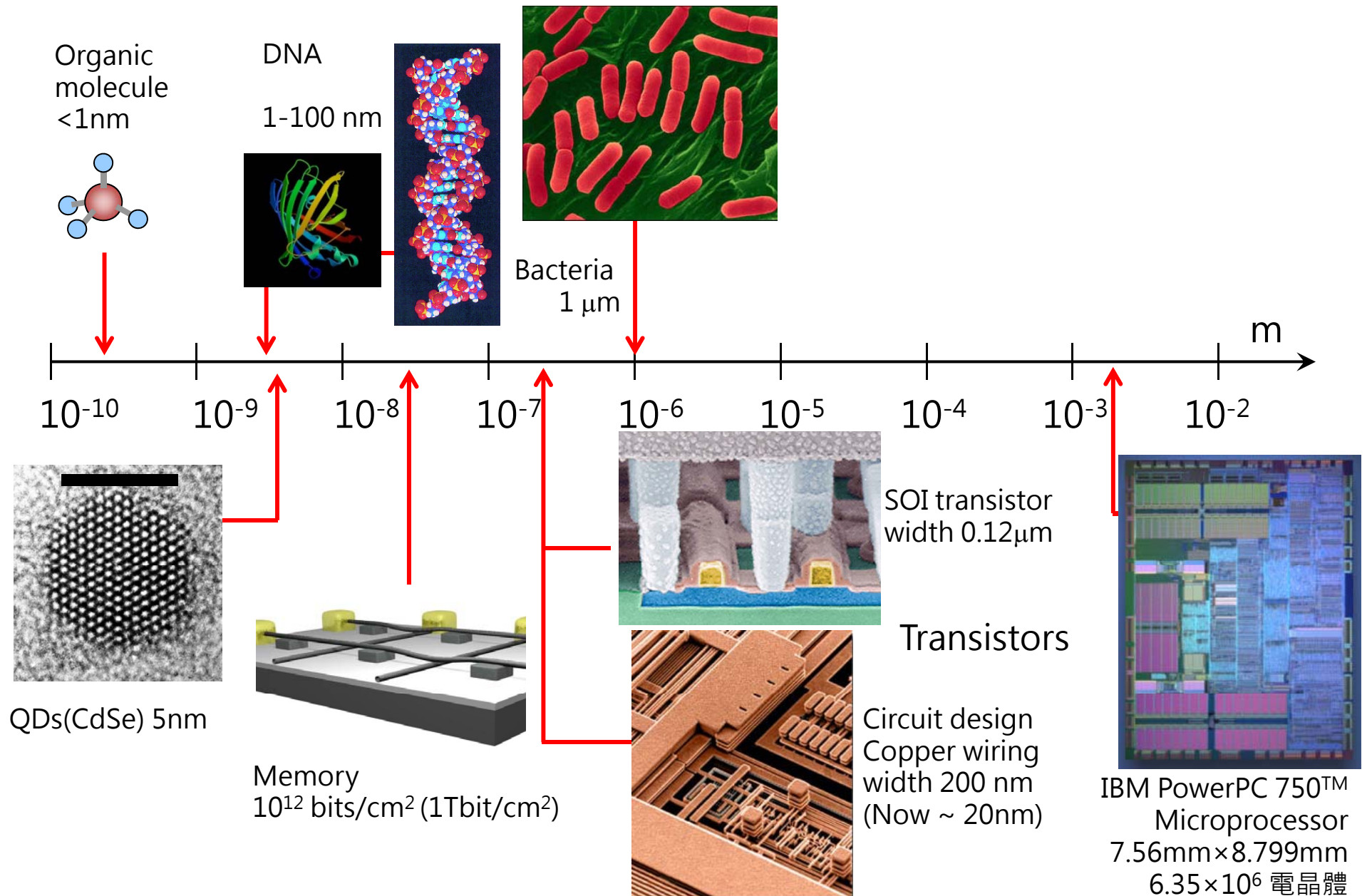
Quantum Nature of the Nano-world

Chun-Wei Chen

Department of Materials Science and Engineering,
National Taiwan University

TIGP Course, 10/30/2014

Size of Nano??



Definition of Nanomaterial

Original : “[quantum](#) size effect” where the electronic properties of solids are altered with great reductions in particle size

◦

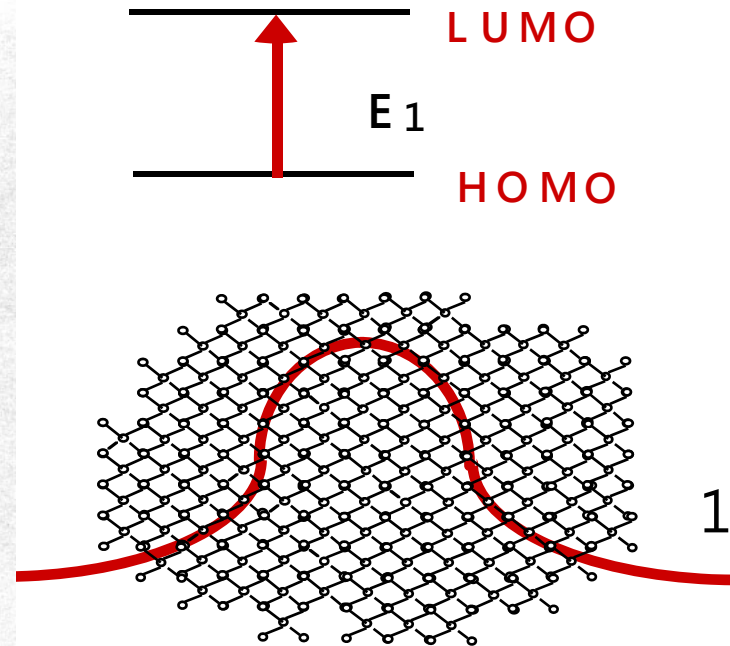
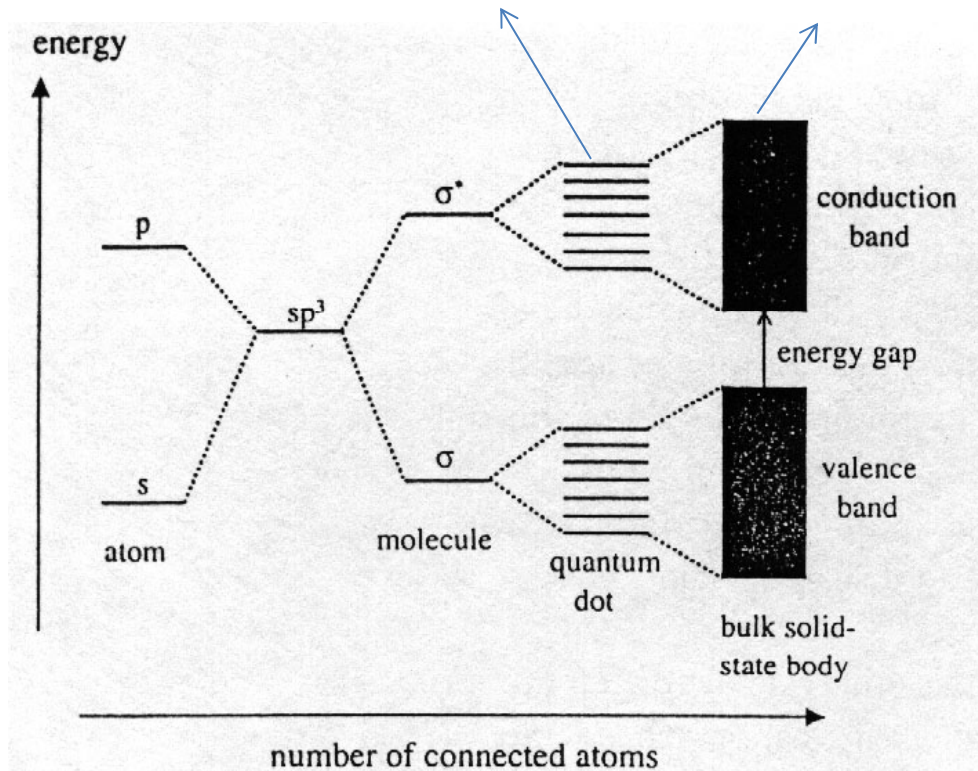
(**New**)

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*.¹

”

Quantum confinement effect

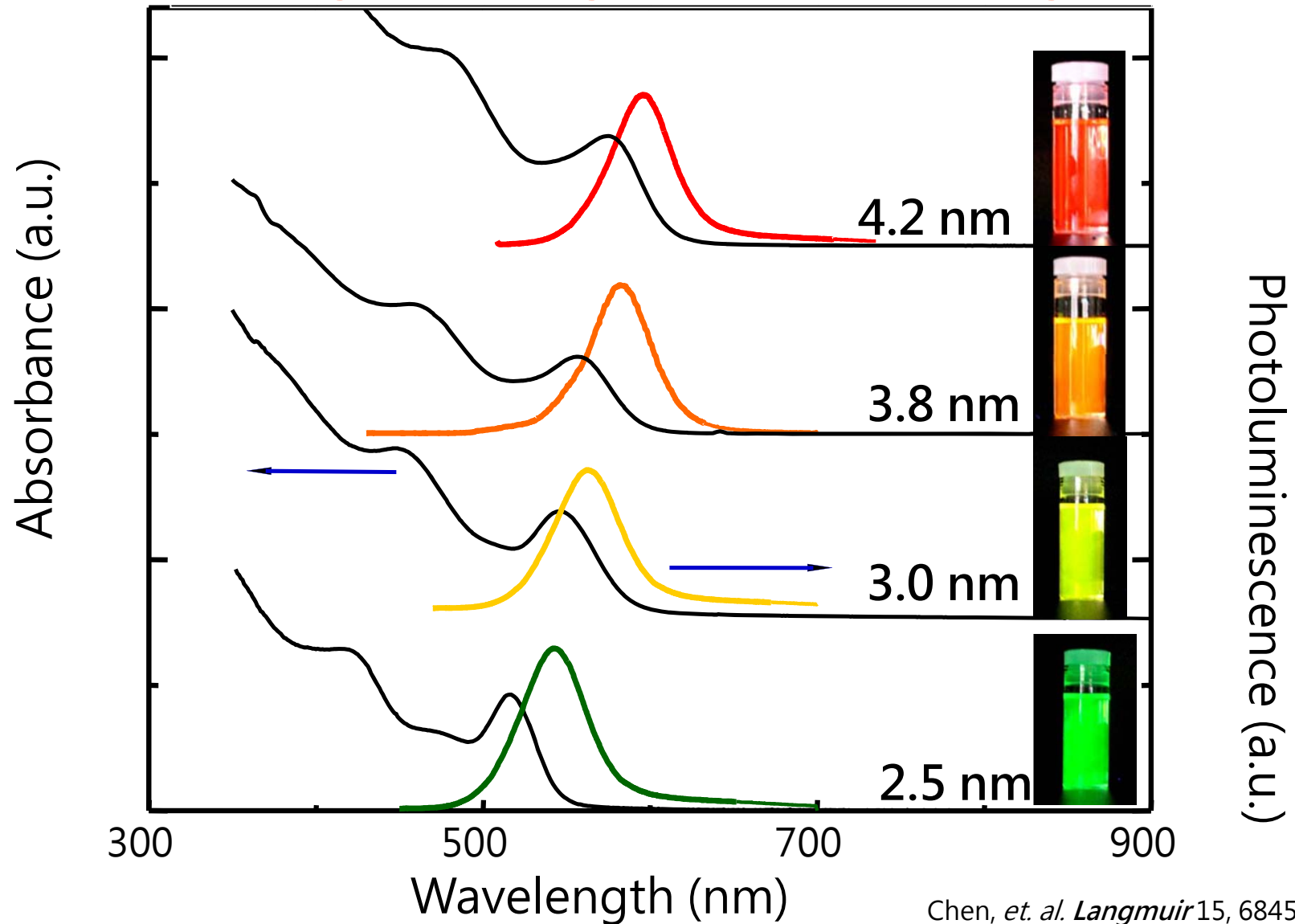


$$E(R) = E_g + \frac{\hbar^2 \pi^2}{2R^2} \left[\frac{1}{m_e} + \frac{1}{m_h} \right] - \frac{1.8e^2}{\epsilon R}$$

m_e and m_h : effective masses
 e : bulk optical dielectric coefficient

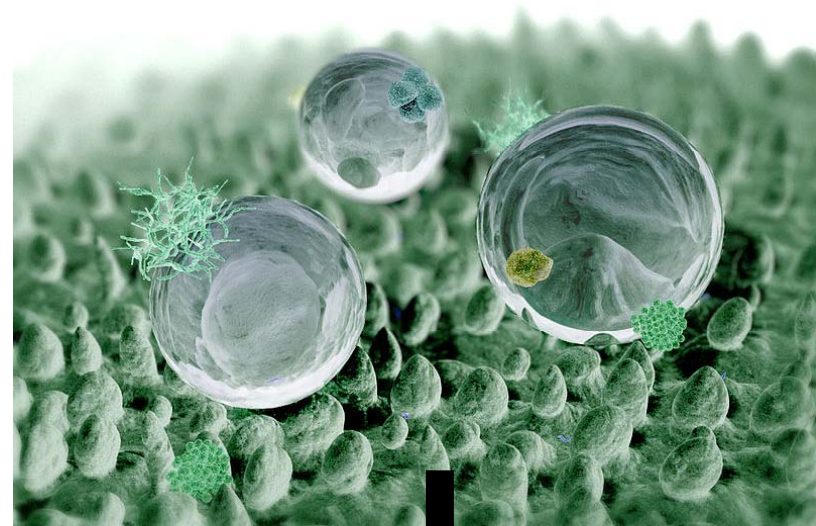
Size-dependent optical properties of CdSe QDs

Band gaps change with their average sizes

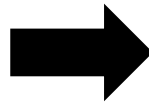
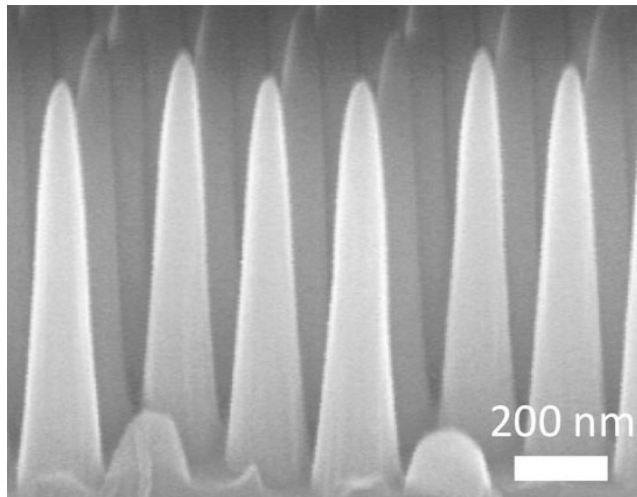


Lotus Effect

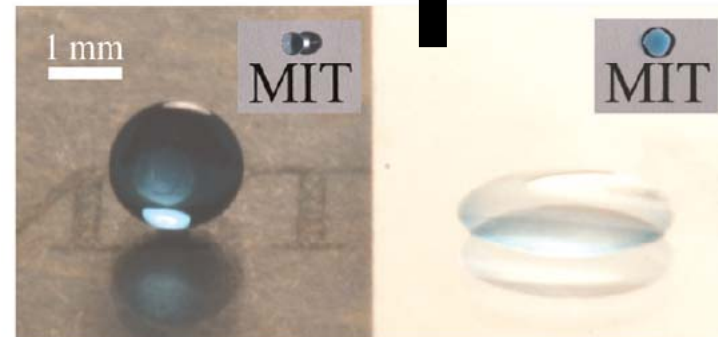
Lotus



Nano array on glass substrate



Self-cleaning



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

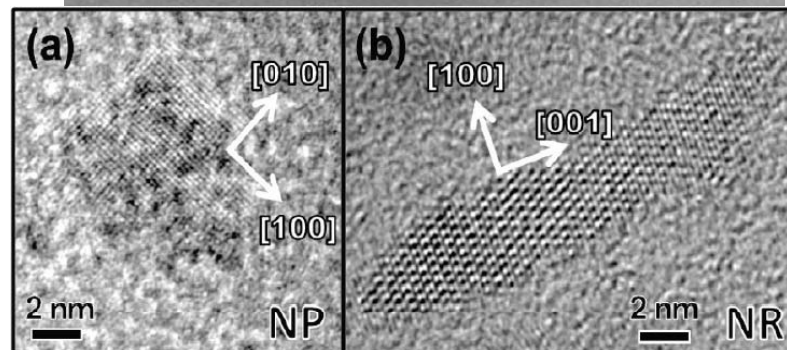
Photocatalysts using Nanomaterials

- Bulk TiO_2 V.S. TiO_2 nanorods/nanoparticles



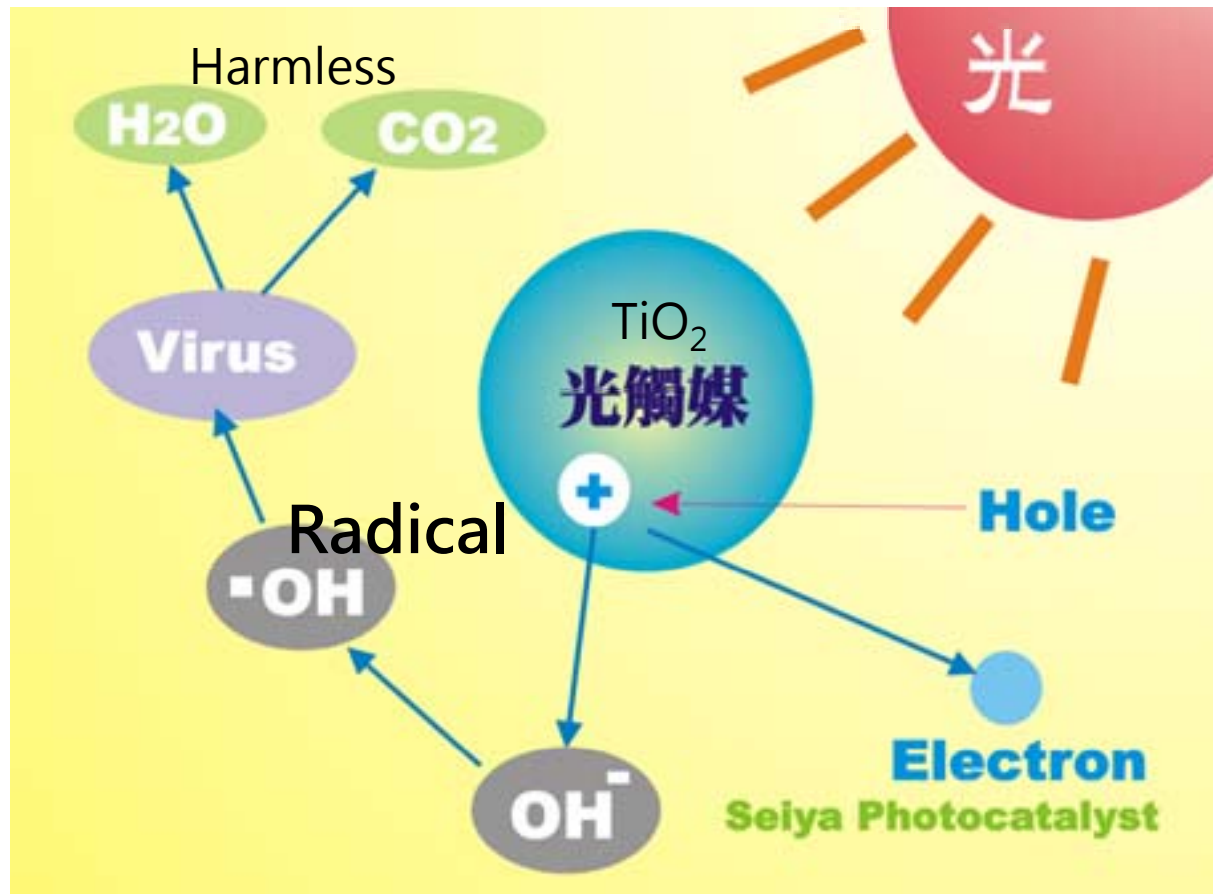
<http://www.35664.net/new/public/tag.php?name=%E4%B8%93%E9%A2%98&page=14>

<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>

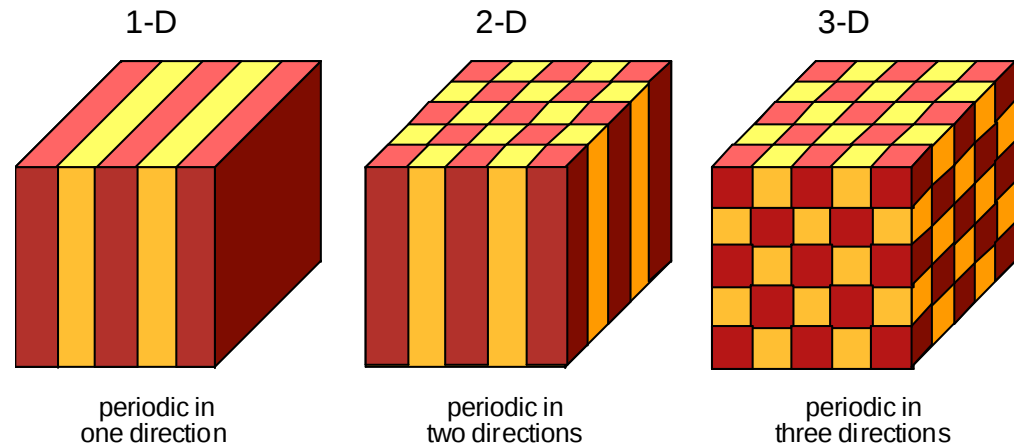
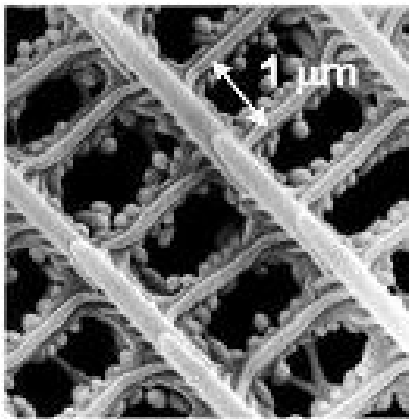


光觸媒
ARC-FLASH
L型口罩 藍色/粉紅色





Photonic crystals

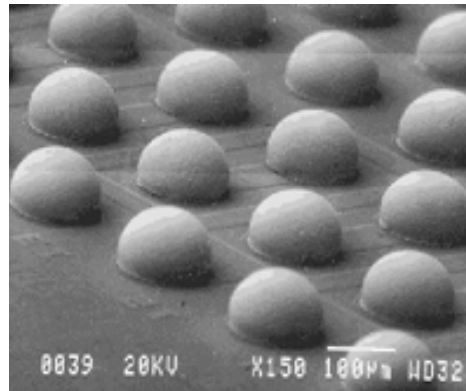
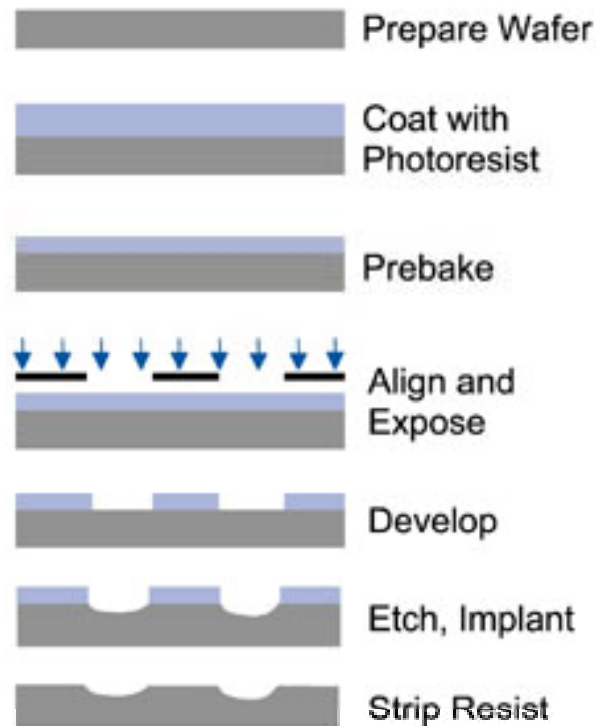


periodic electromagnetic media

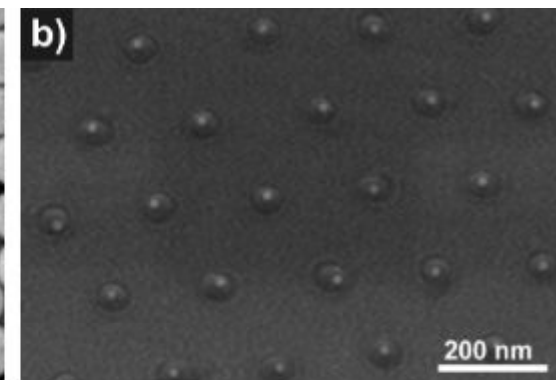
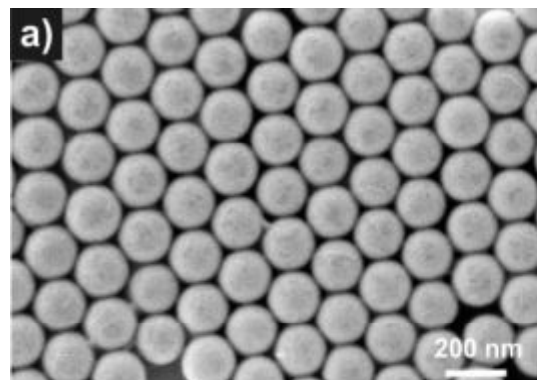
From 《奈米科學網》

How to make Nanomaterials ??

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

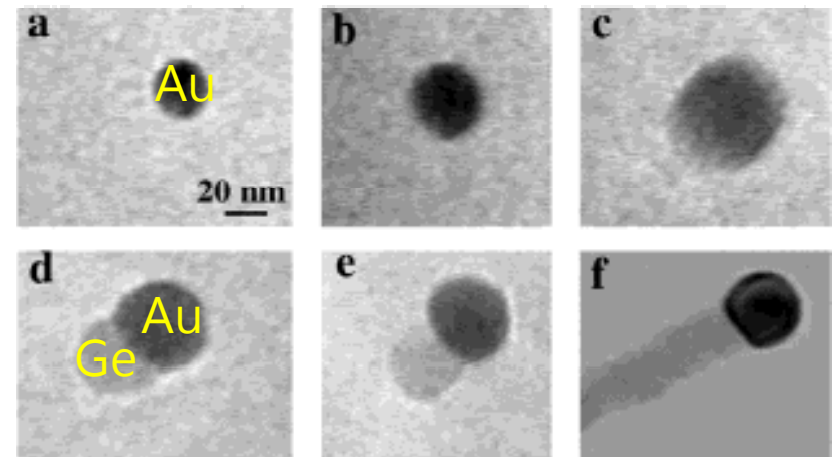
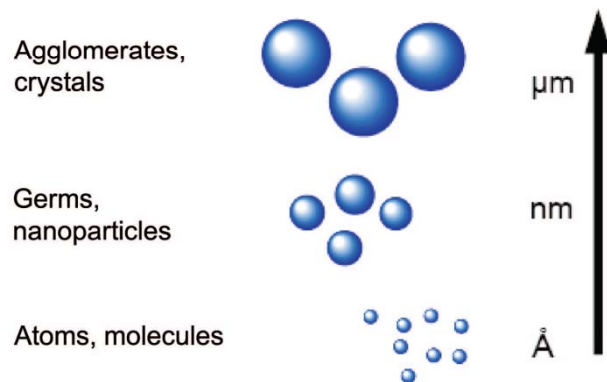
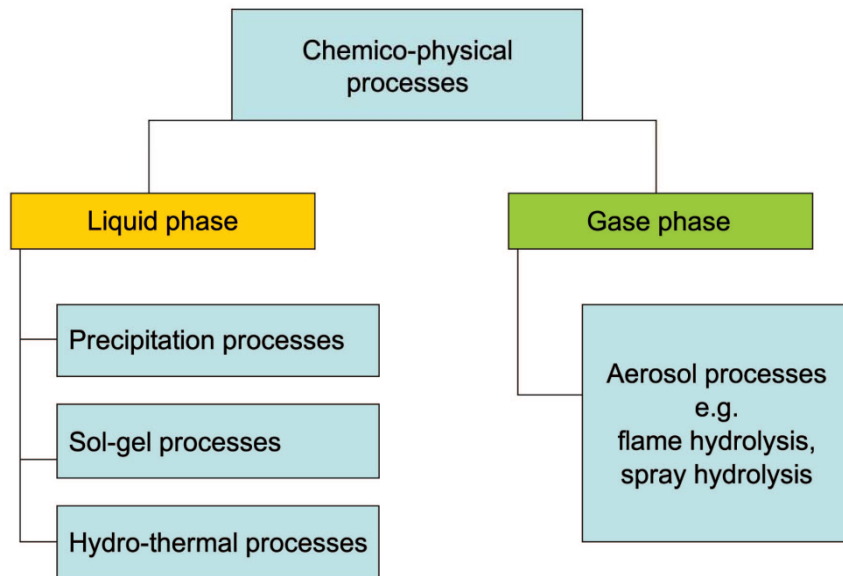


<http://www.beilstein-journals.org/bjnano/single/articleFullText.htm?publicId=2190-4286-2-50>

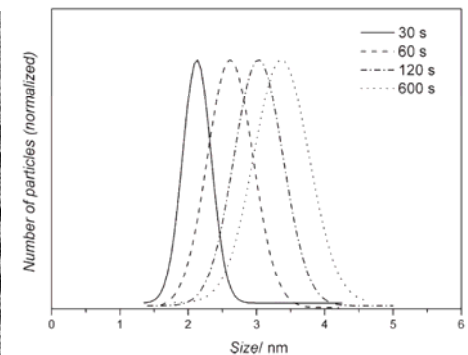
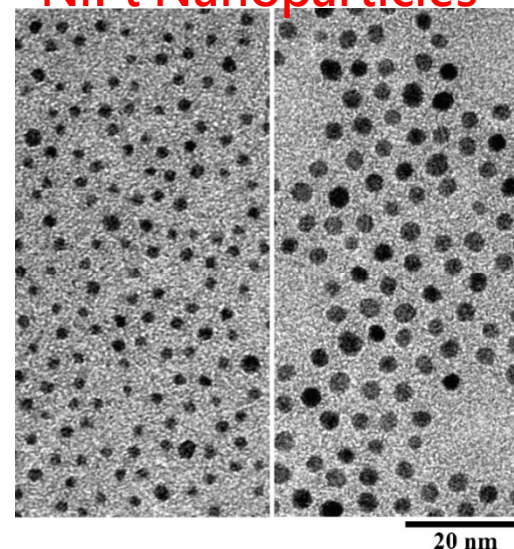


<http://spie.org/x32391.xml>

Bottom up (Chemical Method)



NiPt Nanoparticles

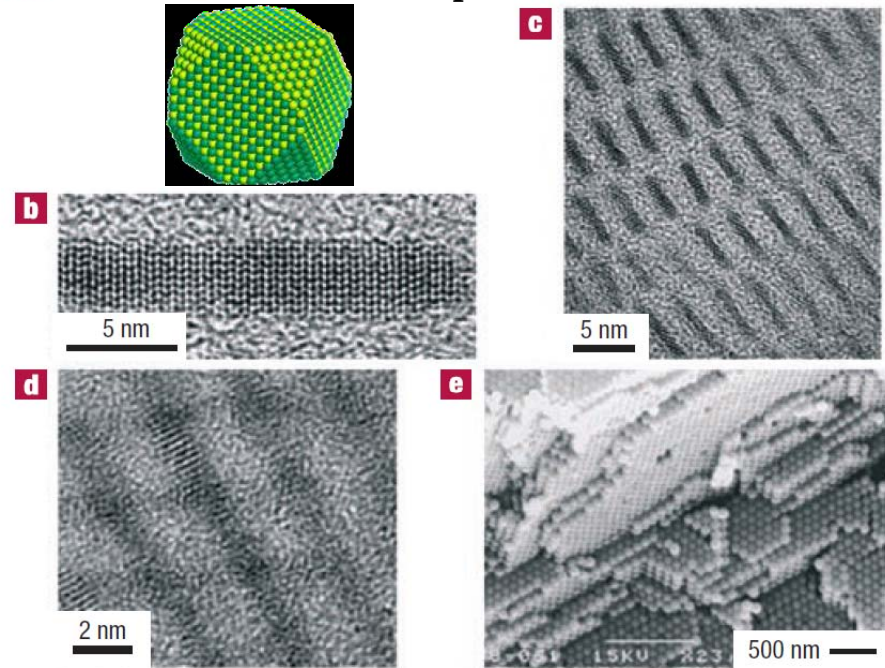
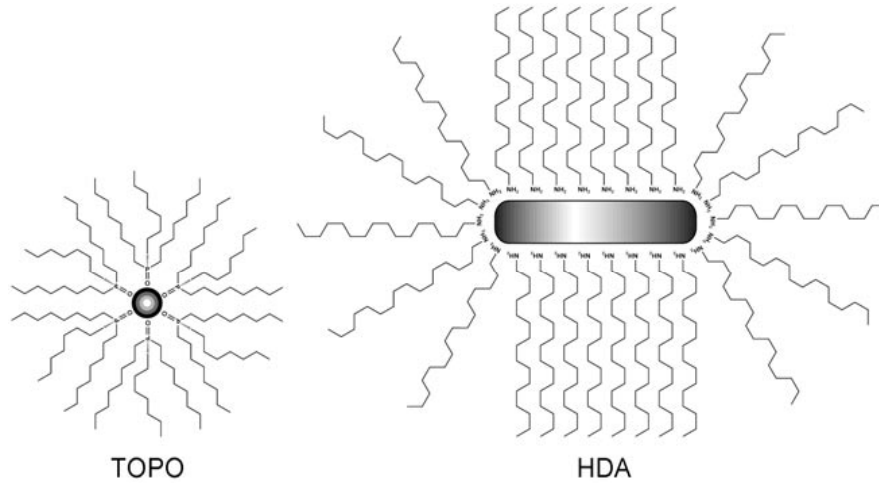


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The Japan Society of Mechanical
Engineers

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

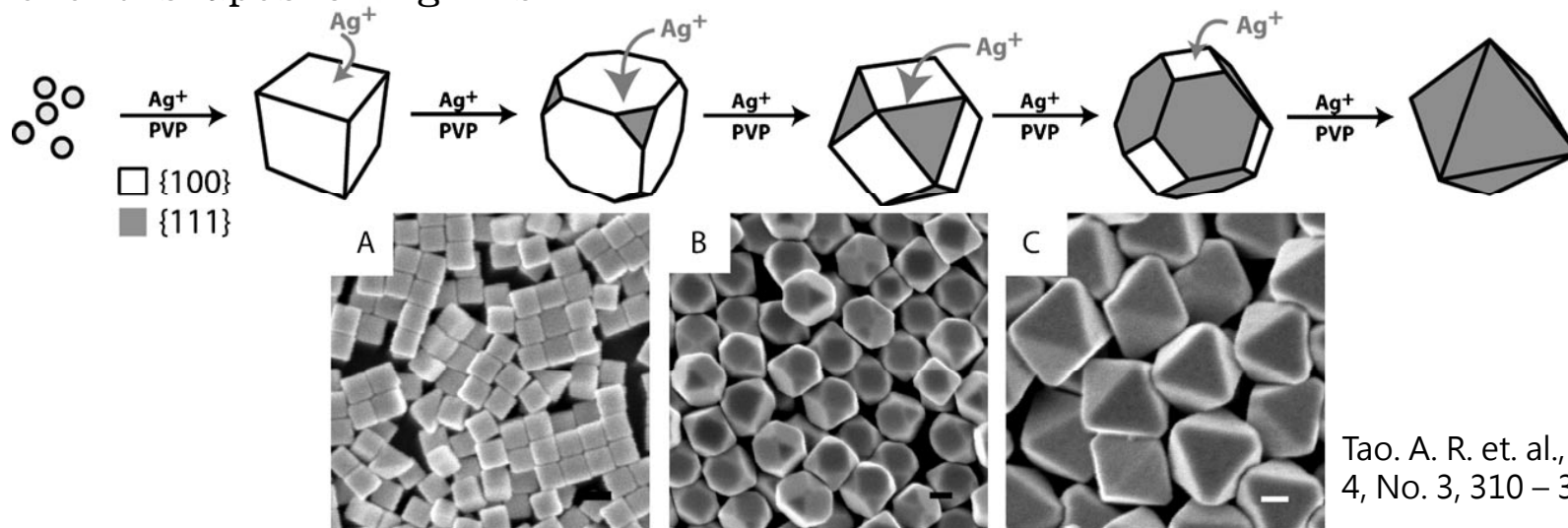
Atomic Foundry

Different shapes of CdSe



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

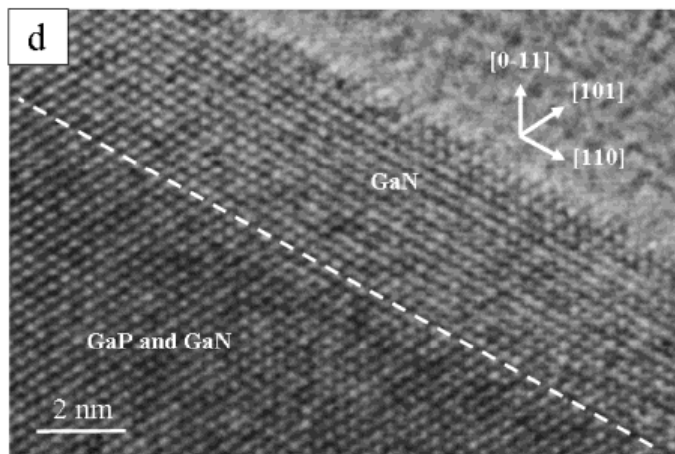
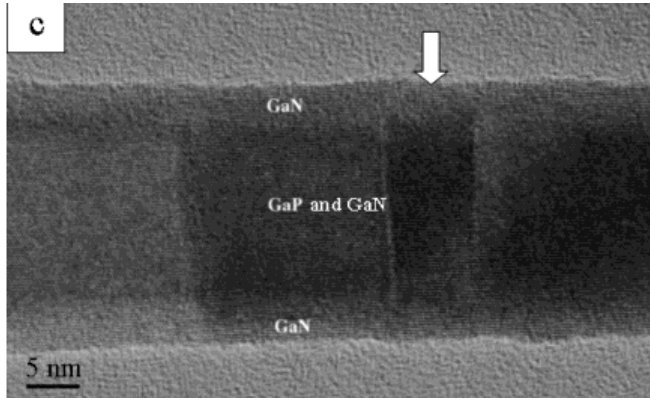
Different shapes of Ag NPs



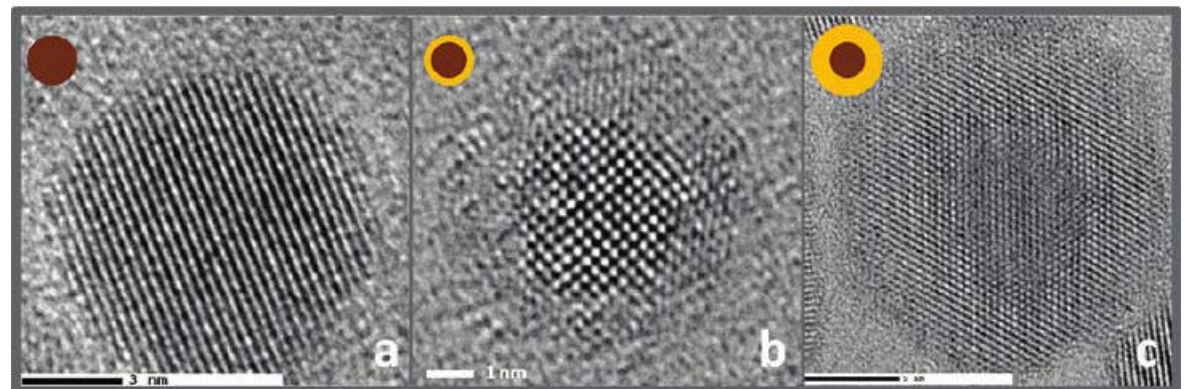
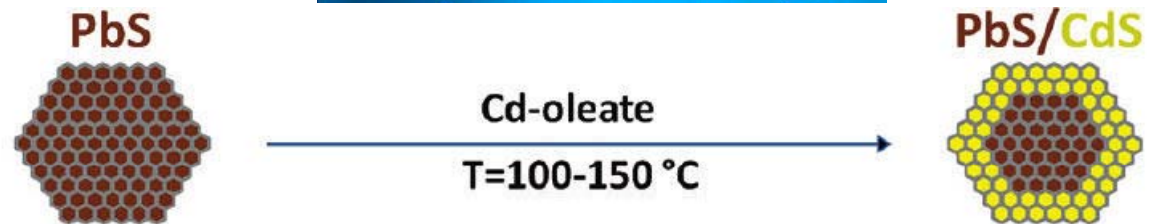
Tao. A. R. et. al., small 2008,
4, No. 3, 310 – 325

How to observe Nanomaterials??

Transmission electron microscopy(TEM)

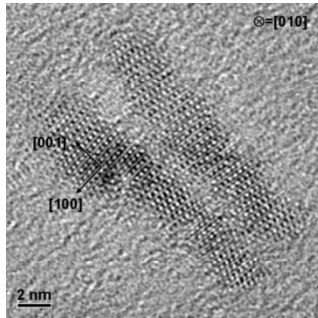


Lin, H. M. et. al., *Nano Lett.*, Vol. 3, No. 4, 2003



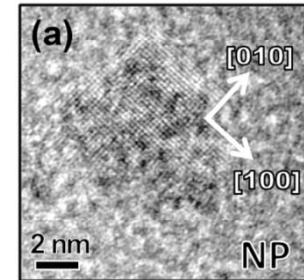
Kinder, E. et. al., *J. Am. Chem. Soc.* 2011, 133, 20488–20499

3D STEM Tomography images of P3HT/TiO₂ hybrids



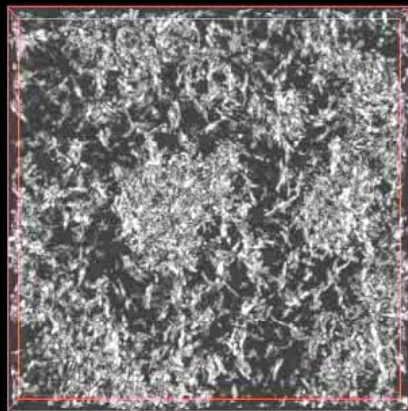
TiO₂ nano rod
(NR)
4nm x 20nm

TiO₂ nano particle
(NP)
5nm x 5nm

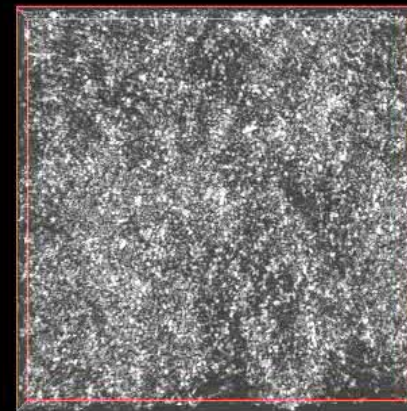


STEM-HAADF electron tomography (2 Å resolution)

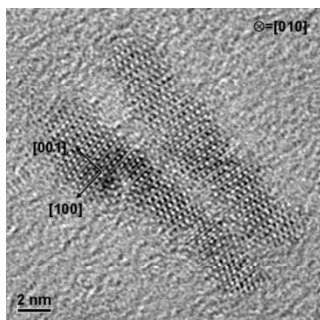
Phase separated domain



Well-dispersed

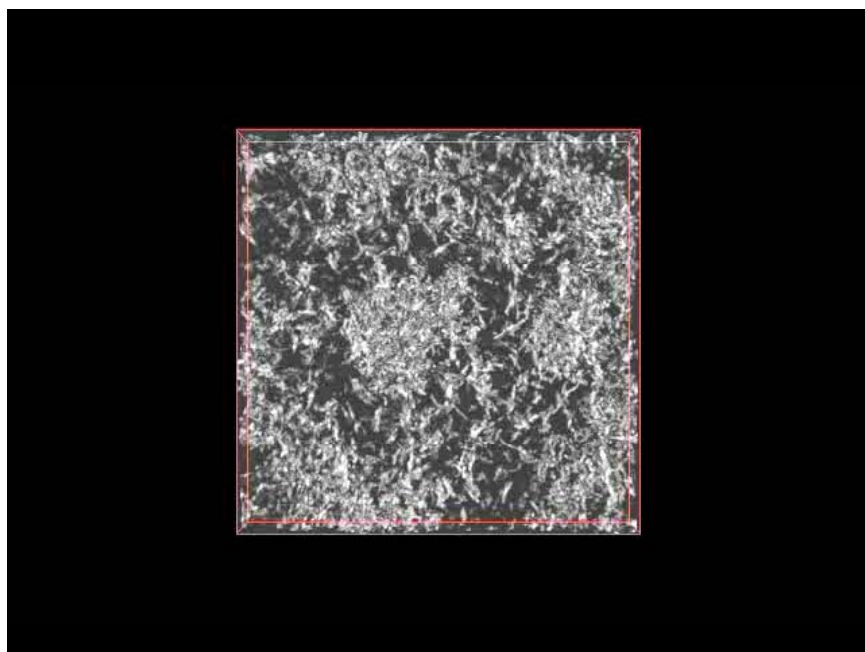
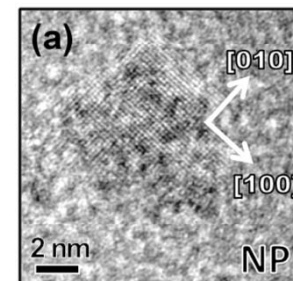


3D STEM Tomography images of P3HT/TiO₂ hybrids

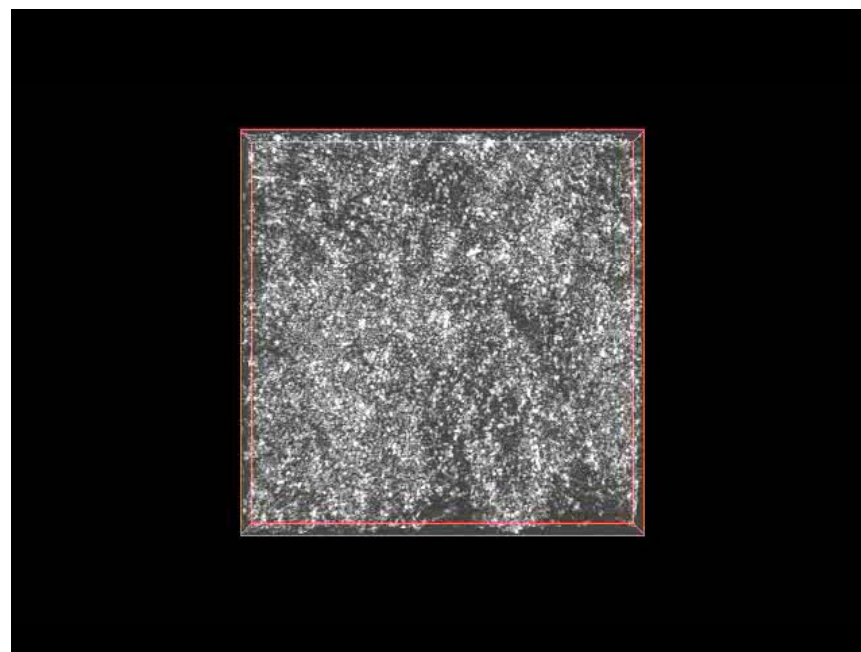


TiO₂ nano rod
(NR)
4nm x 20nm

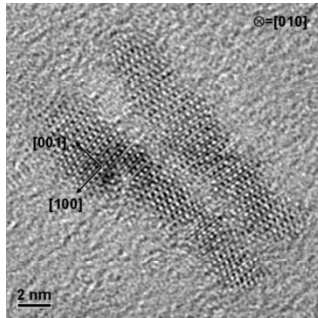
TiO₂ nano particle
(NP)
5nm x 5nm



Phase separated domain

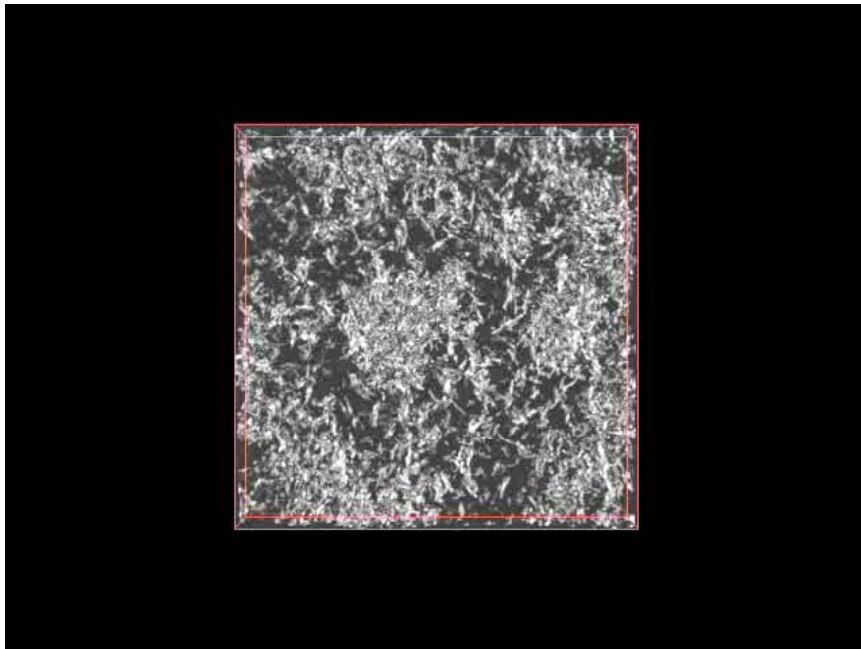
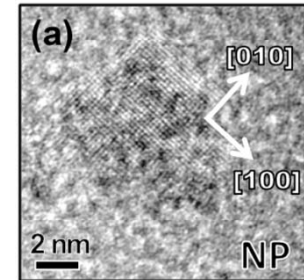


3D STEM Tomography images of P3HT/TiO₂ hybrids

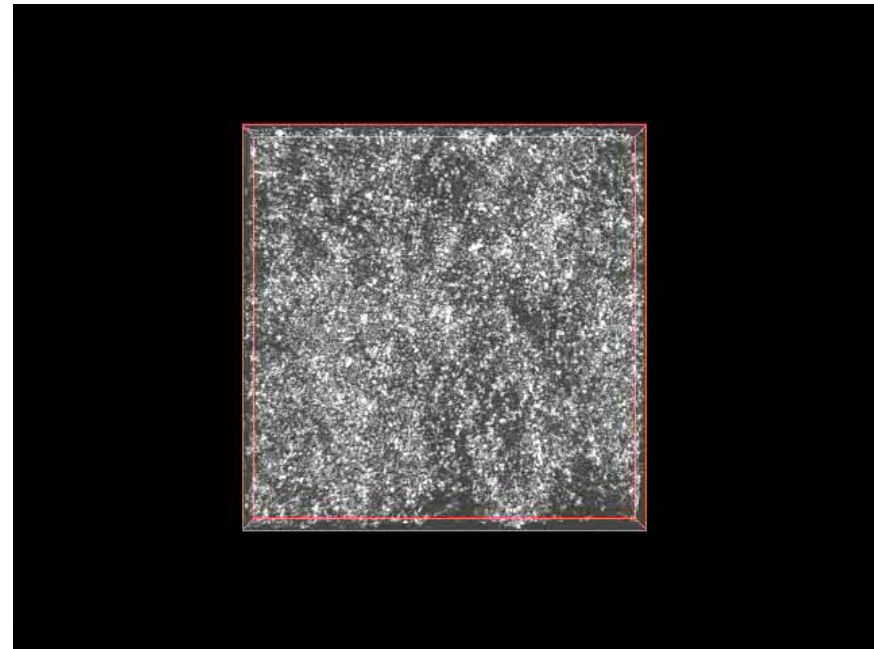


TiO₂ nano rod
(NR)
4nm x 20nm

TiO₂ nano particle
(NP)
5nm x 5nm



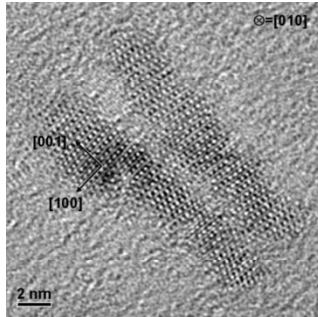
Phase separated domain



Well-dispersed

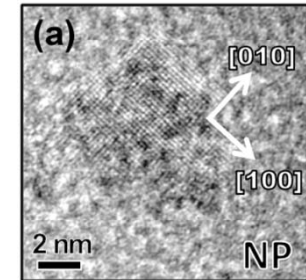
3D scanning transmission electron microscopy (STEM)

Electron tomography of P3HT/TiO₂ hybrids



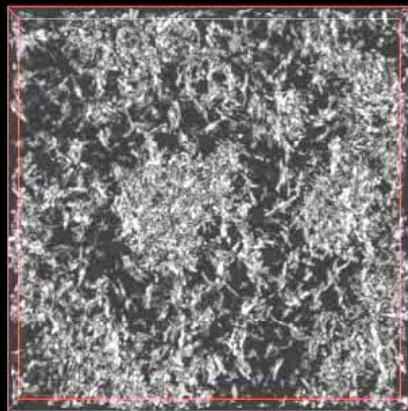
TiO₂ nanorod
(NR)
4nm x 20nm

TiO₂ nanoparticle
(NP)
5nm x 5nm

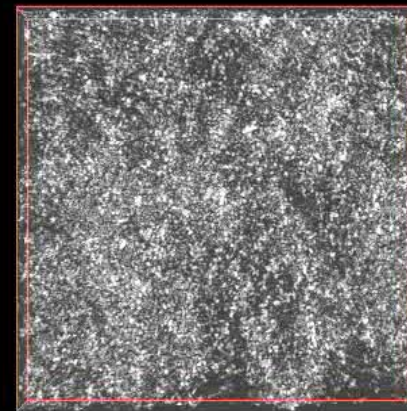


STEM-HAADF electron tomography

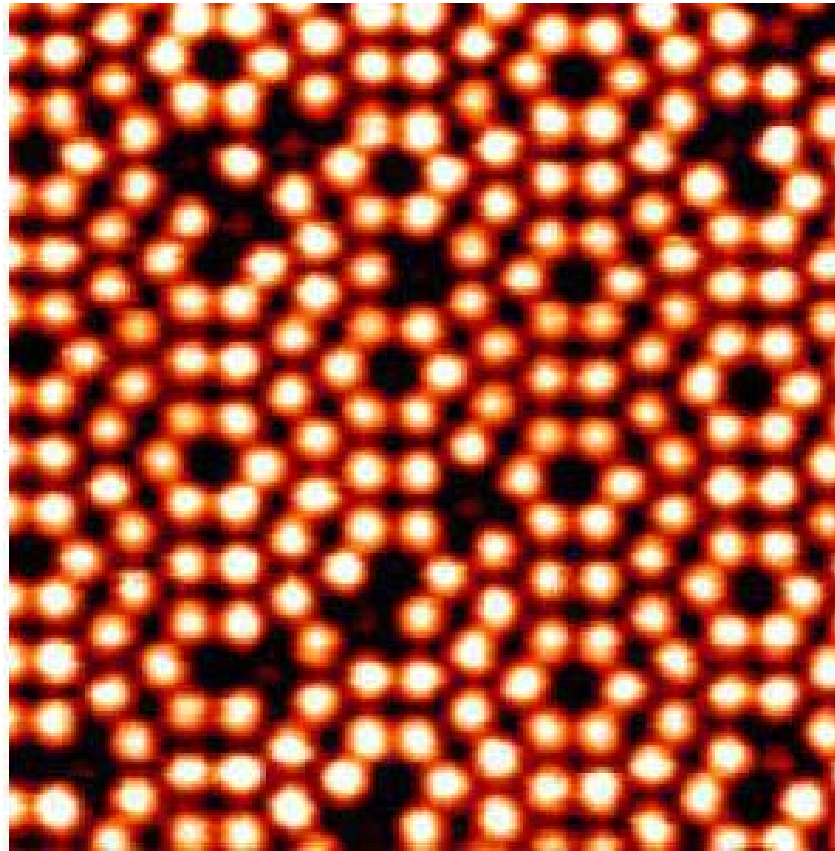
Phase separated domain



More dispersed



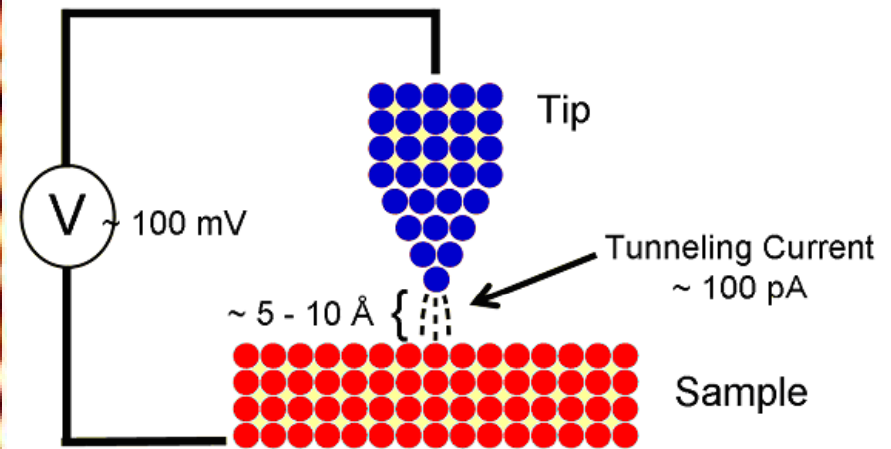
Scanning electron microscopy(STM)



Silicon atoms on a surface

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

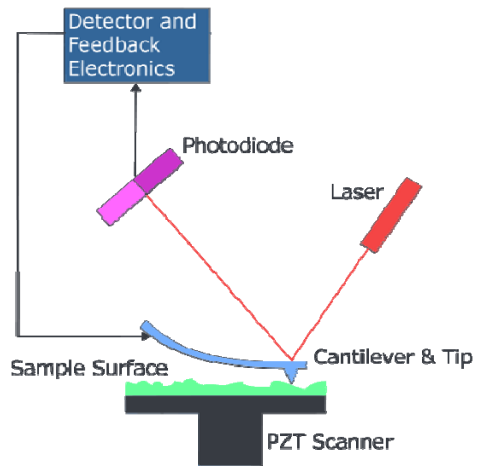
(Quantum tunneling effect)



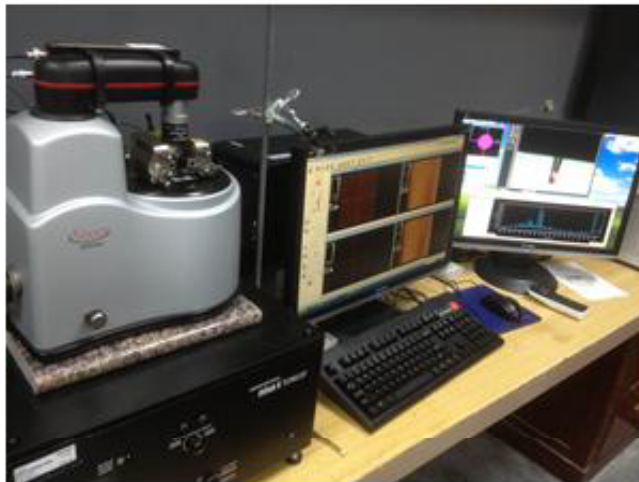
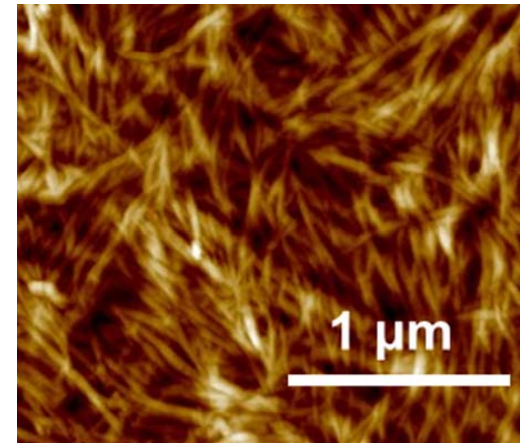
<http://www.personal.psu.edu/ewh10/ResearchBackground.htm>

Atomic Force Microscopy (AFM)

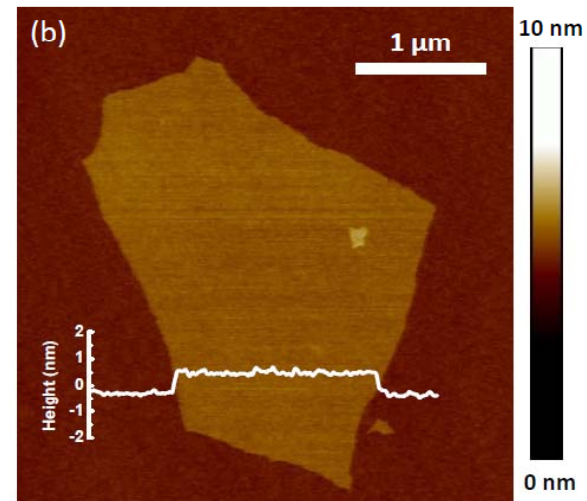
Atomic Force Microscopy (AFM)



single wall carbon nanotube



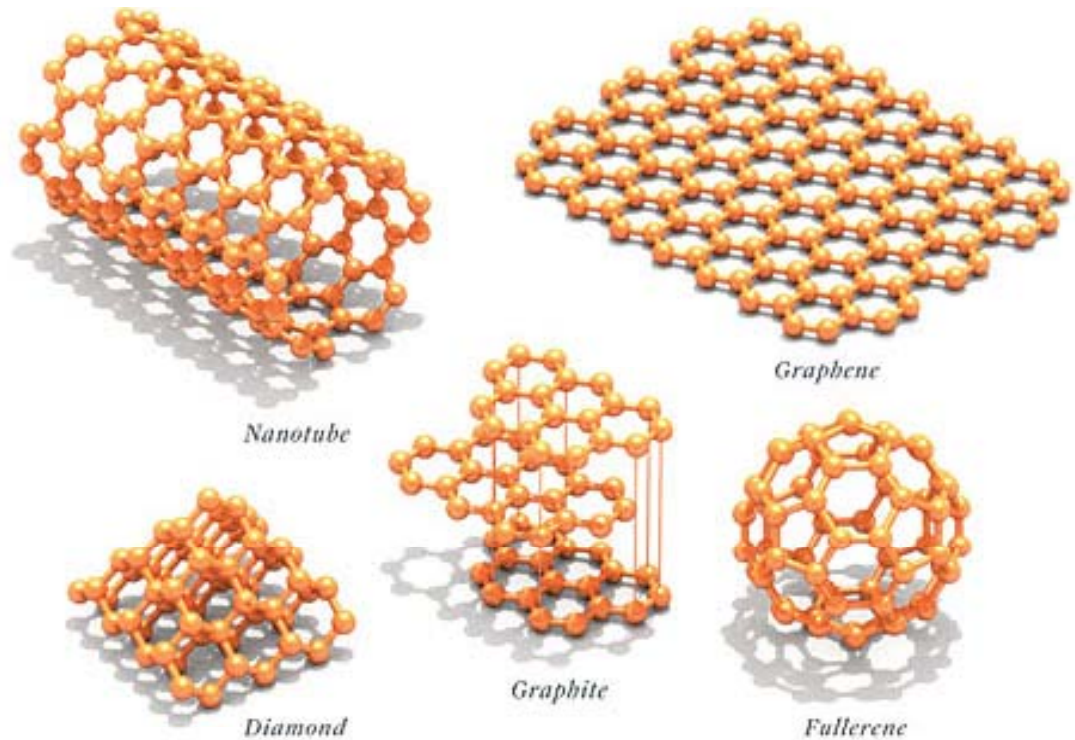
(Graphene oxide)



Nanomaterials-- Carbon nanotubes (CNTs) and Graphene

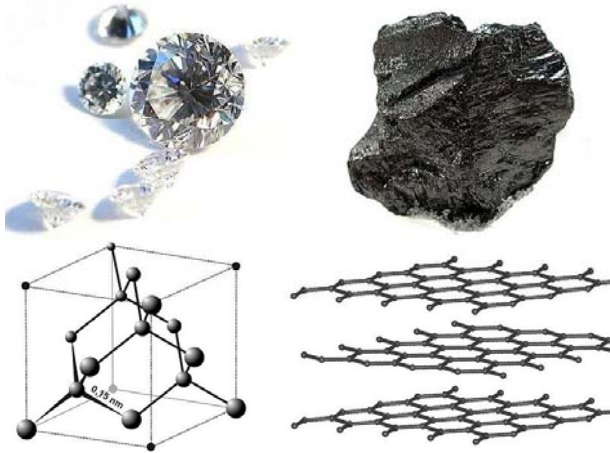
Carbon Nanomaterials

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

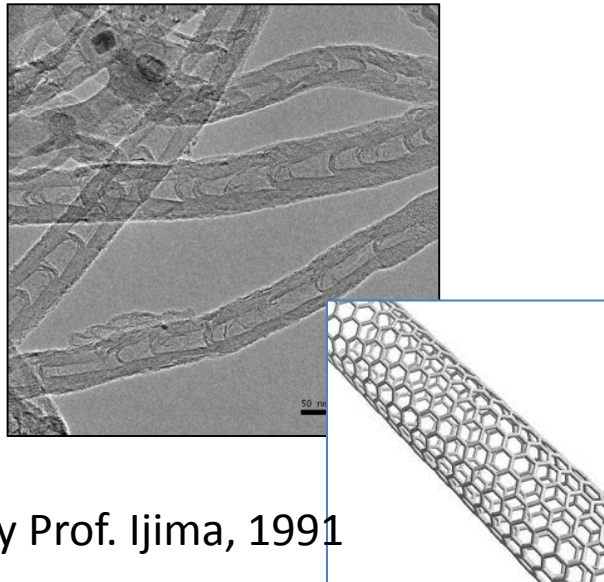


Carbon-related materials

3D Diamond and Graphite

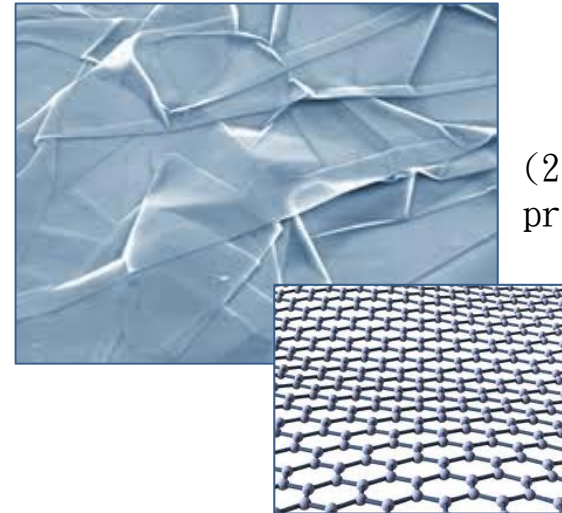


1D Carbon nanotube



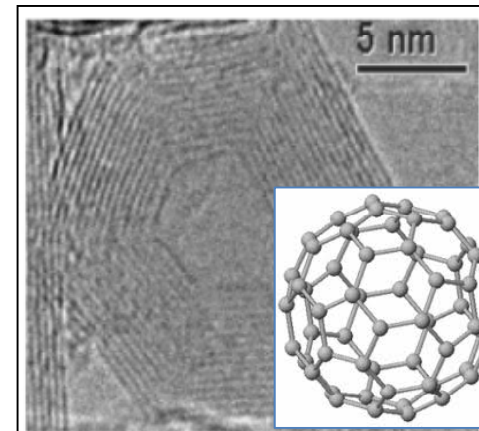
discovered by Prof. Iijima, 1991

2D Graphene



(2010 Nobel prize in physics)

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

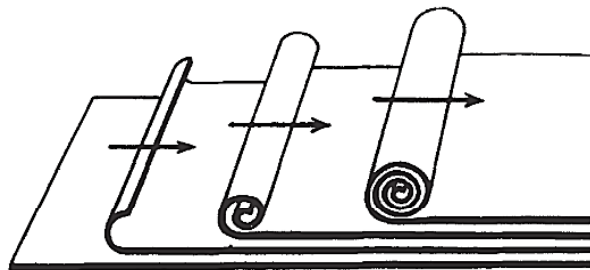
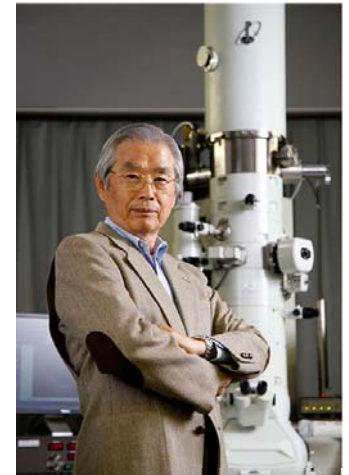
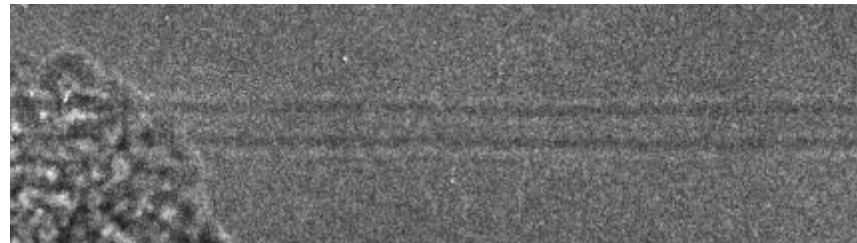
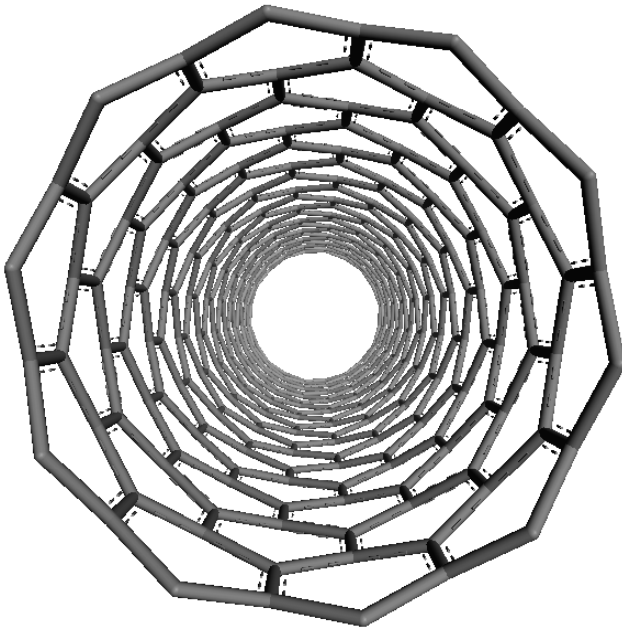


Fig. 3. Schematic illustration of rollers



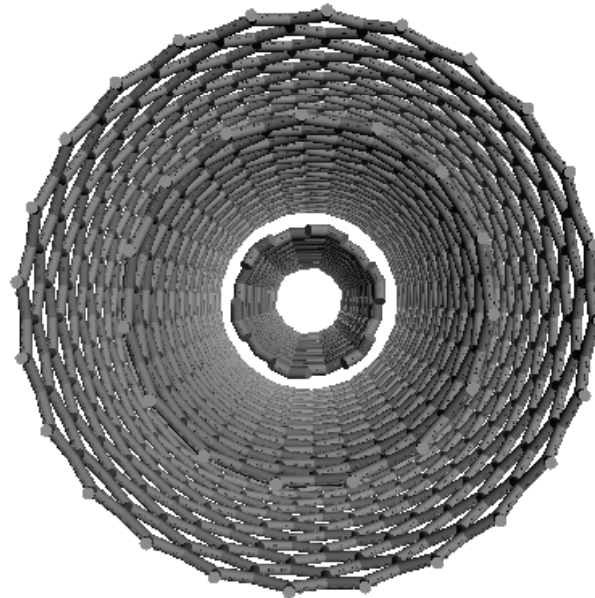
Structure of CNT

Single-Walled CNT
(SWCNT)



$(10,0)$

Multi-Walled CNT
(MWCNT)

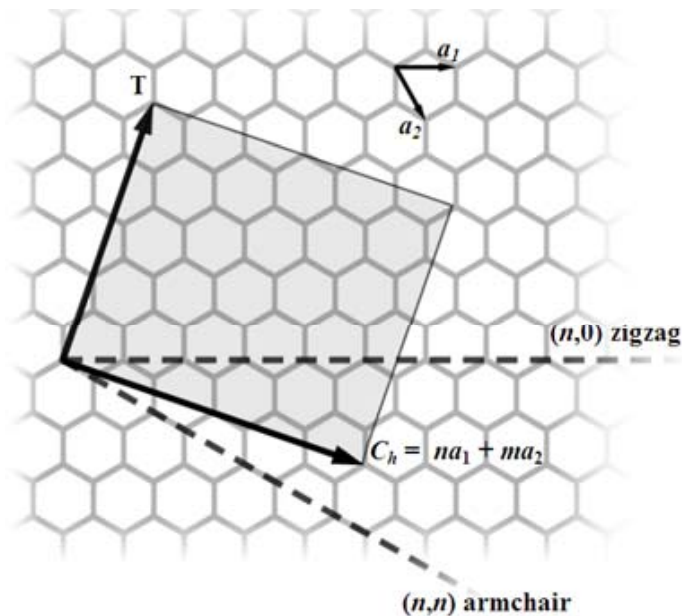


$(6,0)+(15,0)+(24,0)$

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

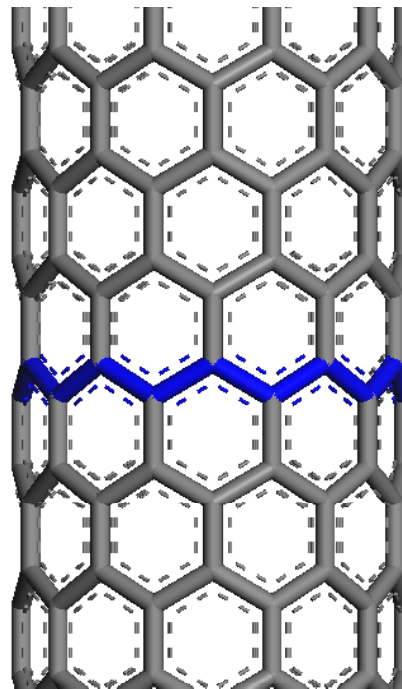
Structure of CNT

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

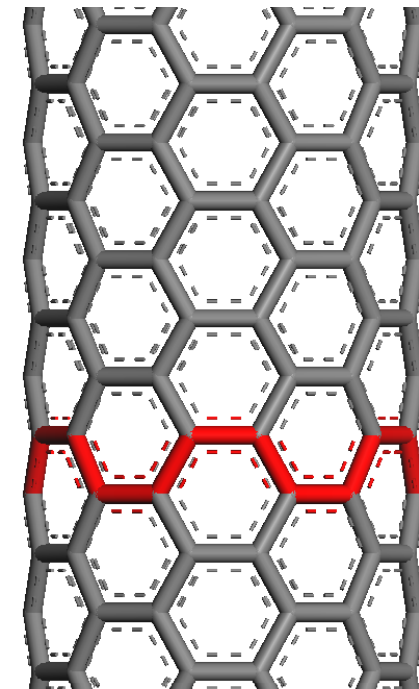


The diameter of $[n,m]$ CNT:

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



(10,0) Z-CNT

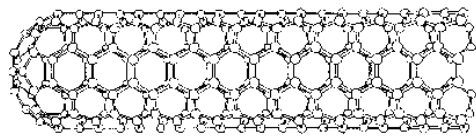
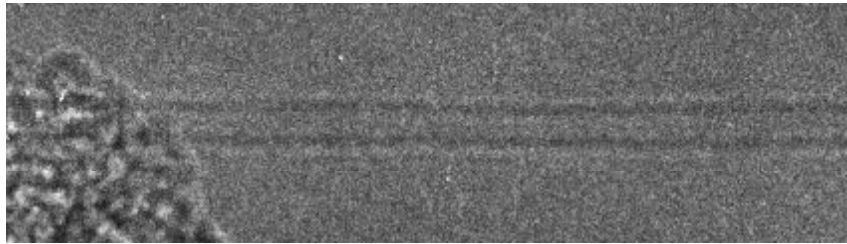


(6,6) A-CNT

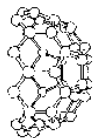
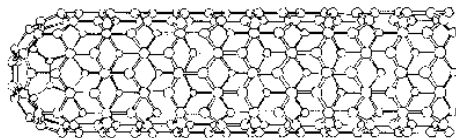
Physical Properties of CNT

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

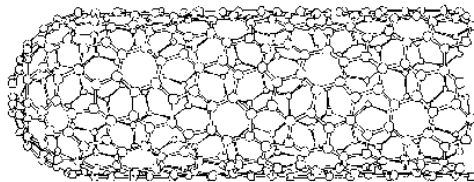
1-D nanomaterials (Carbon nanotube)



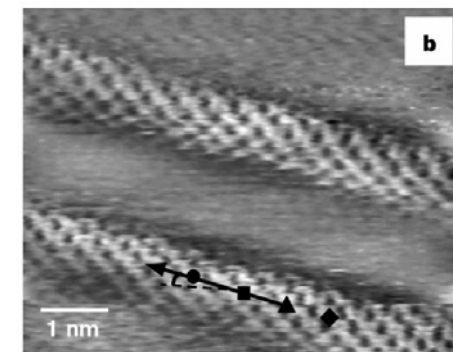
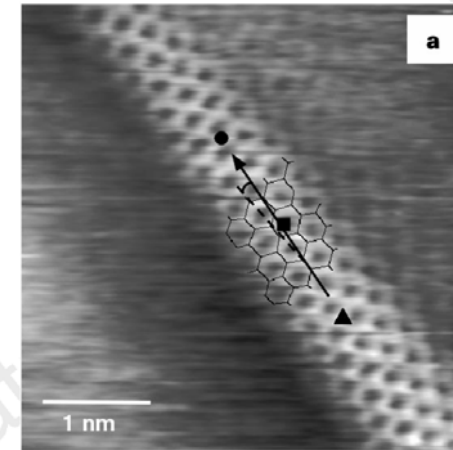
Armchair (n,n)



Zig-zag $(n,0)$

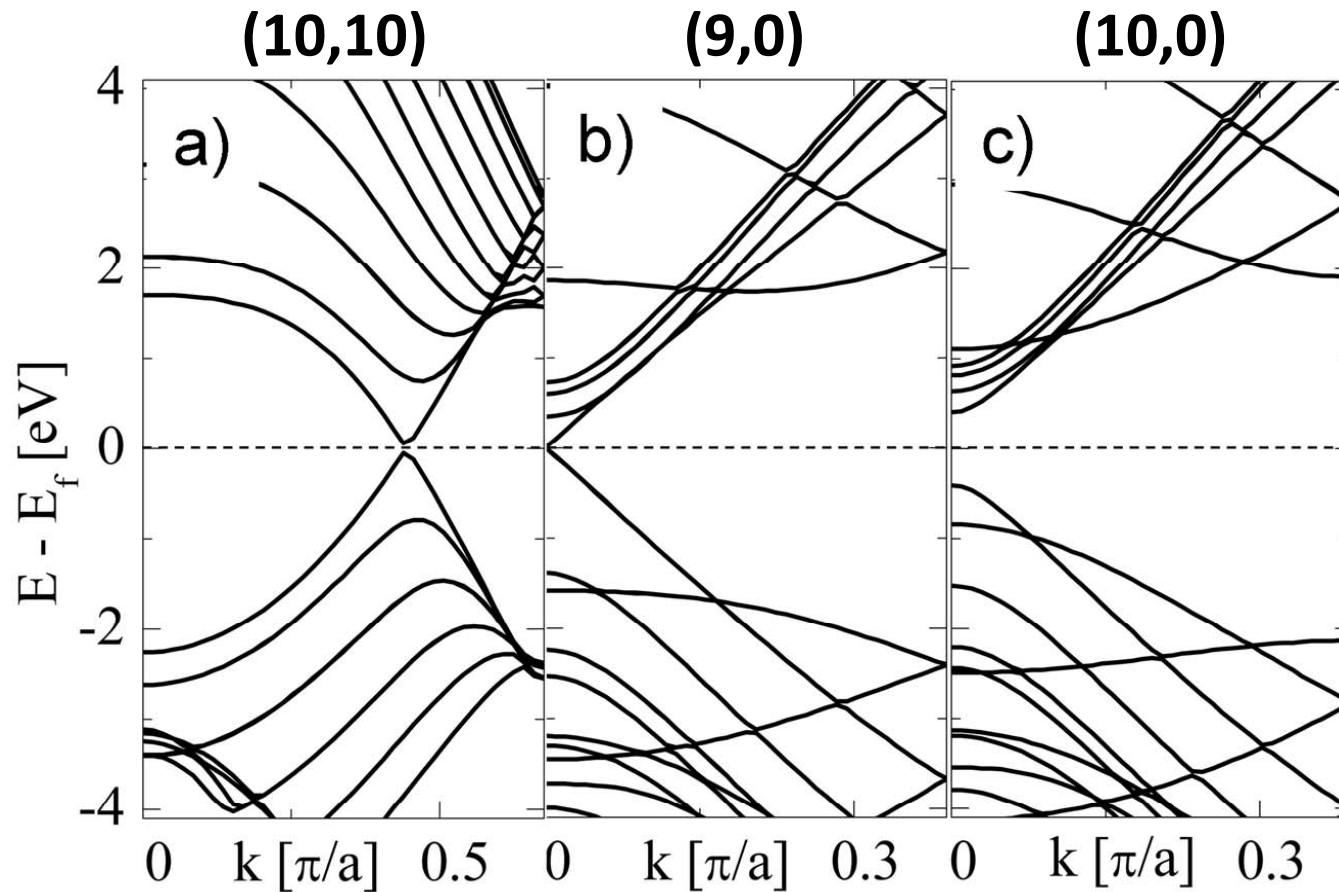


Chiral (n,m)



Discovered by Iijima (1991)

Band Structures of CNT

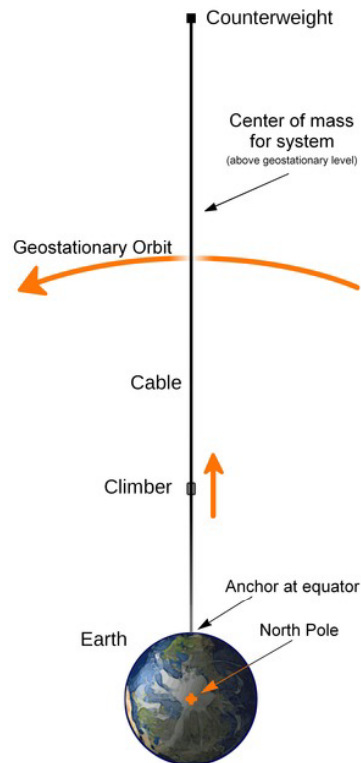


Band structures of (a) (10,10) (b) (9,0) (c) (10,0) CNTs

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

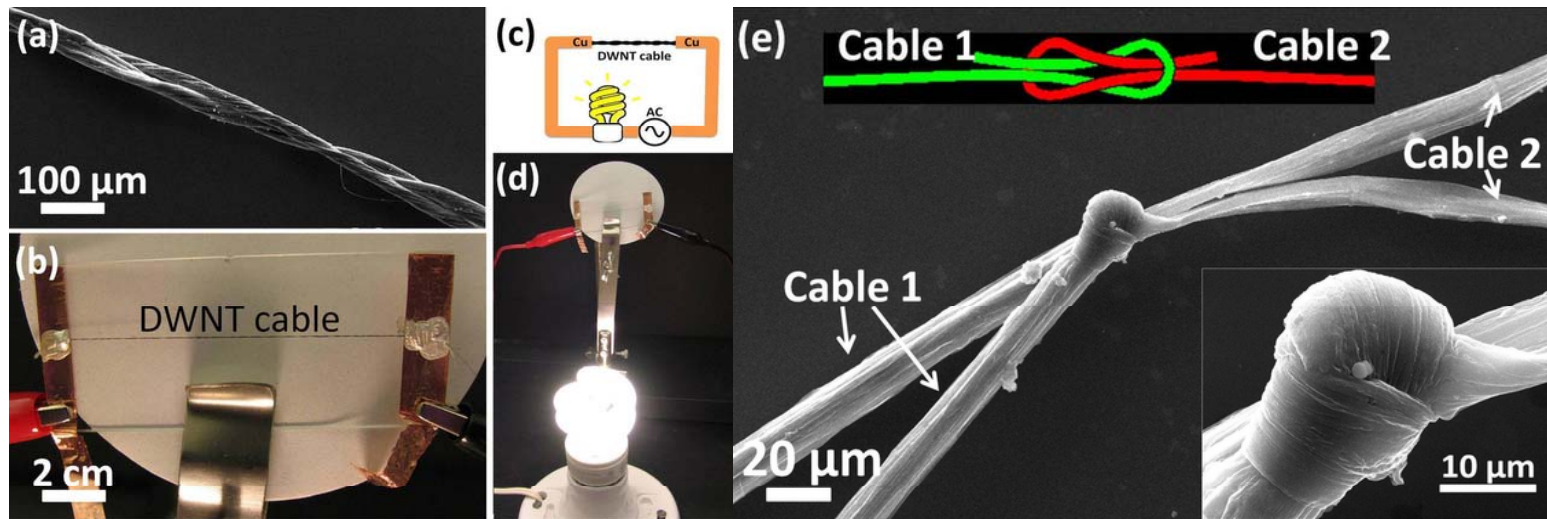
Belluci, S. et al., *Phys. Status Solidi C* **2** (1), 34 (2005)
Sinnott, S.B. et al., *Crit. Rev. Solid State* **26** (3), 145 (2001)

Electronic Properties

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

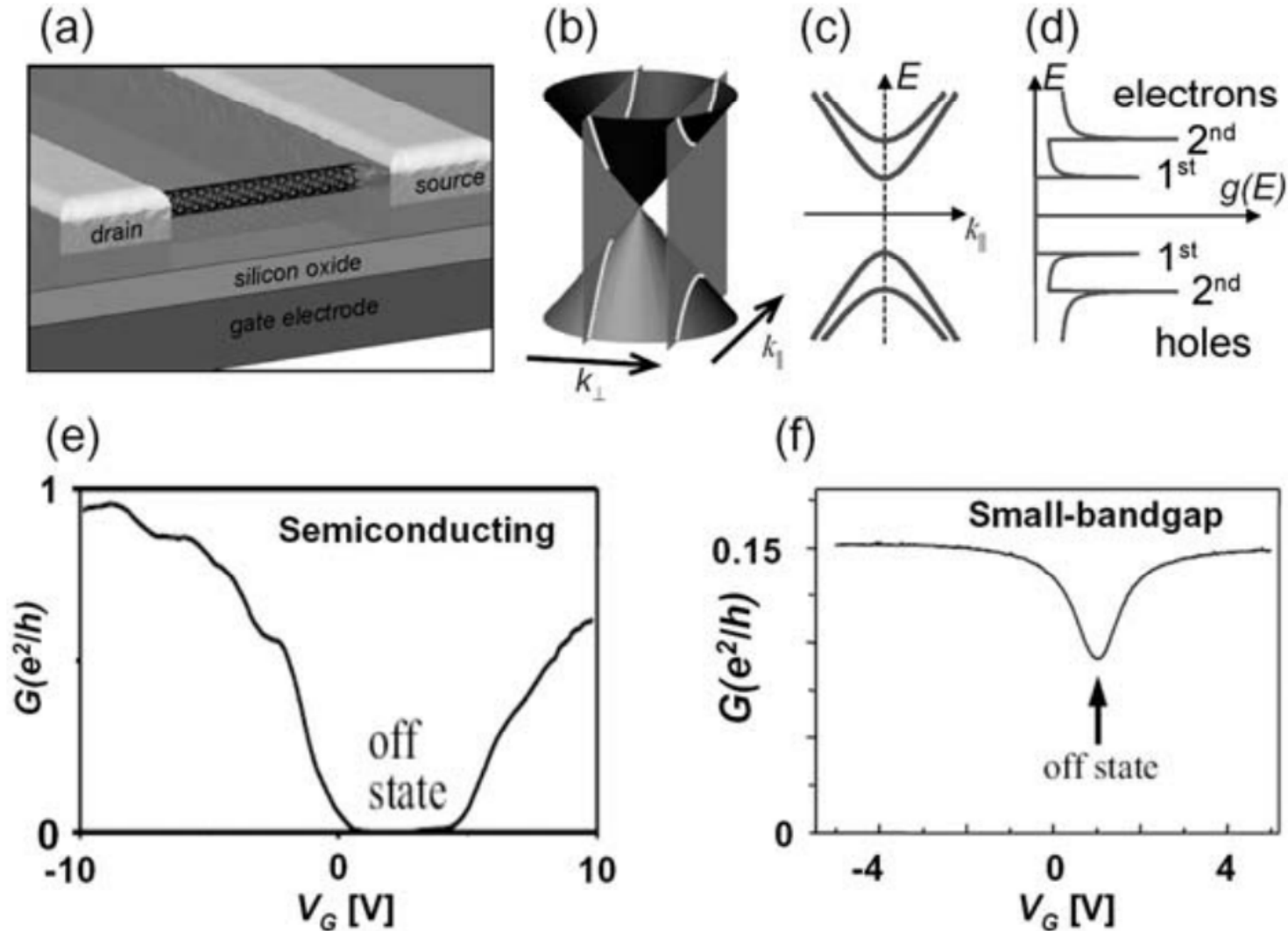
Interconnects

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



Transport of CNT

Nanotube field-effect transistor

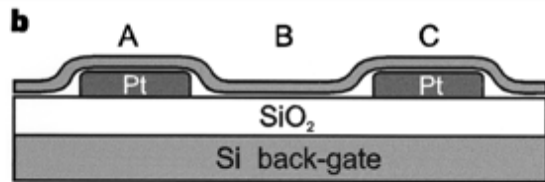


Ambipolar Electrical Transport in
Semiconducting Single-Wall Carbon Nanotubes

CNT Transistor

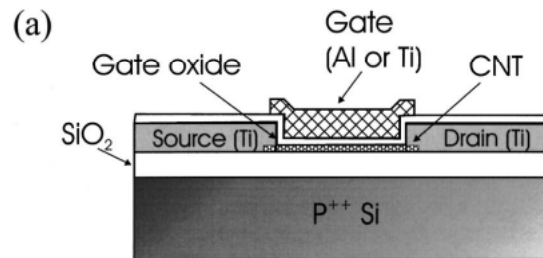
- Various type of CNT transistors had been developed

Back-gated



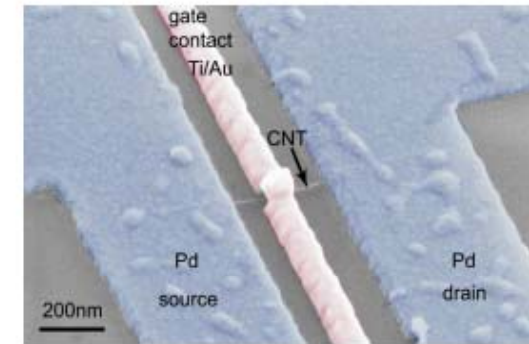
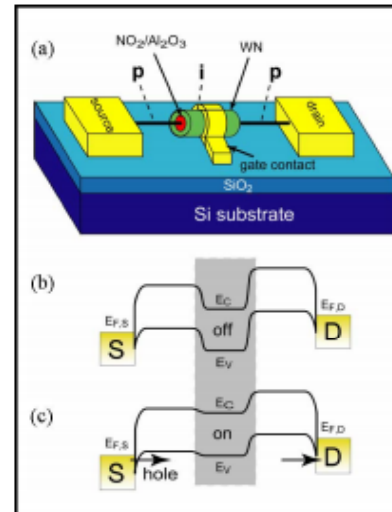
Sander J. Tans, et. al., *Nature* 1998, **393**, 49-52

Top-gated



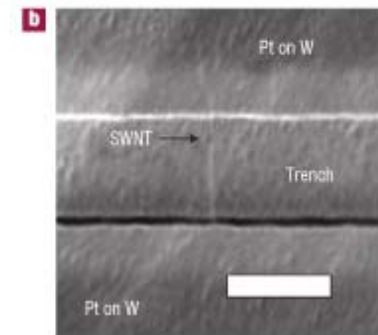
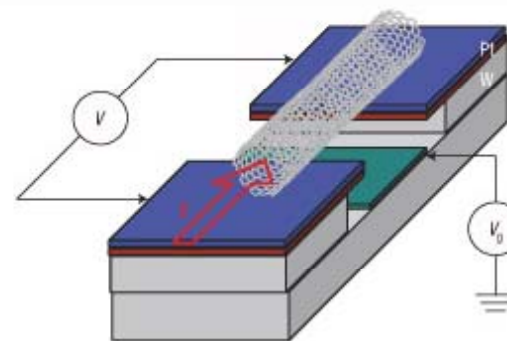
Wind, S. J. et. al., 2002 *Applied Physics Letters* **80** (20): 3817

Wrap-around gate



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

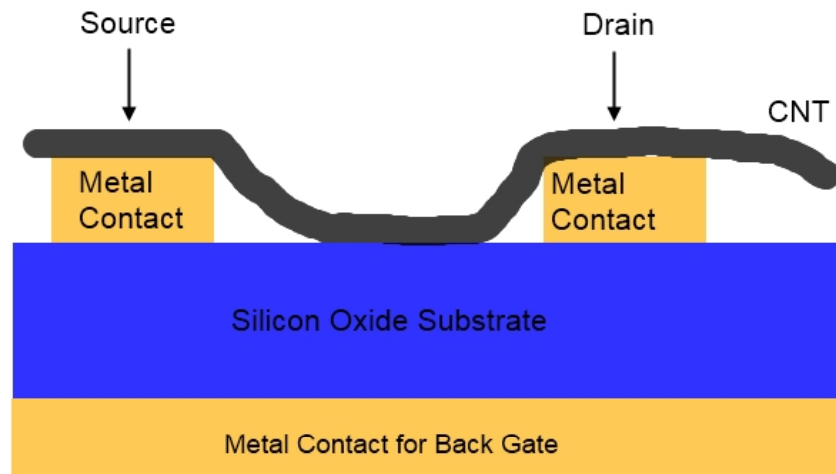
Suspended



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

Designs of CNT Transistors

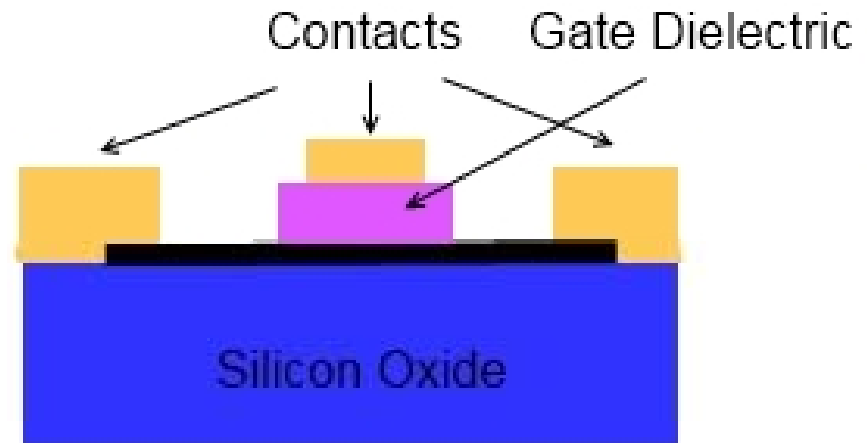
Back-gated



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

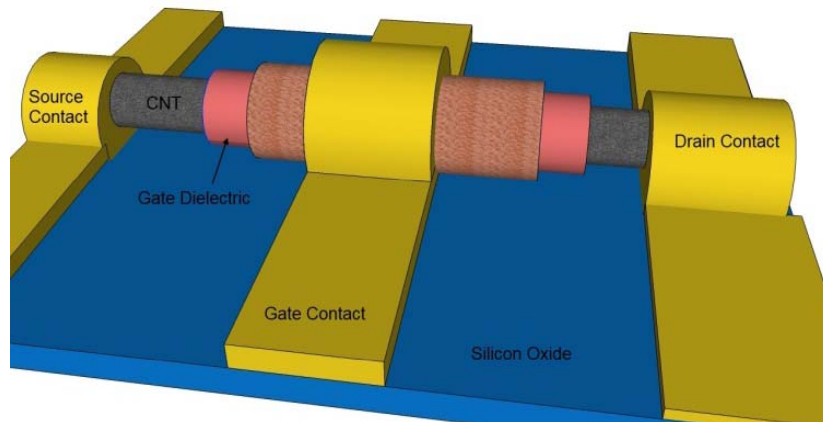
Top-gated



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



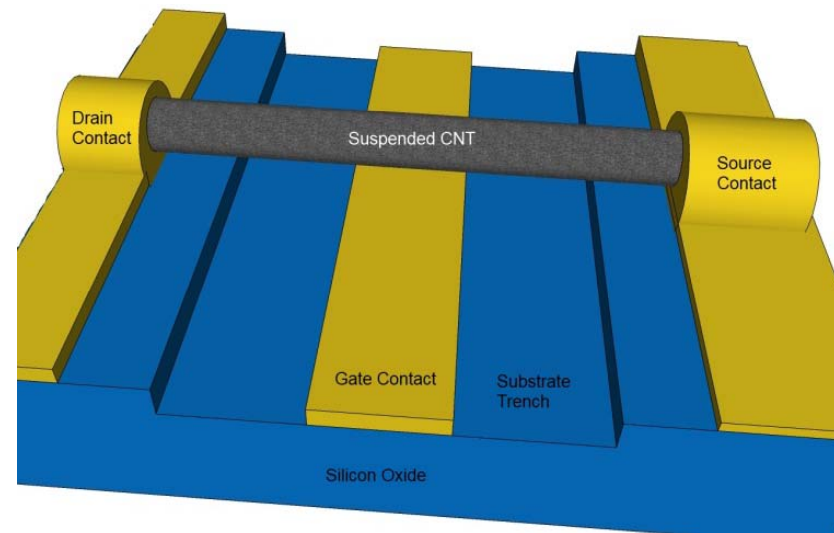
Developed in 2008. This design

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)

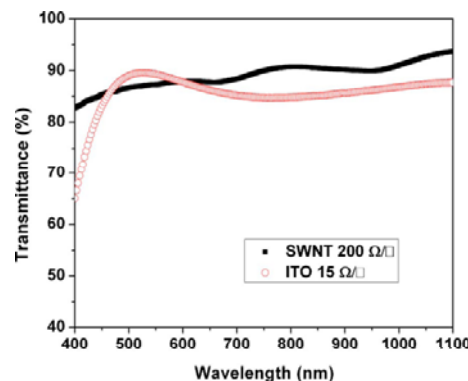
Suspended



Developed in 2005. This design reduces the scattering at the interface of the CNT-substrate.

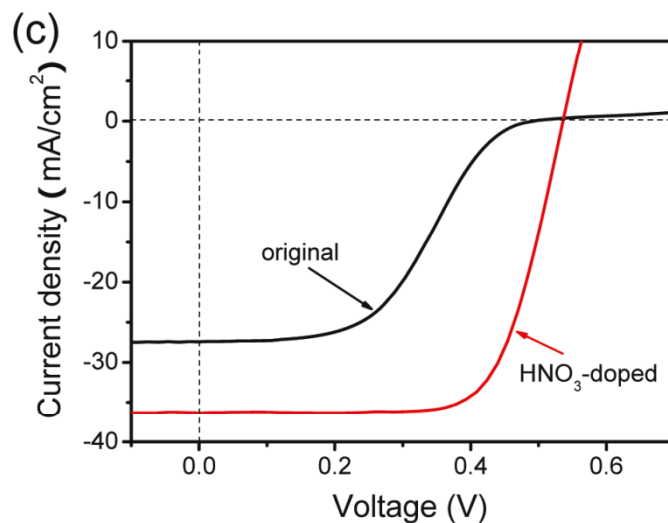
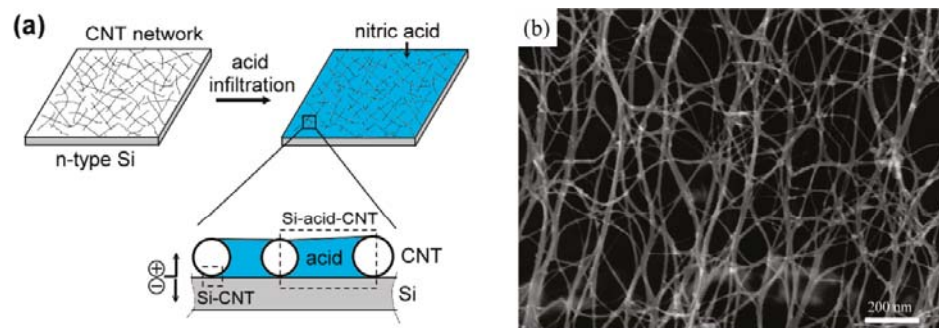
However, materials of devices are limited. It is only for studying the properties of clean CNT and cannot be commercialized.

Carbon Nanotube on photovoltaic and LED applications



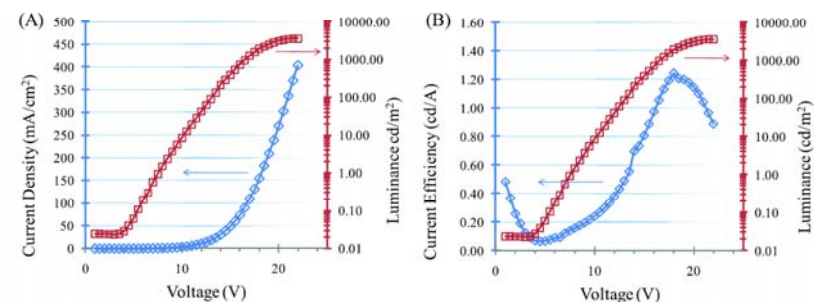
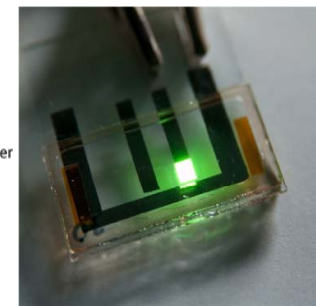
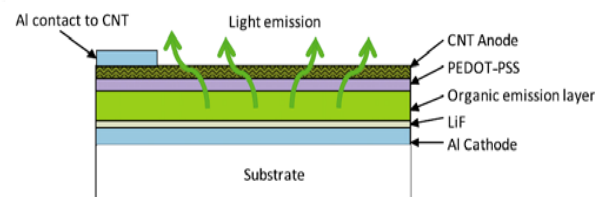
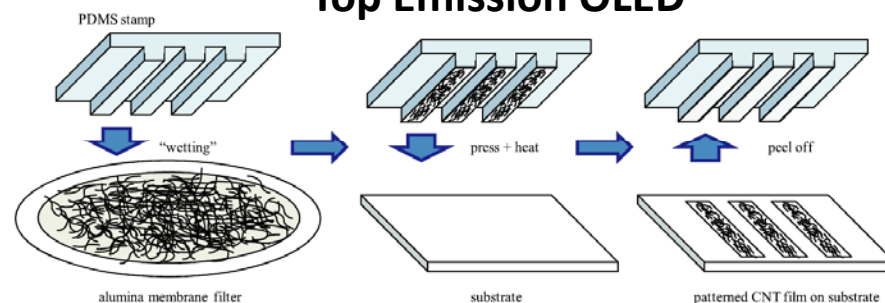
- ✧ High transparency on visible and NIR range
- ✧ Good conductivity
- ✧ Flexible

Silicon-CNT heterojunction solar cell



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

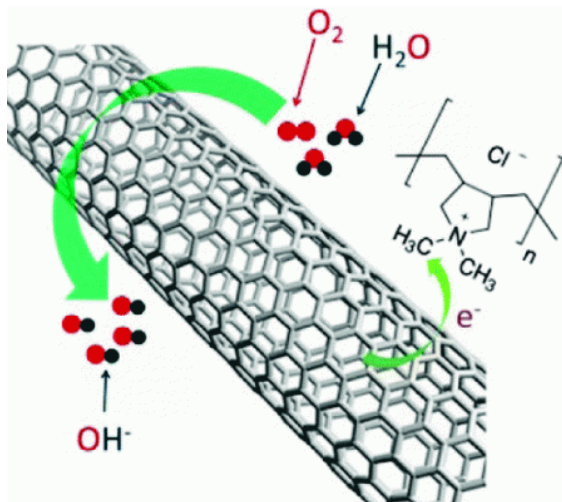
Top Emission OLED



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

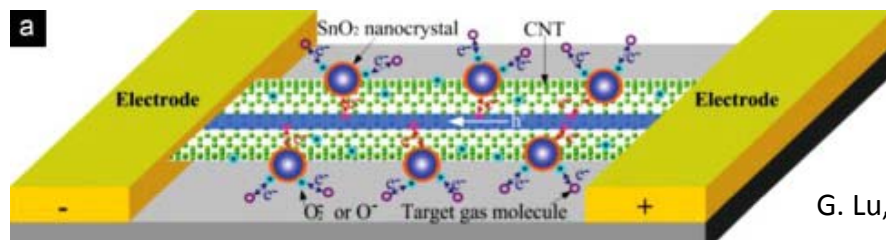
Other Applications

- Fuel cells
 - Store H_2 in CNT



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

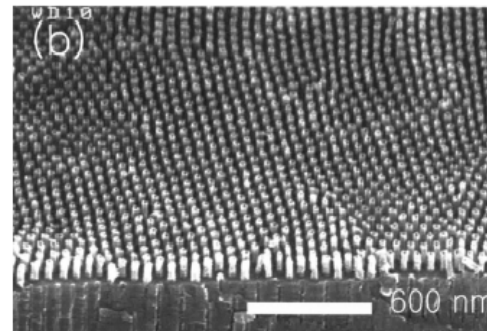
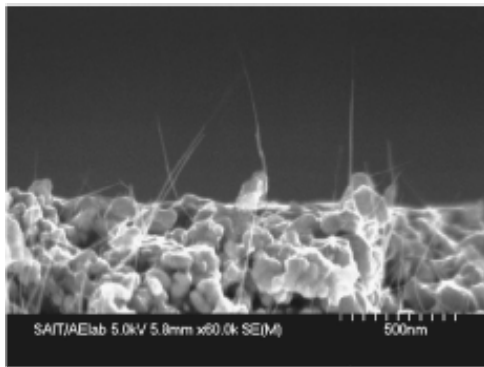
- Gas detector
 - Molecules adsorb on the channel of CNT FET, modifying the electrical properties of CNT



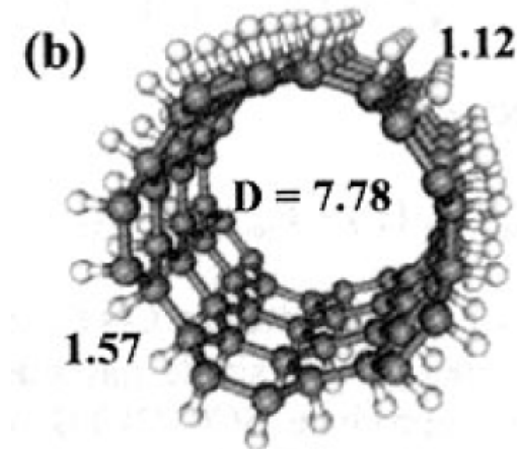
G. Lu, L.E. Ocola J. Chen, *Adv. Mater.*, 2009, 21, 2487

Applications of Carbon Nanotube

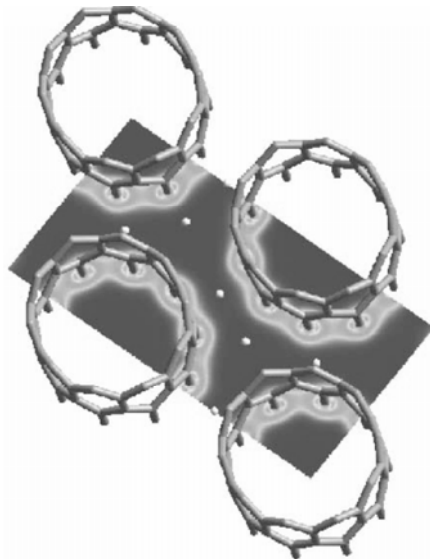
Field Emitter



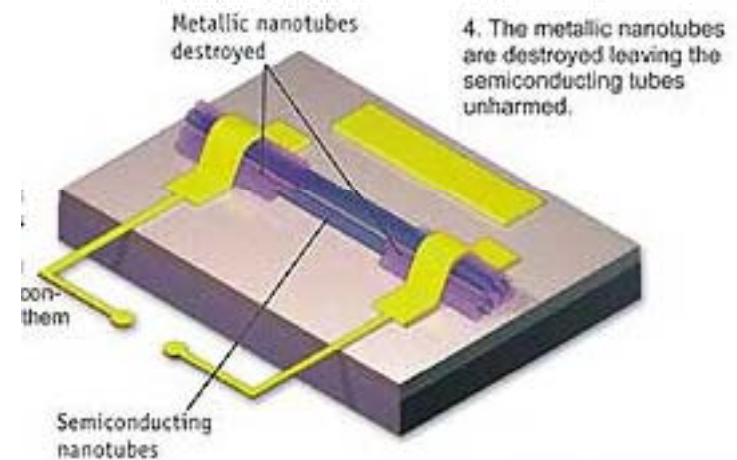
Hydrogen Storage



Li-ion battery anode

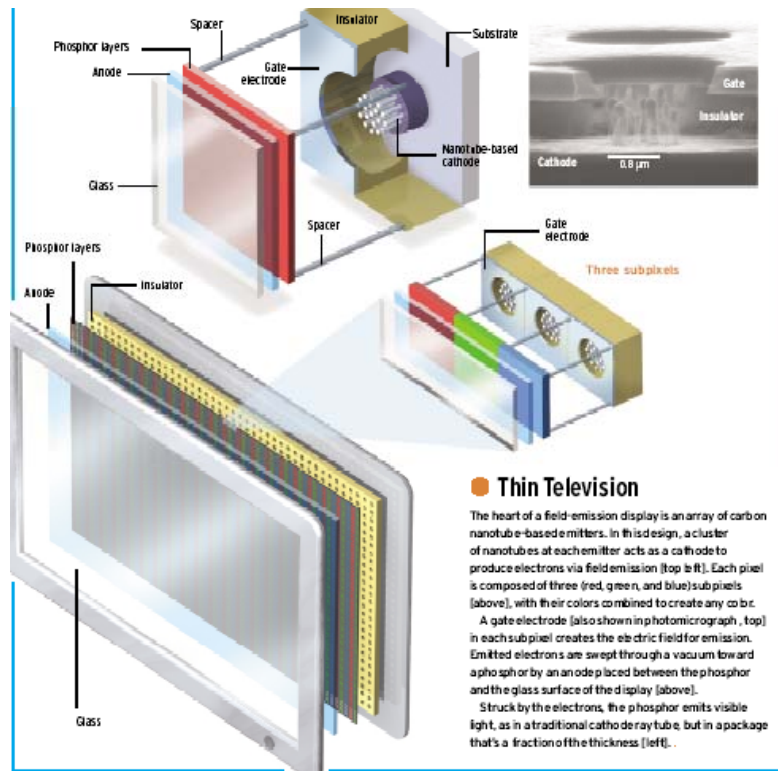


Logic gate by IBM



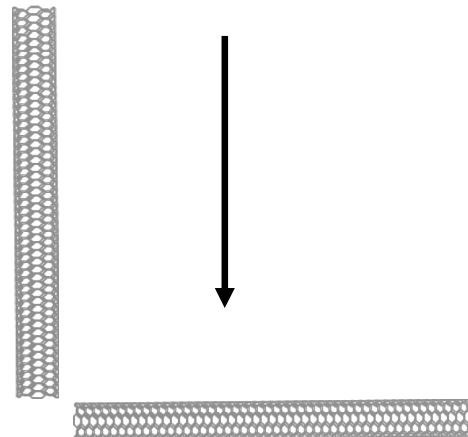
Applications of CNTs in electronic devices

CNT field emission display



From IEEE spectrum 2003

E field

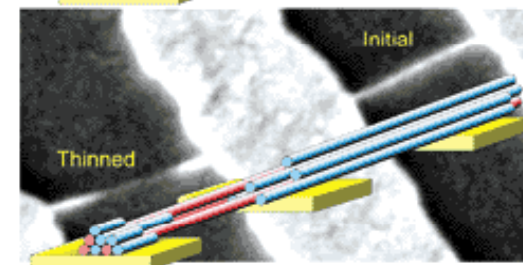
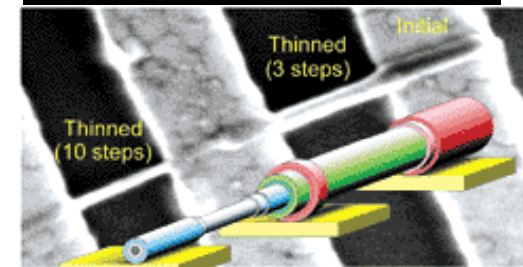
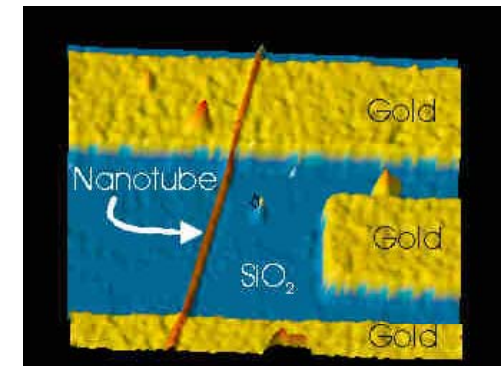


Small dimension

→ High local field

→ Electronic structure changes

CNT Field effect transistor



From IBM