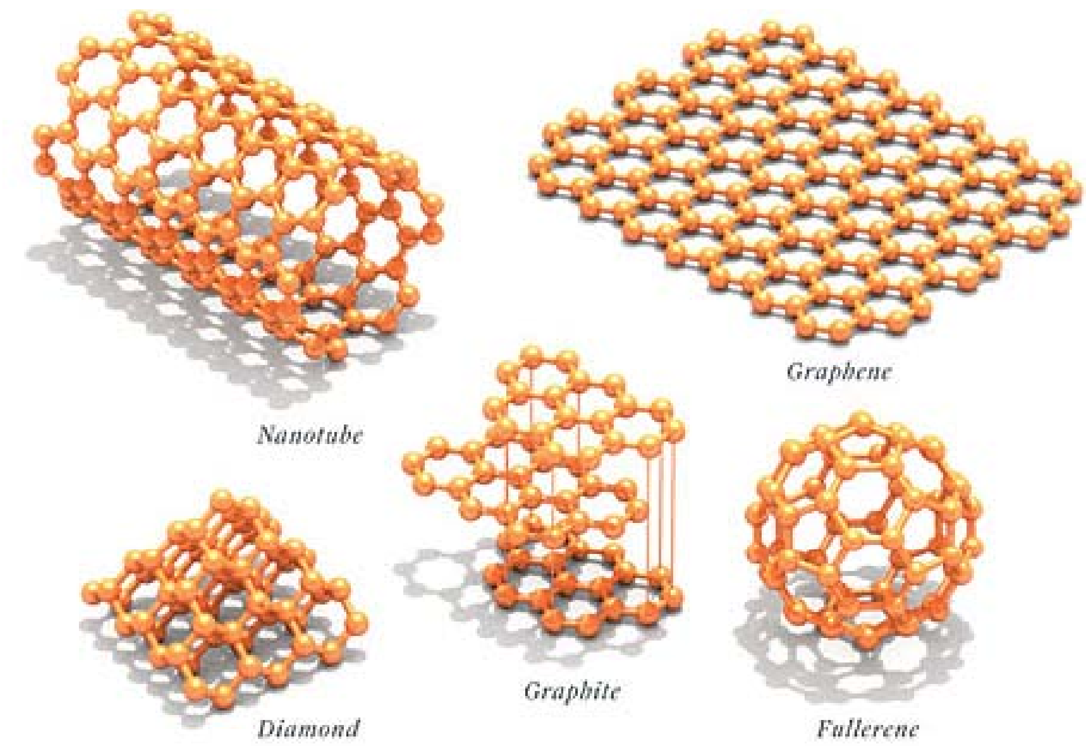
Part II
Low-dimensional carbon materials--Carbon nanotubes (CNTs) and Graphene

Outline

- Carbon nanomaterials
  - Types of carbon nanomaterials
- Graphene and CNT
  - Introduction
  - Synthesis
  - Specific topics
  - Application

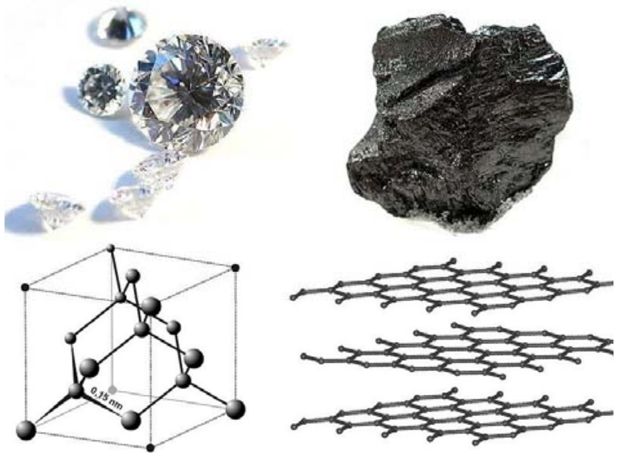
Carbon Nanomaterials

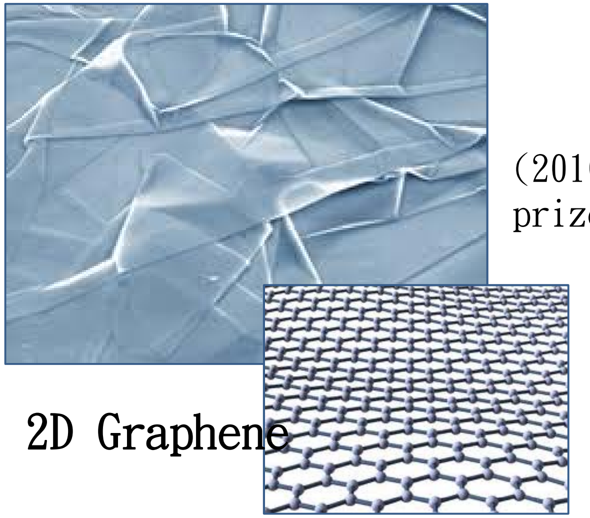
- 3D
  - Graphite
  - Diamond
- 2D
  - **Graphene**
- 1D
  - **Carbon nanotube**
- 0D
  - Fullerene



Cabon-related nanomaterials

3D Diamond and Graphite

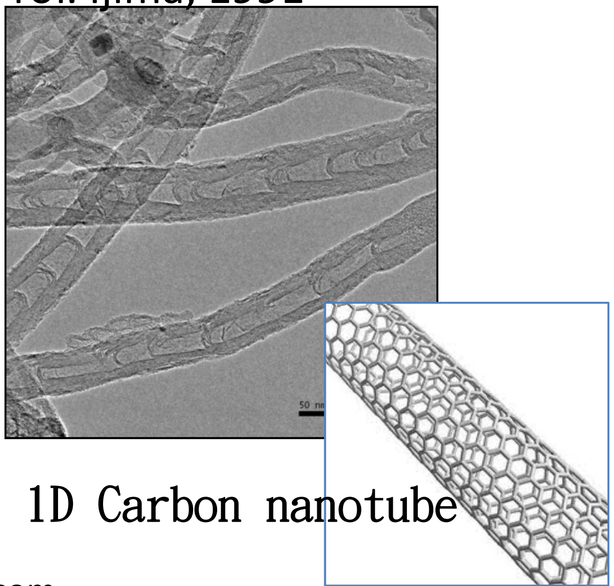




2D Graphene

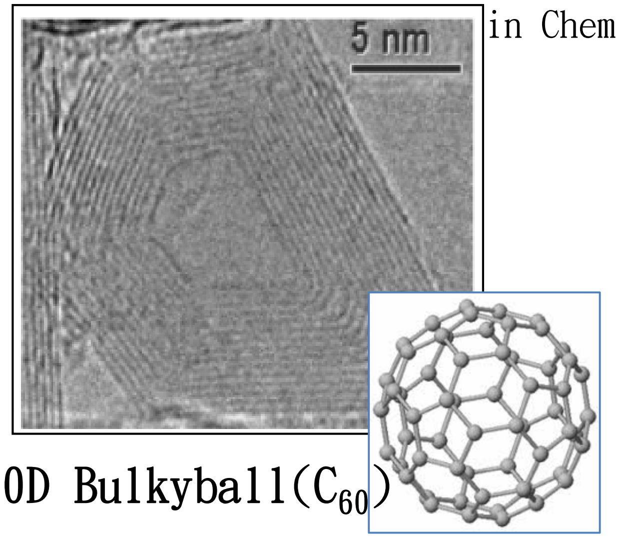
(2010 Nobel prize in physics)

discovered by Prof. Ijima, 1991



1D Carbon nanotube

(1996 Nobel priz in Chemistry)



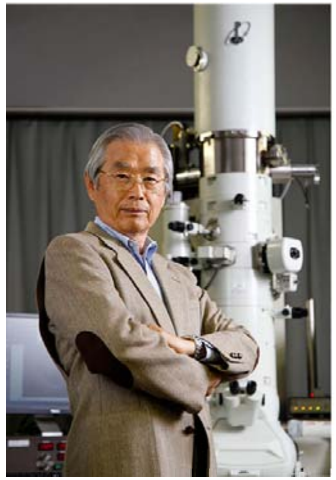
0D Bulkyball(C_{60})

en.wikipedia.org
craigbanksresearch.com
grapheneindustries.com

2-1. Introduction of CNT

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



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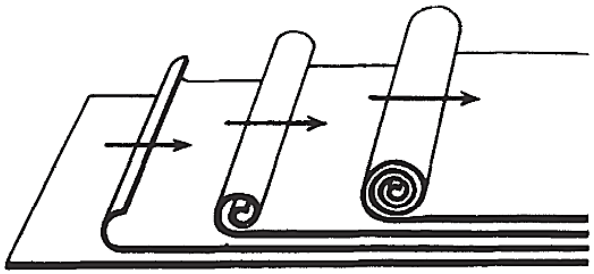
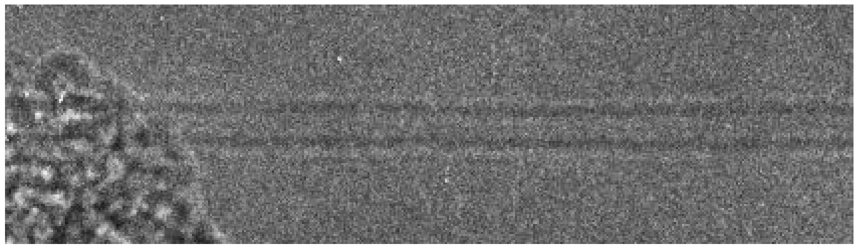
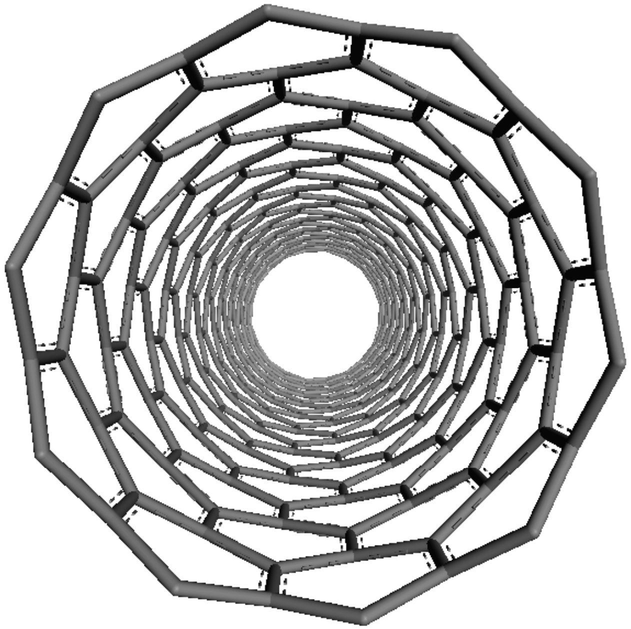


Fig. 3. Schematic illustration of rollers



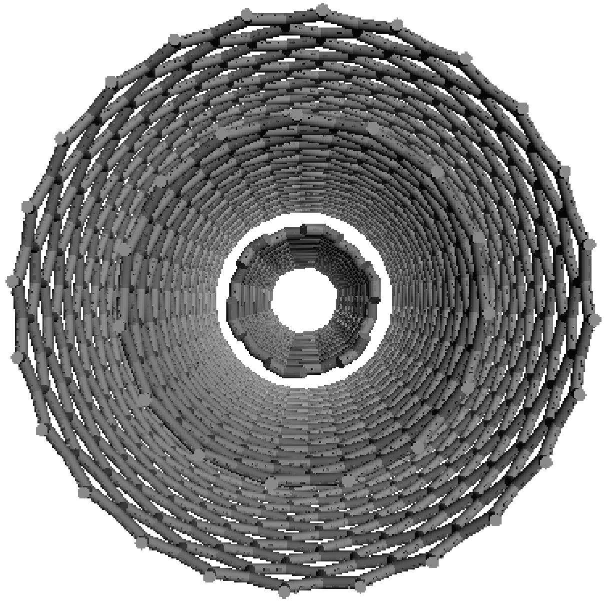
Structure of CNT

Single-Walled CNT
(SWCNT)



(10,0)

Multi-Walled CNT
(MWCNT)

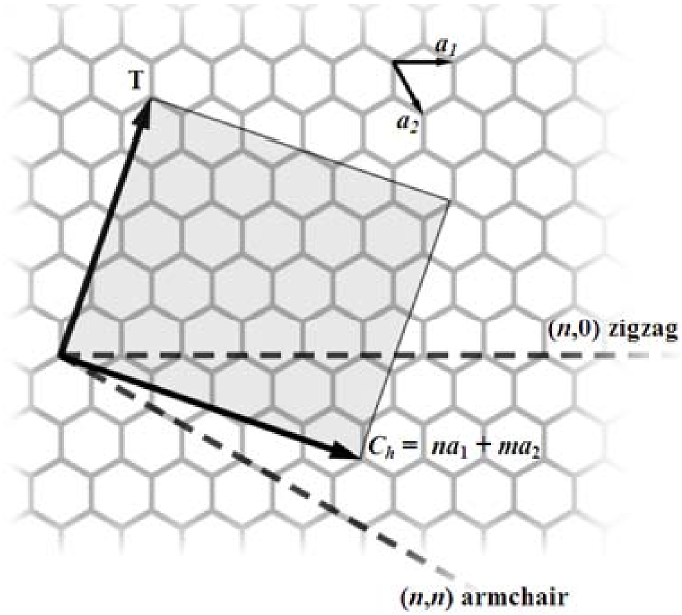


(6,0)+(15,0)+(24,0)

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

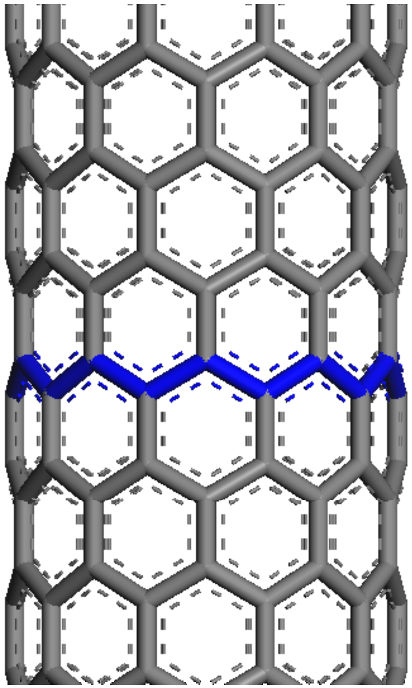
Structure of CNT

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

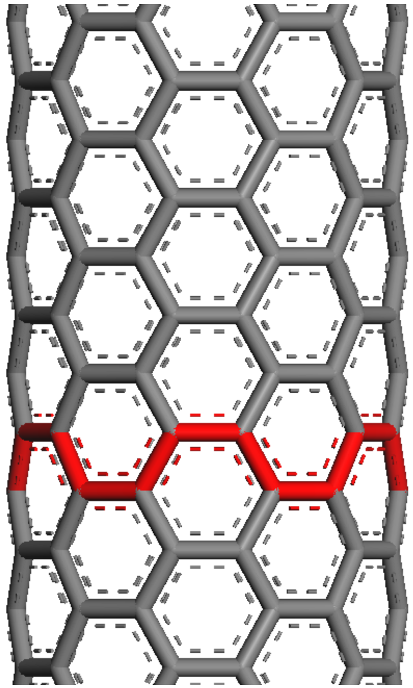


The diameter of [n,m] CNT:

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



(10,0) Z-CNT

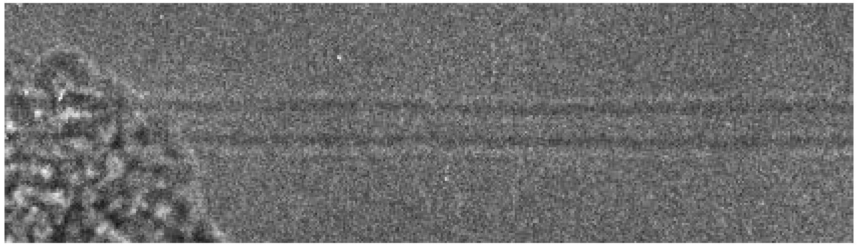


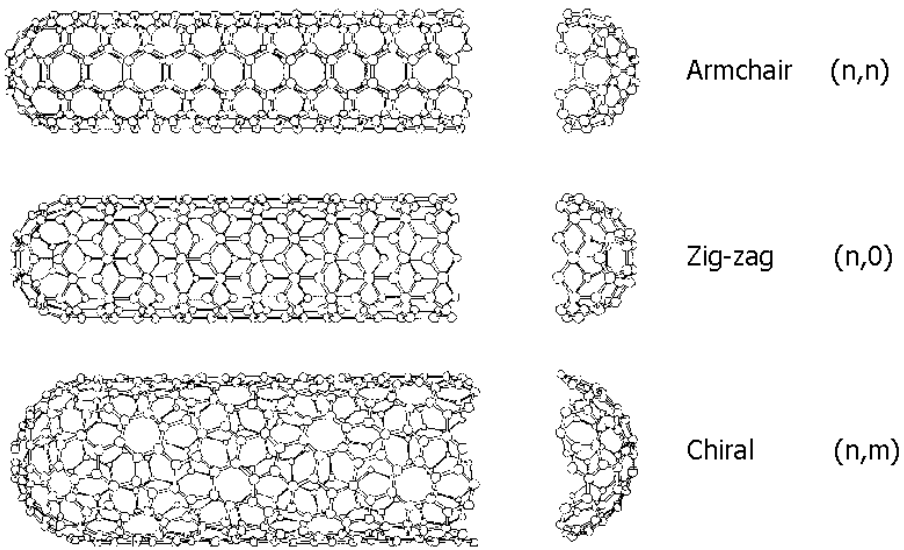
(6,6) A-CNT

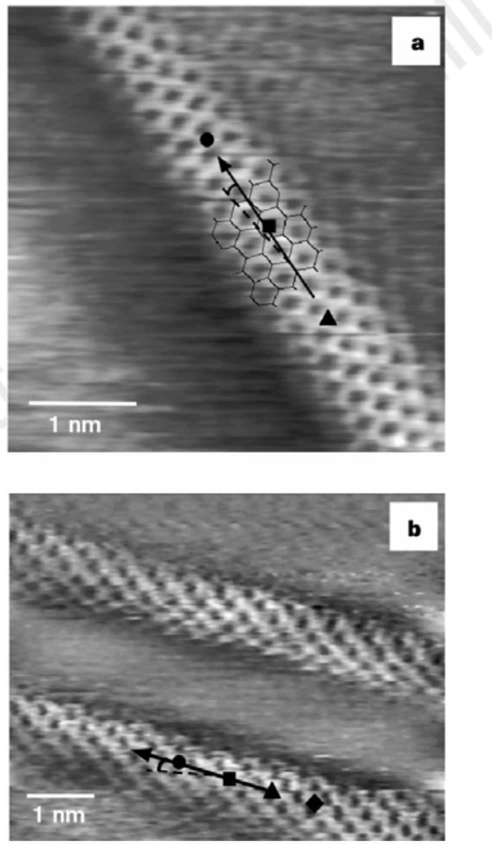
Physical Properties of CNT

- 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)

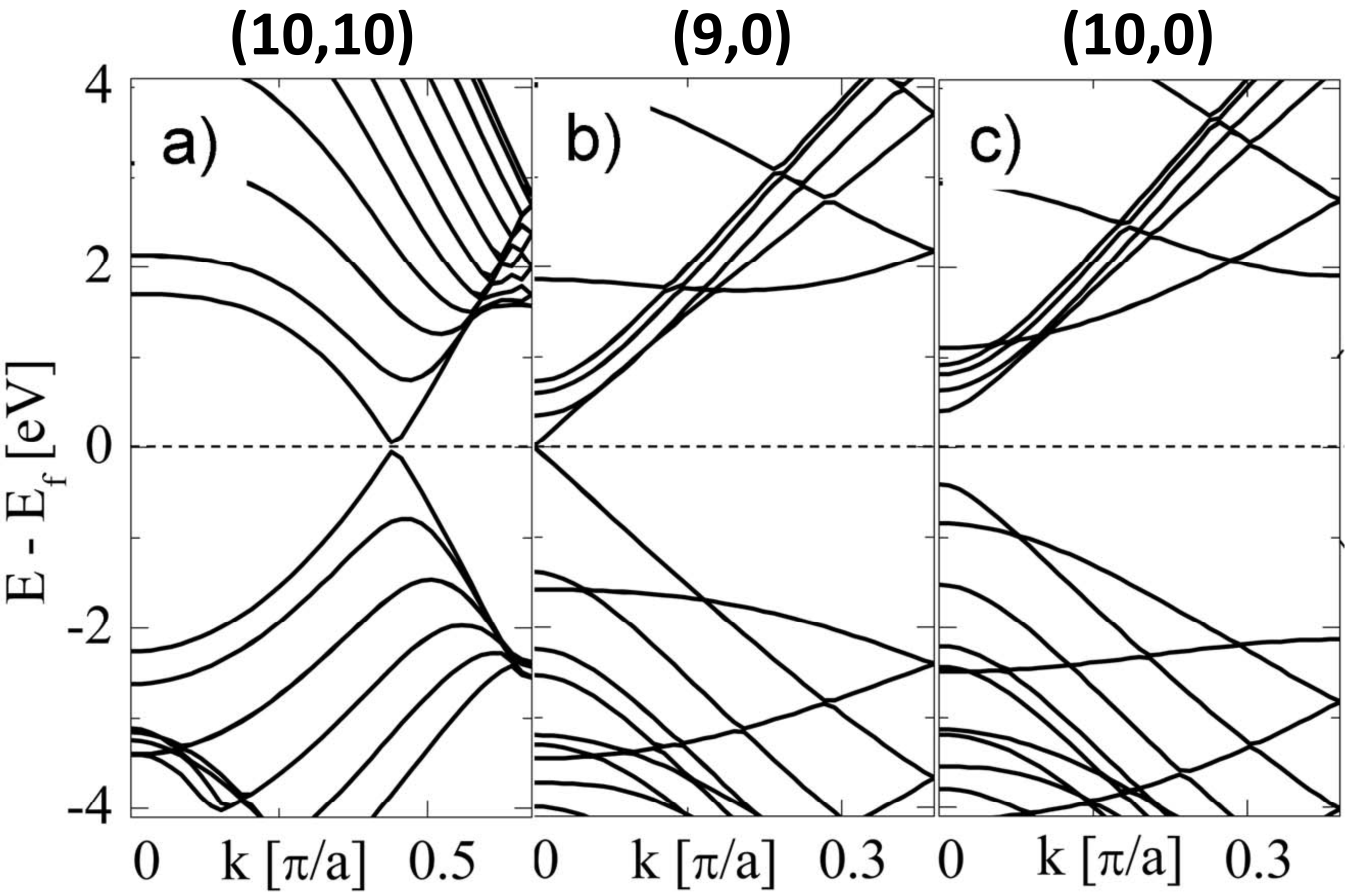






Discovered by Iijima (1991)

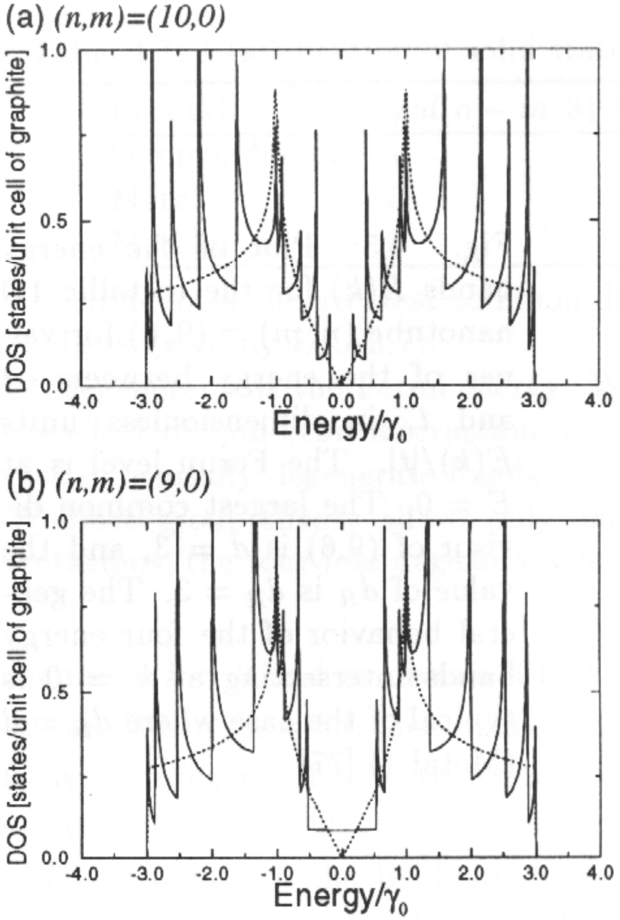
Band Structures of CNT



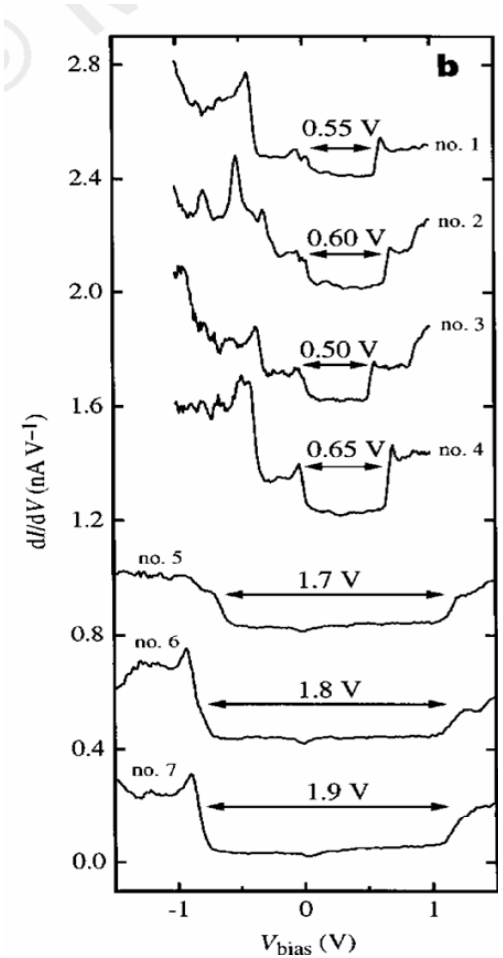
Band structures of (a) (10,10) (b) (9,0) (c) (10,0) CNTs

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

Electronic Properties of CNT



Tight-binding calculations



Experiments

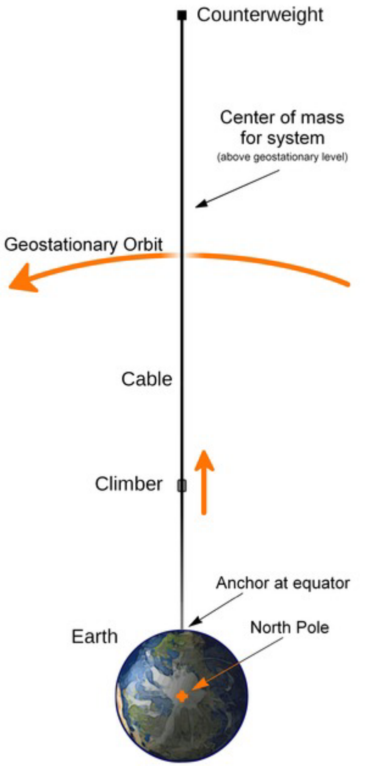
Energy gap changes with *chirality* and *diameter*

Nature 391,62, 1998

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)

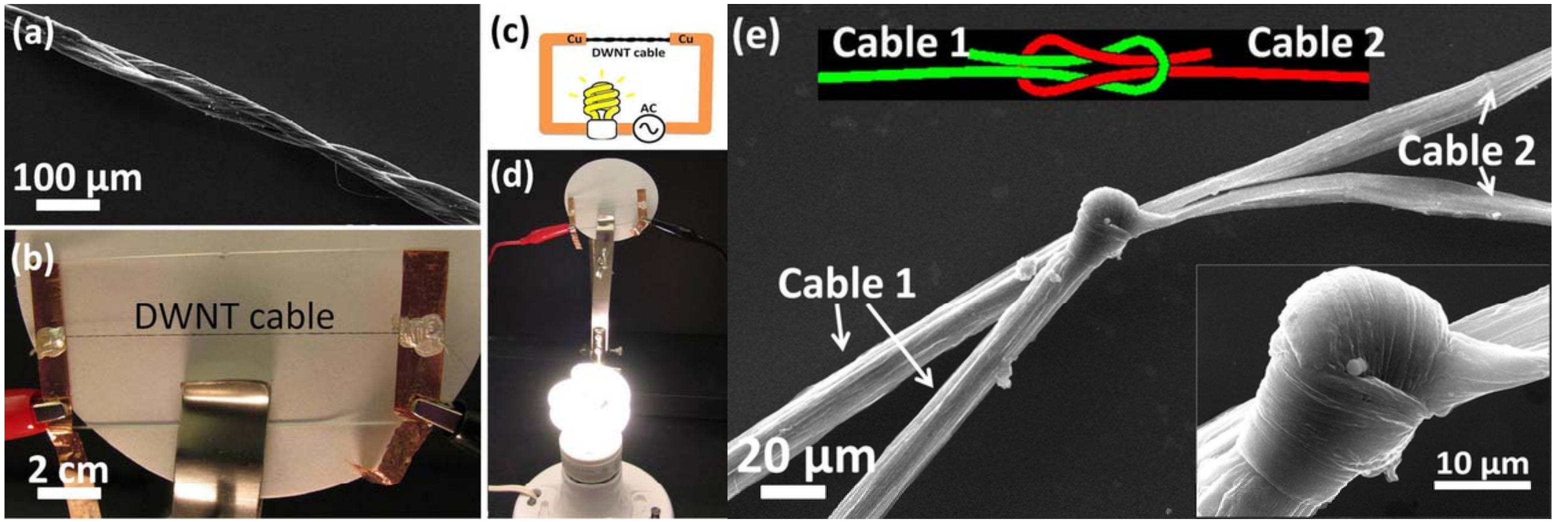
Electronic Properties

- 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

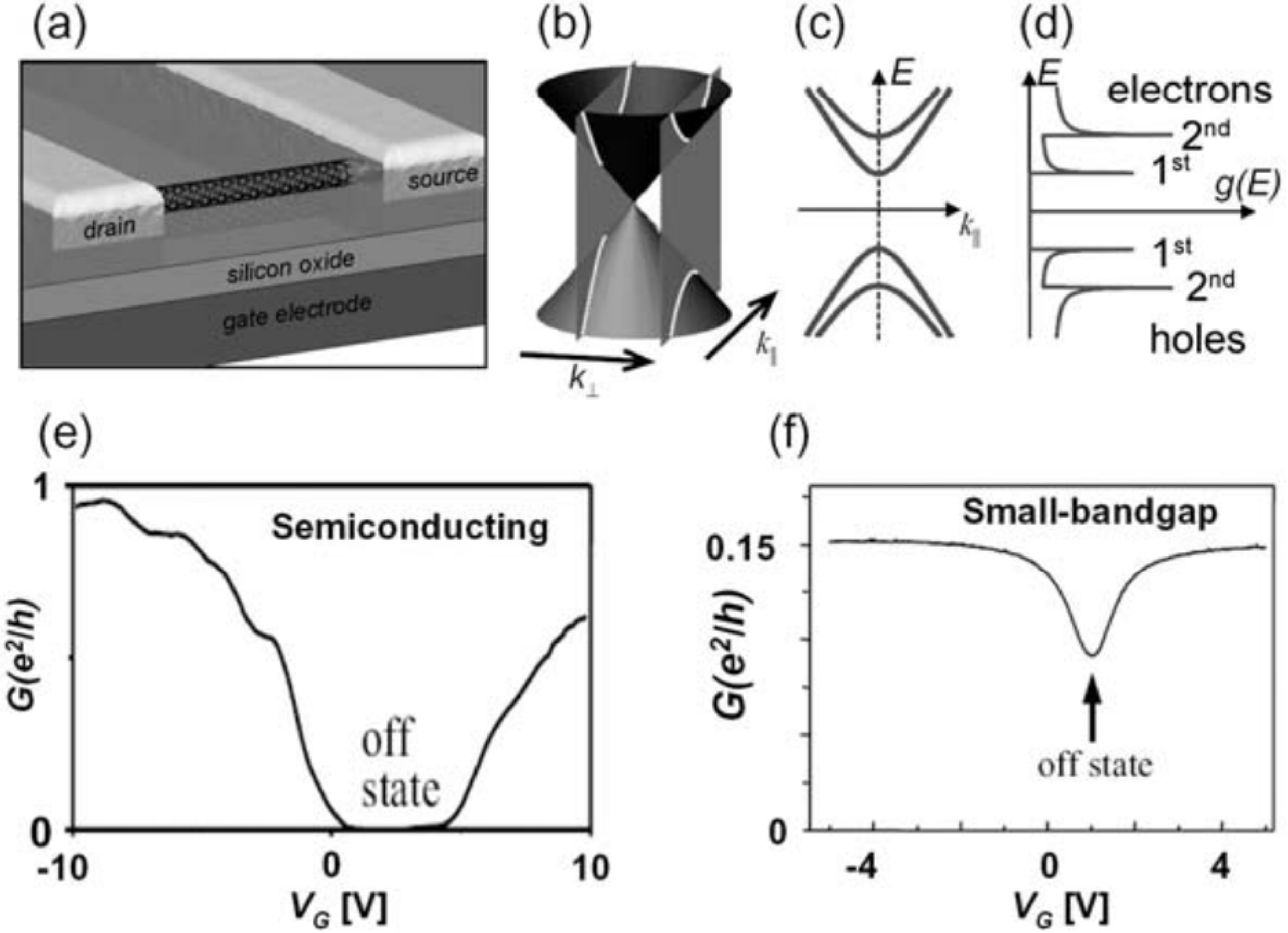
- Similar to GNRs, CNTs are potential materials to replace metal (such that Cu, Au) as non-metal high-conductivity interconnects in the integrated circuits



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

Transport of CNT

Nanotube field-effect transistor



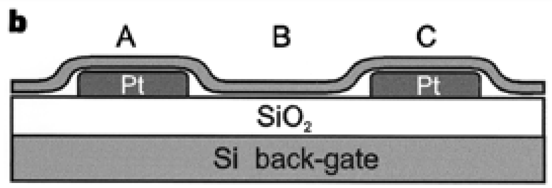
Ambipolar Electrical Transport in Semiconducting Single-Wall Carbon Nanotubes

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

CNT Transistor

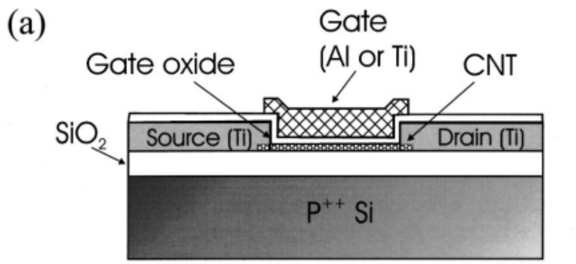
- Various type of CNT transistors had been developed

Back-gated



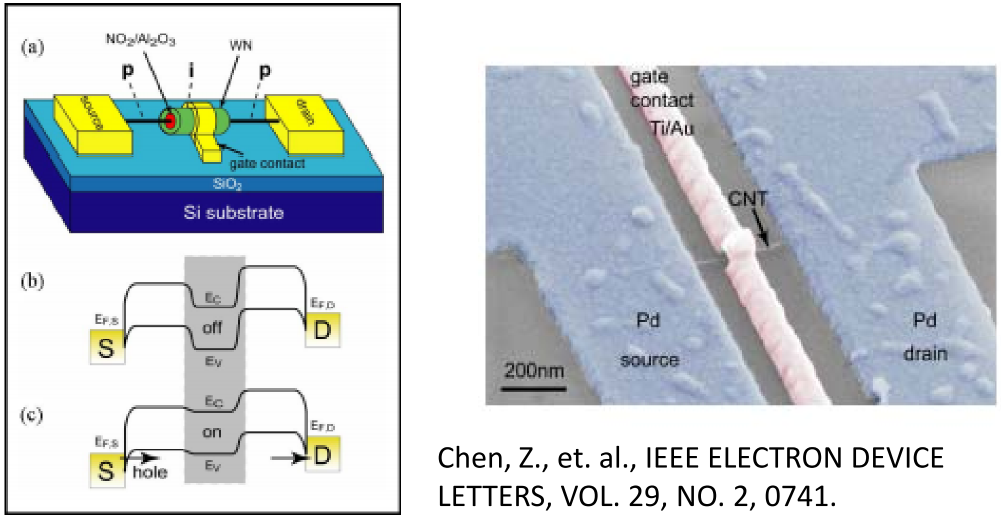
Sander J. Tans, et. al., *Nature* 1998, **393**, 49-52

Top-gated



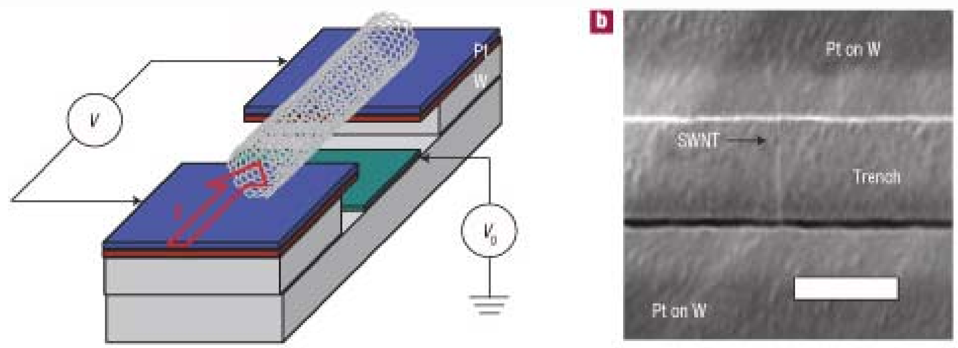
Wind, S. J. et. al., 2002 *Applied Physics Letters* **80** (20): 3817

Wrap-around gate



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

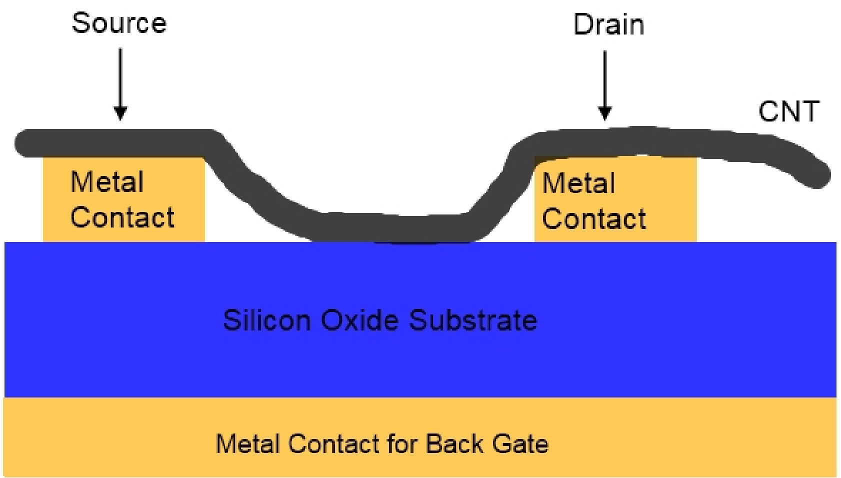
Suspended



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

Designs of CNT Transistors

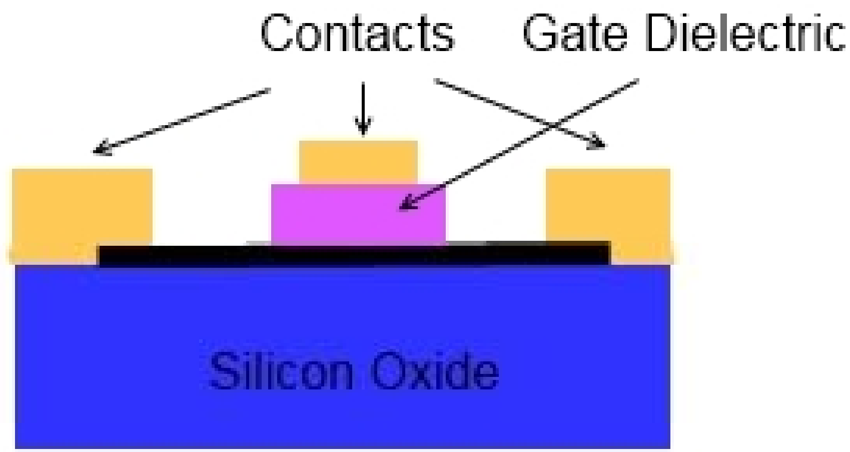
Back-gated



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

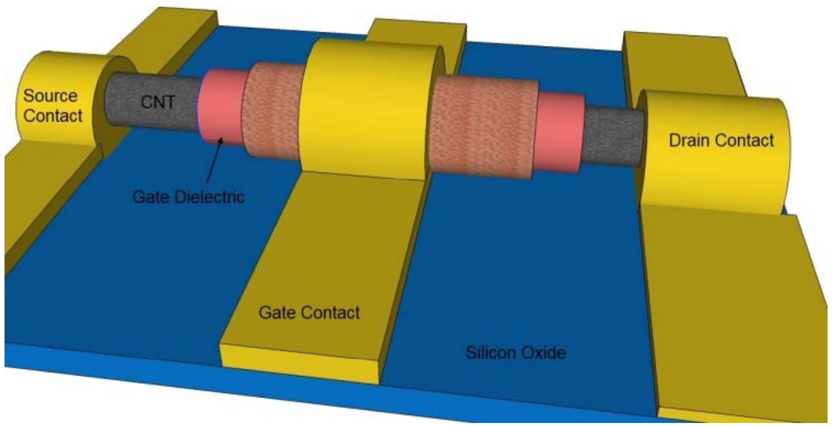
Top-gated



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

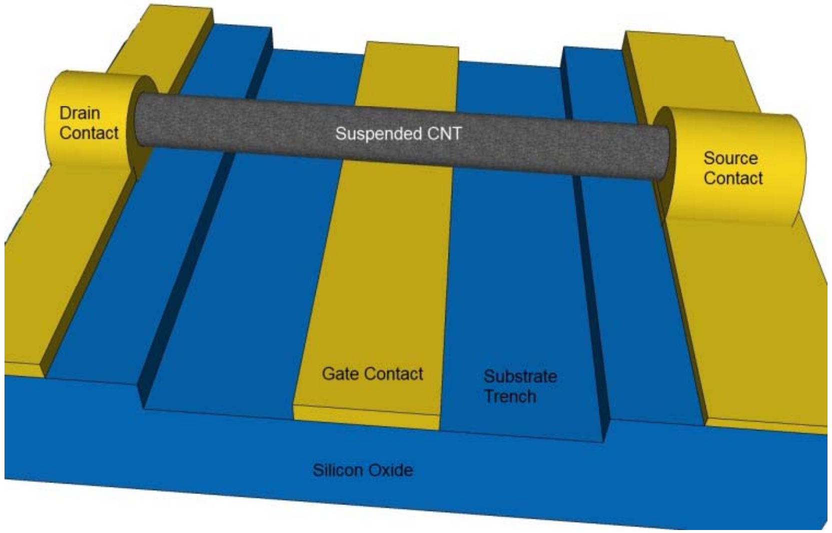
Wrap-around gate



Developed in 2008. This design
1. Improve the on/off ratio and the performance
2. Reduce the leakage current

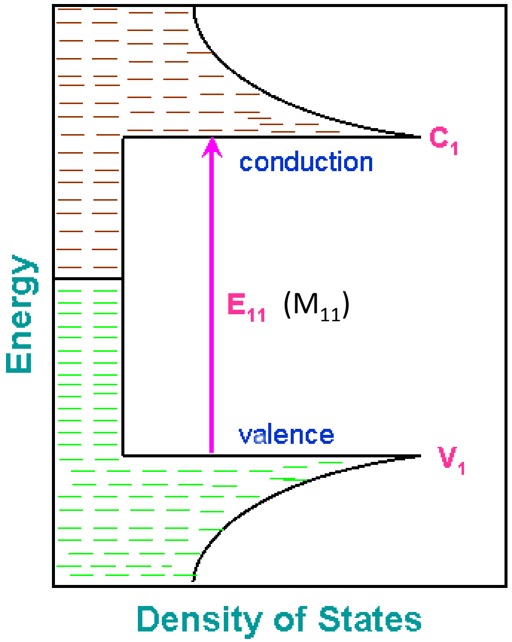
Z. Chen et al., *EDL* **29** (2), 183 (2008)
J. Cao et al., *Nature Materials* **4**, 745 (2005)

Suspended



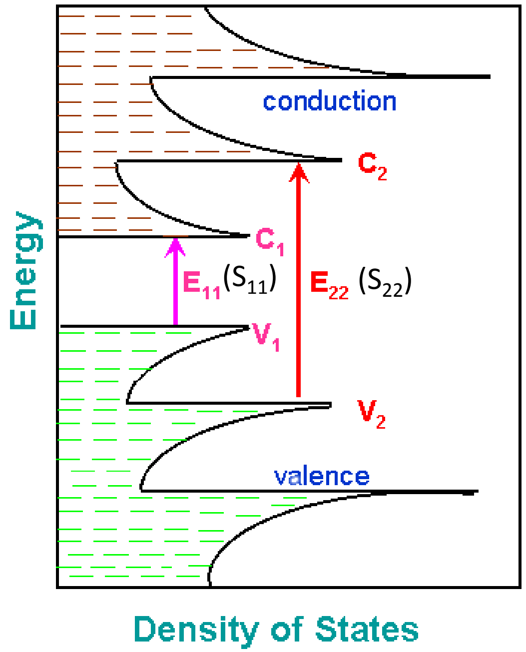
Developed in 2005. This design reduces the scattering at the interface of the CNT-substrate.
However, materials of devices are limited. It is only for studying the properties of clean CNT and cannot be commercialized.

Optical Properties of CNT



Metallic SWNT

$v_1 \rightarrow c_1$ corresponds to the "first van Hove" optical transition



Semiconducting SWNT

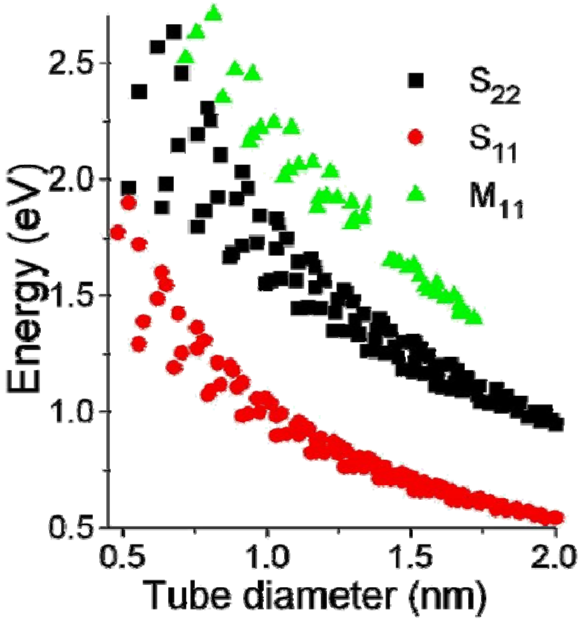
$v_2 \rightarrow c_2$ corresponds to the "second van Hove" optical transition

Van Hove singularity: The discontinuity of DOS of 1D materials

Optical Properties

- Because of the sharp transitions, we can selectively excite (n,m) CNT; namely, we can detect optical signals in order to identify (n,m) CNT

Kataura plot



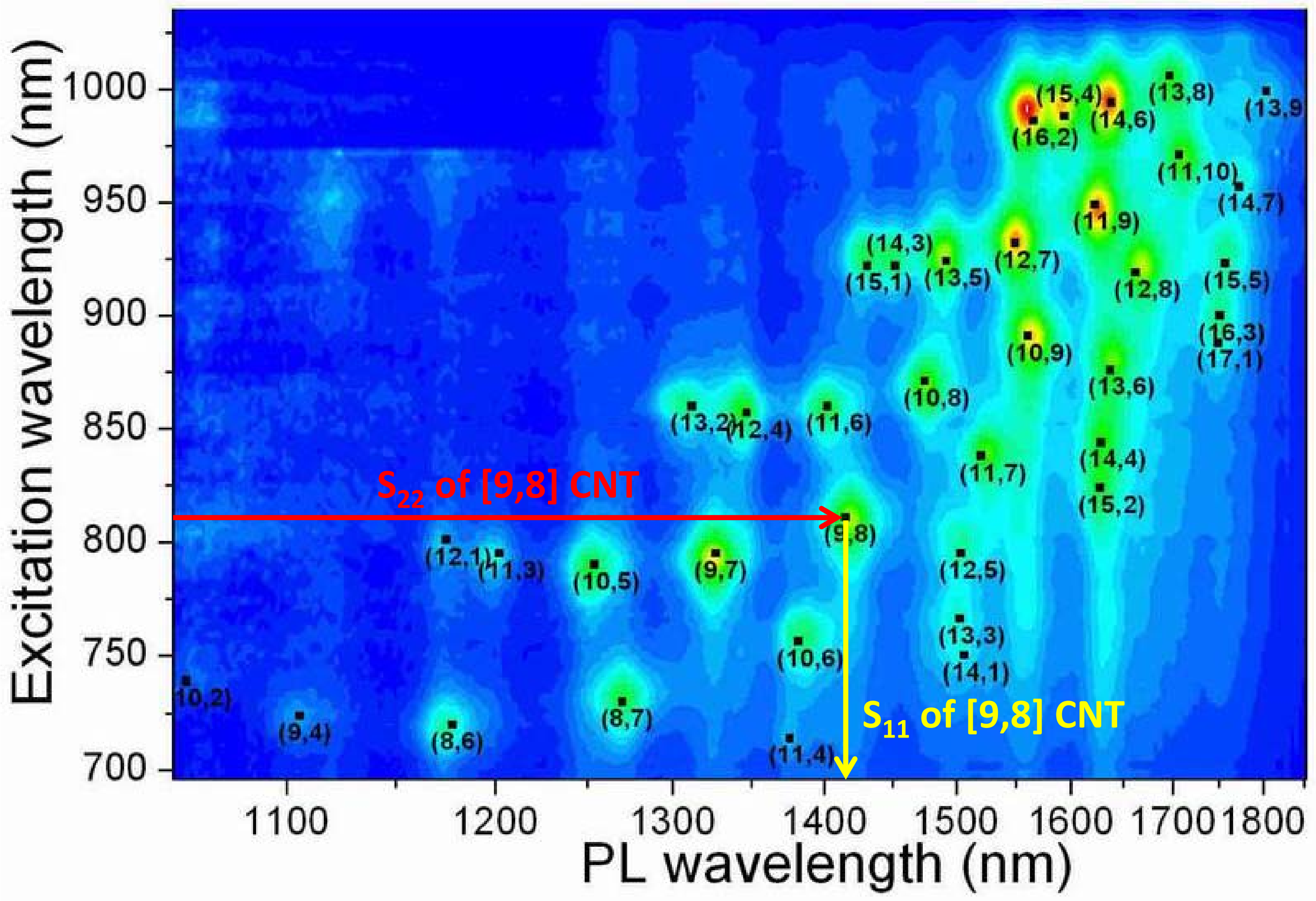
R. B. Weisman and S. M. Bachilo, *Nano Lett.* **3** (9), 1235 (2003)

Photoluminescence of CNT

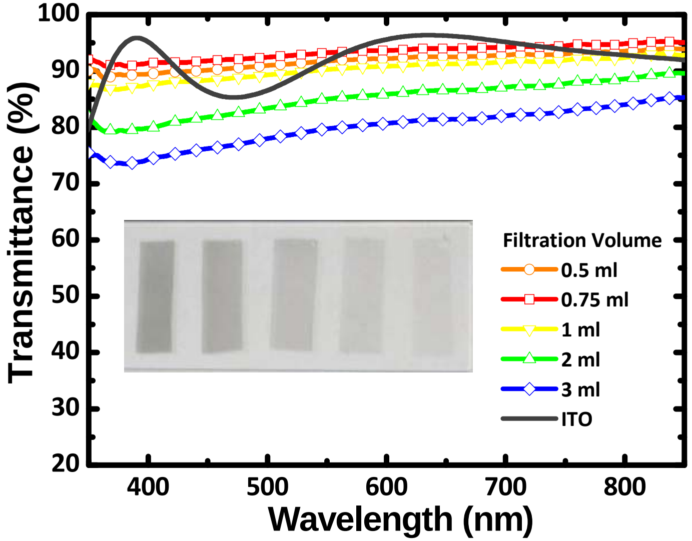
- Process of PL
  1. Excite S_{22} (C_2-V_2) and create the exciton pair
  2. Relax to C_1 and V_1 respectively
  3. Recombine and emit light with S_{11} (C_1-V_1) energy
- An important tools for characterizing semiconducting CNT

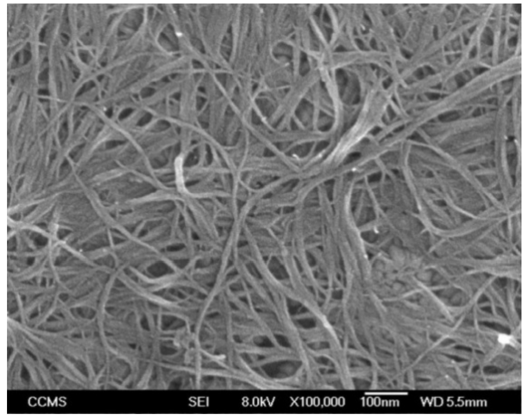
R. B. Weisman and S. M. Bachilo, *Nano Lett.* **3**, 1235 (2003)

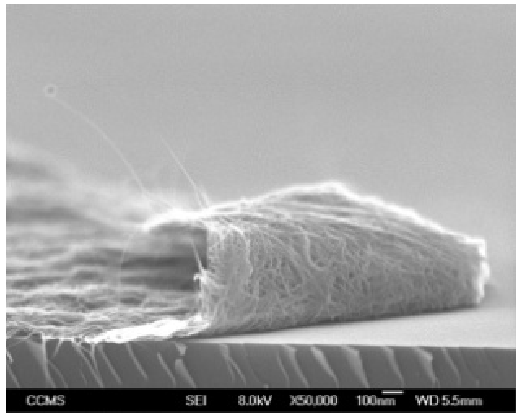
PL Mapping of CNT

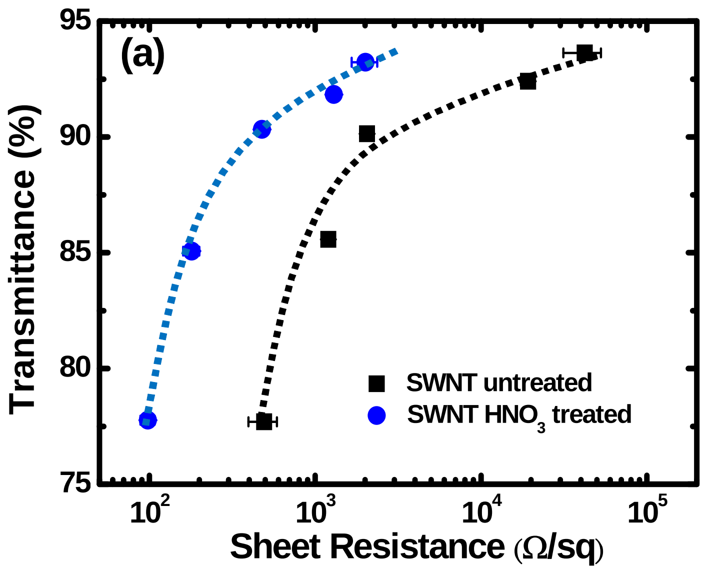


Applications: Optical and Electrical Properties of SWNT Electrode





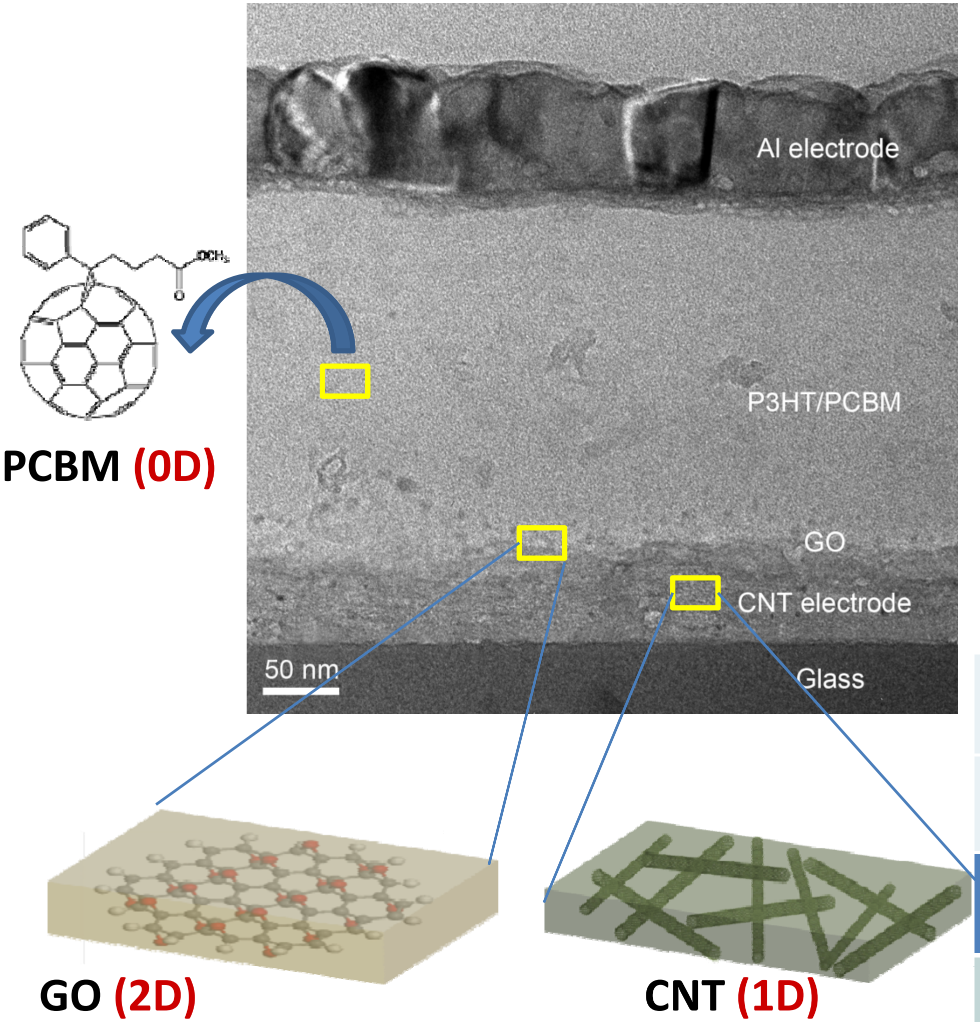


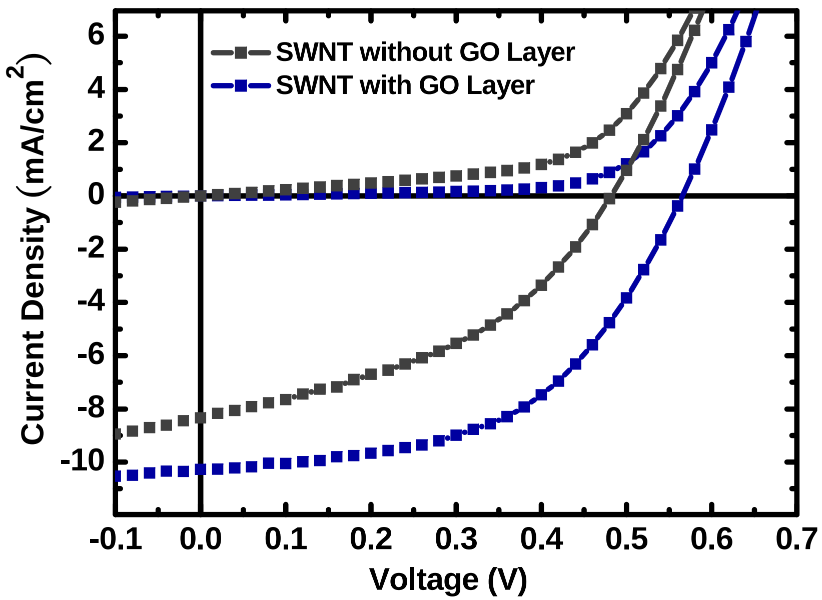


- SWNT electrode has high flexibility and excellent mechanical strength
- Sheet resistance of SWNT electrode can be further reduced by HNO_3 treatment
- Sheet resistance ~100 Ω/sq with 75% transparency @ 550nm

Energy and Environmental Science, 4.3521, (2011)

"Cocktail" nanocarbon polymer solar cell !

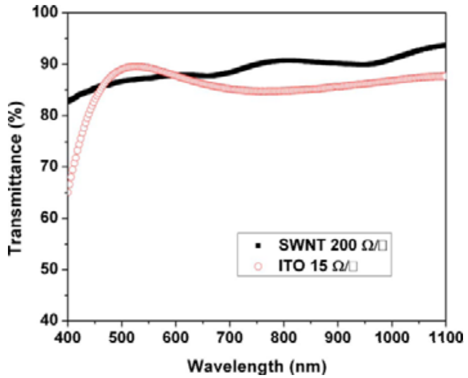




SWNT	Voc (V)	Jsc (mA)	Fill Factor	PCE (%)
Without GO	0.48	8.33	0.42	1.67%
With GO	0.57	10.3	0.53	3.1%
ITO/PEDOT:PSS	0.57	11.0	0.57	3.57%

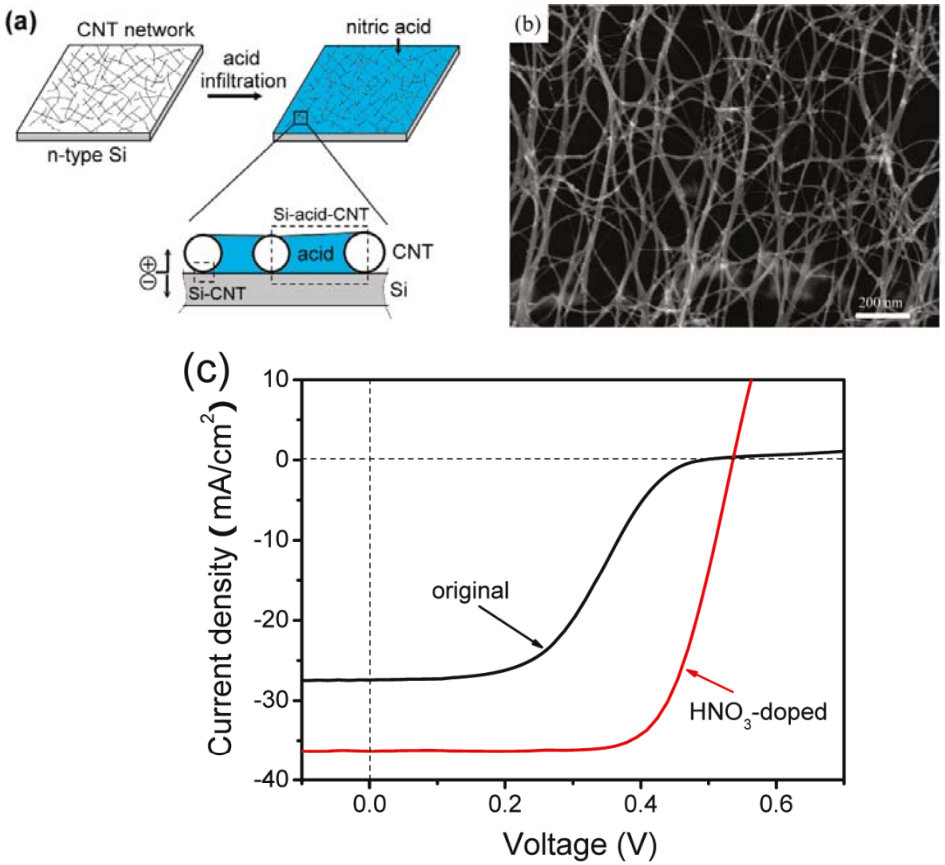
Energy and Environmental Science, 4,3521 , (2011)

Carbon Nanotube on photovoltaic and LED applications



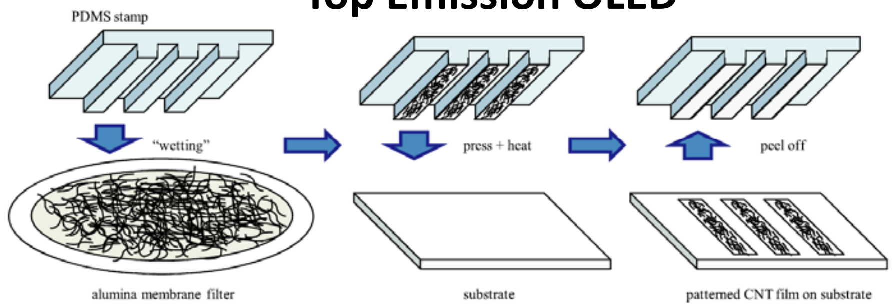
※High transparency on visible and NIR range
※Good conductivity
※Flexible

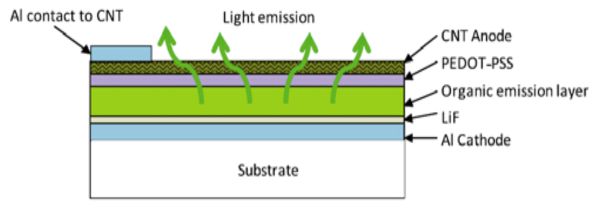
Silicon-CNT heterojunction solar cell

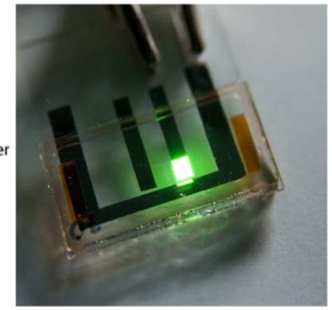


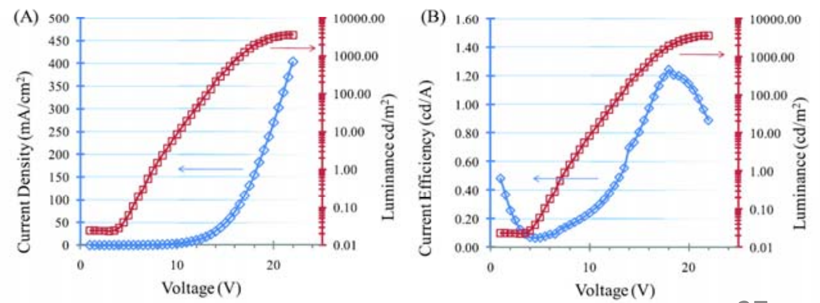
Jia, Y. et. al., *Nano Lett*, **2011**, *11,* 1901.

Top Emission OLED





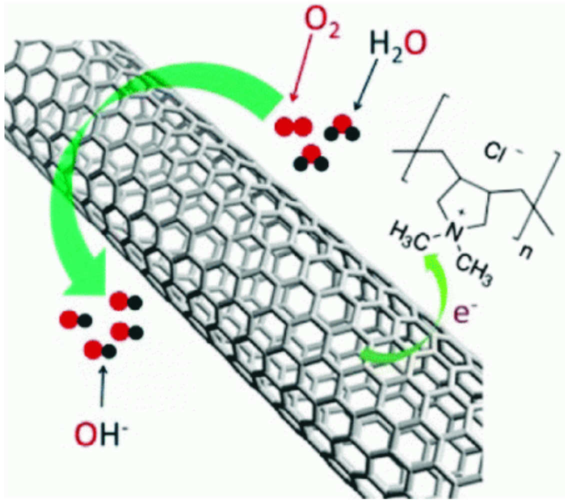




Chien, Y. M. et. al, *Nanotechnology*, **2010**, *21*, 134020

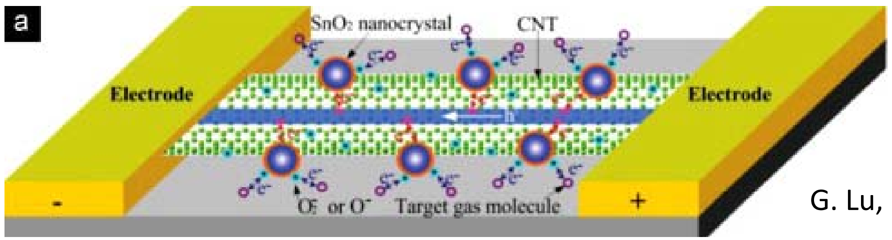
Other Applications

- Fuel cells
  - Store H_2 in CNT



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

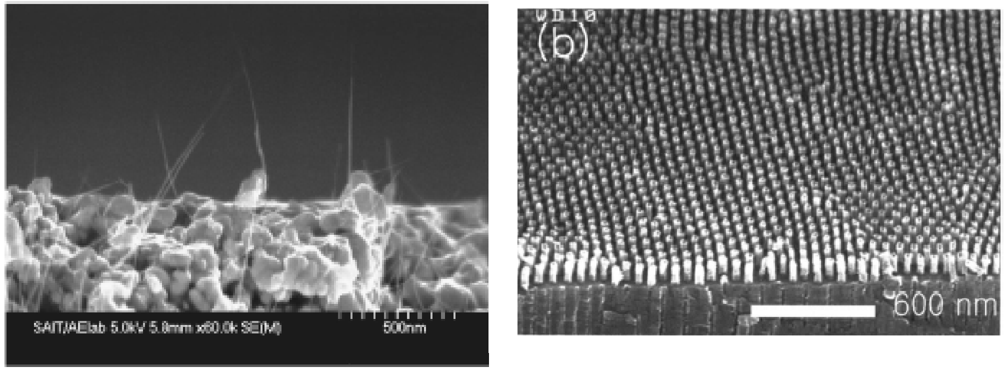
- Gas detector
  - Molecules adsorb on the channel of CNT FET, modifying the electrical properties of CNT



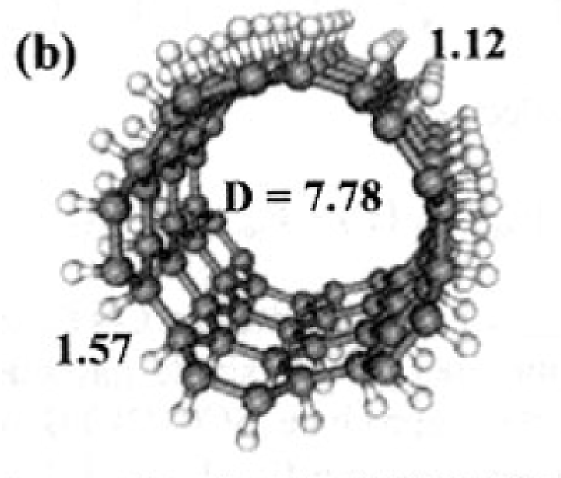
G. Lu, L.E. Ocola J. Chen, Adv. Mater, 2009, 21, 2487

Applications of Carbon Nanotube

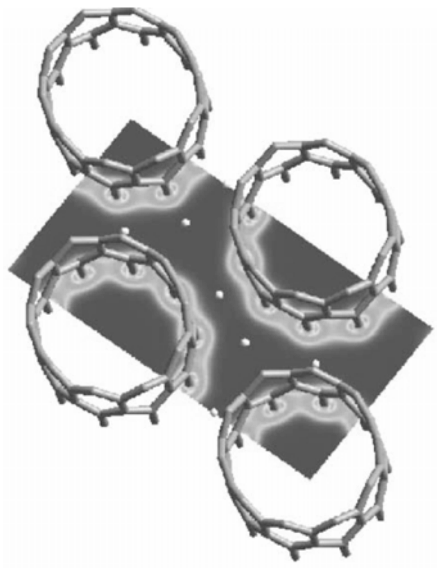
Field Emitter



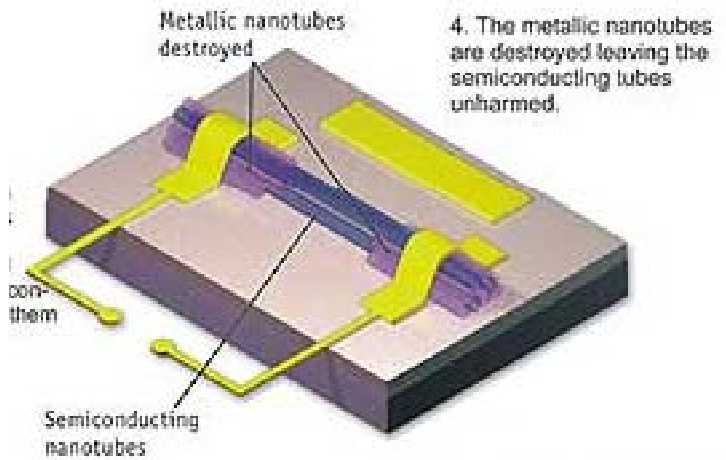
Hydrogen Storage



Li-ion battery anode

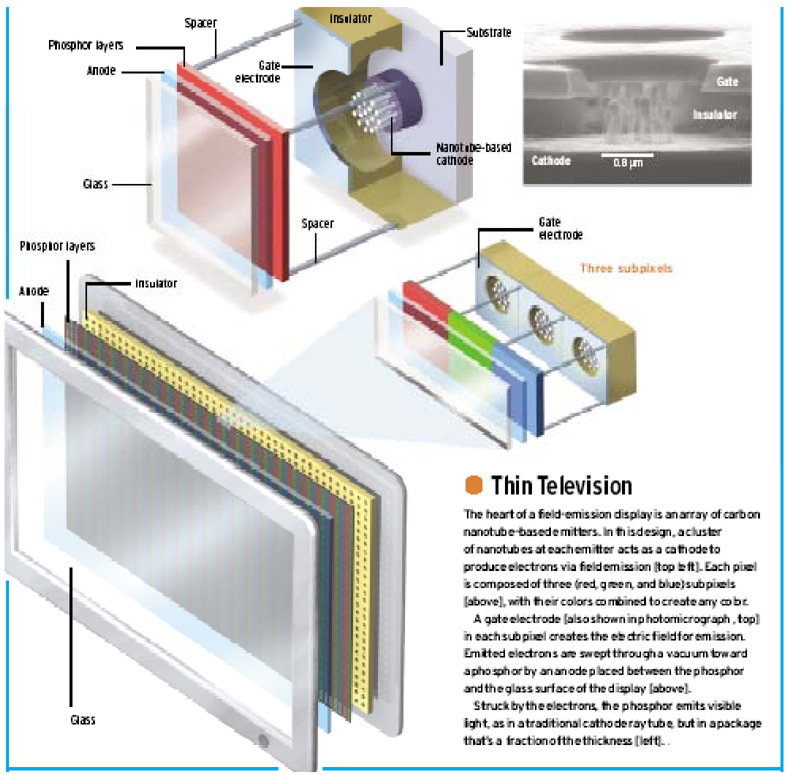


Logic gate by IBM



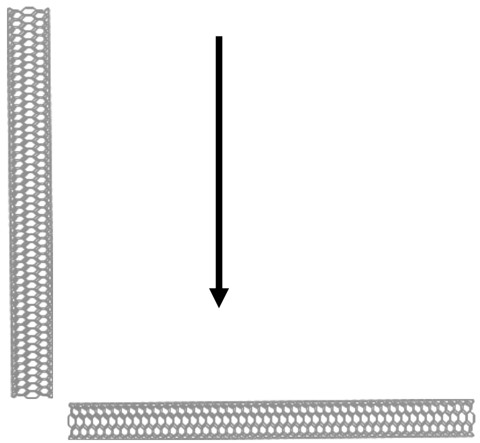
Applications of CNTs in electronic devices

CNT field emission display



From IEEE spectrum 2003

E field

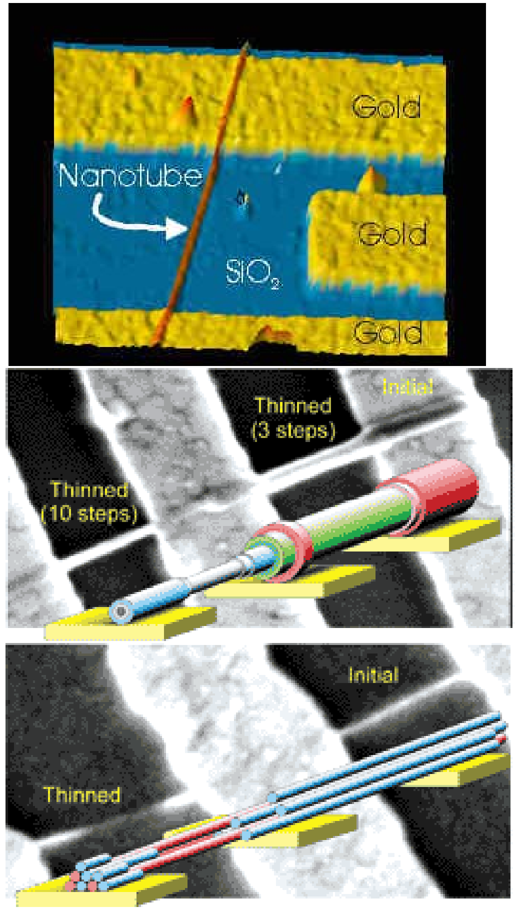


Small dimension

→High local field

→Electronic structure changes

CNT Field effect transistor



From IBM

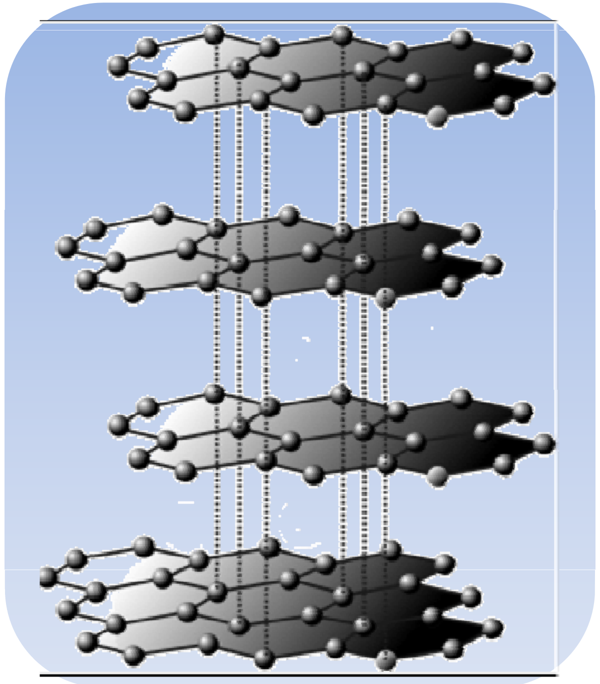
1-1. Introduction of Graphene

Graphene History

- Early: Theoretical description
- 1962: Named by Hanns-Peter Boehm (Graphite + -ene)
- 2004: Single-atom-thick, free-standing graphene is extracted (by Andre Geim and Konstantin Novoselov, Manchester University, U.K.)

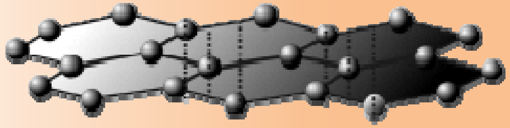
- 2005: Anomalous quantum Hall effect was observed
- 2010: Nobel prize in Physics for Andre Geim and Konstantin Novoselov
- Now: Stimulate wide researches and be applied to various fields

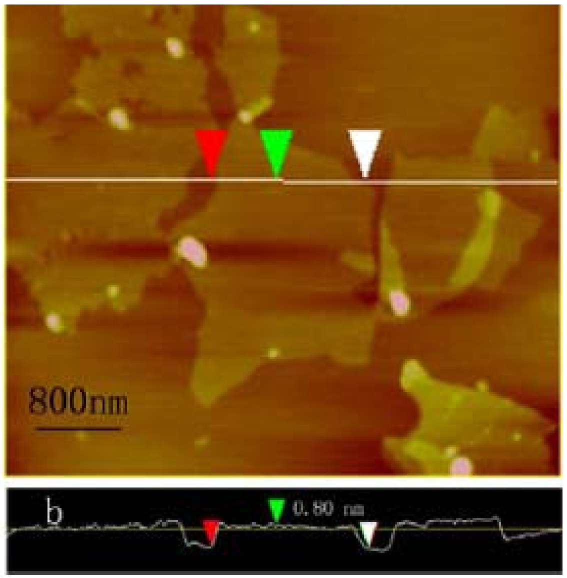
From graphite to graphene



Graphite
Multilayer carbon atom

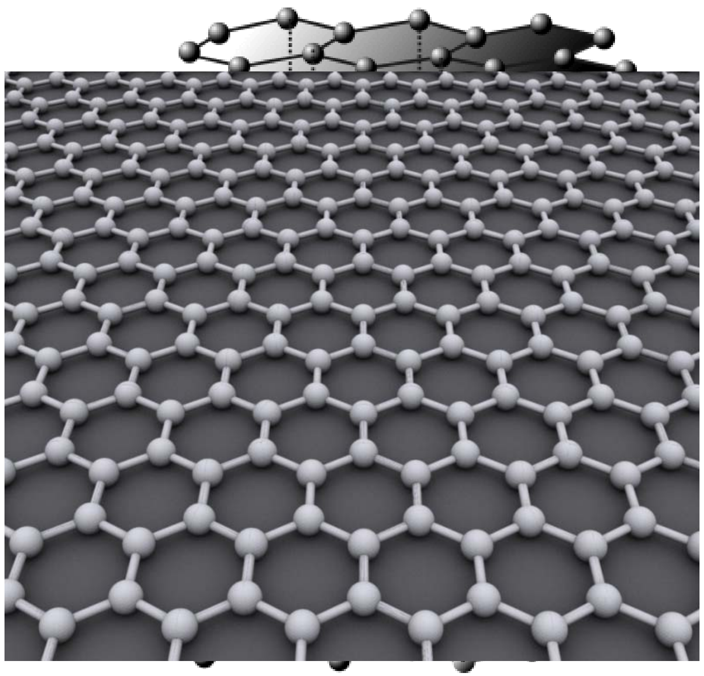
Graphene
Mono-atomic layer~1nm (10^{-9} m)





Graphene

- What is graphene?
  - A single layer of graphite
  - 2D material
- Structure
  - One-atom-thick planar sheet
  - sp^2-bonded carbon atoms
  - Honeycomb lattice



2010 The Nobel Prize in Physics

Photo: Sergeom, Wikimedia Commons

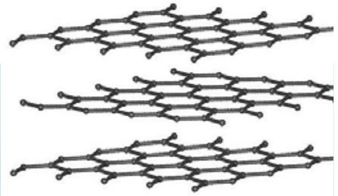
Andre Geim

Photo: University of Manchester, UK

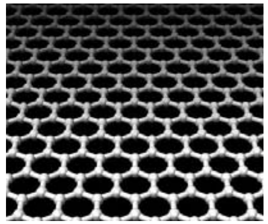
Konstantin Novoselov

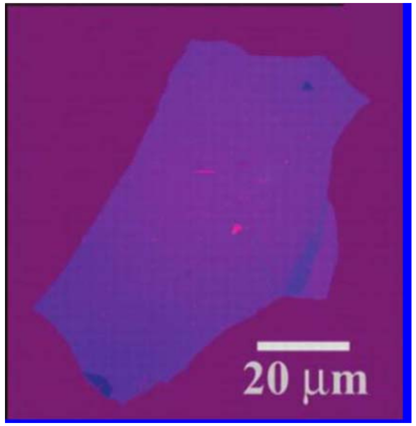
Prof. Andre Geim and Konstantin Novoselov at the U. Manchester for groundbreaking experiments regarding the 2-D material graphene

Graphite



Graphene

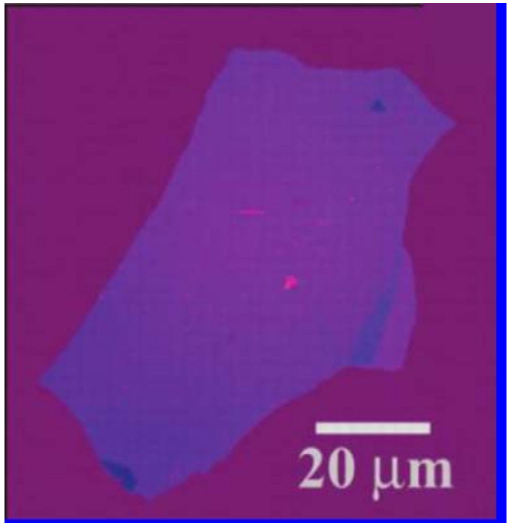


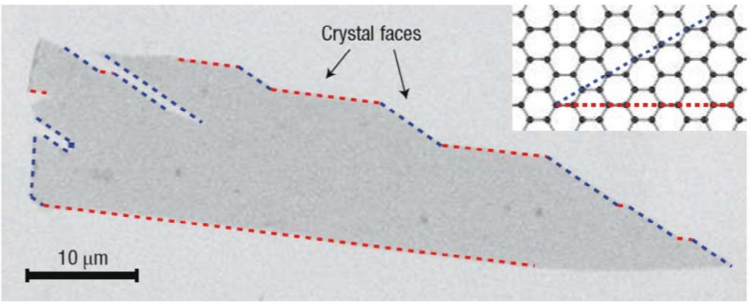


How to find the atomic layer “graphene” from repeatedly split graphite crystals by adhesive tape

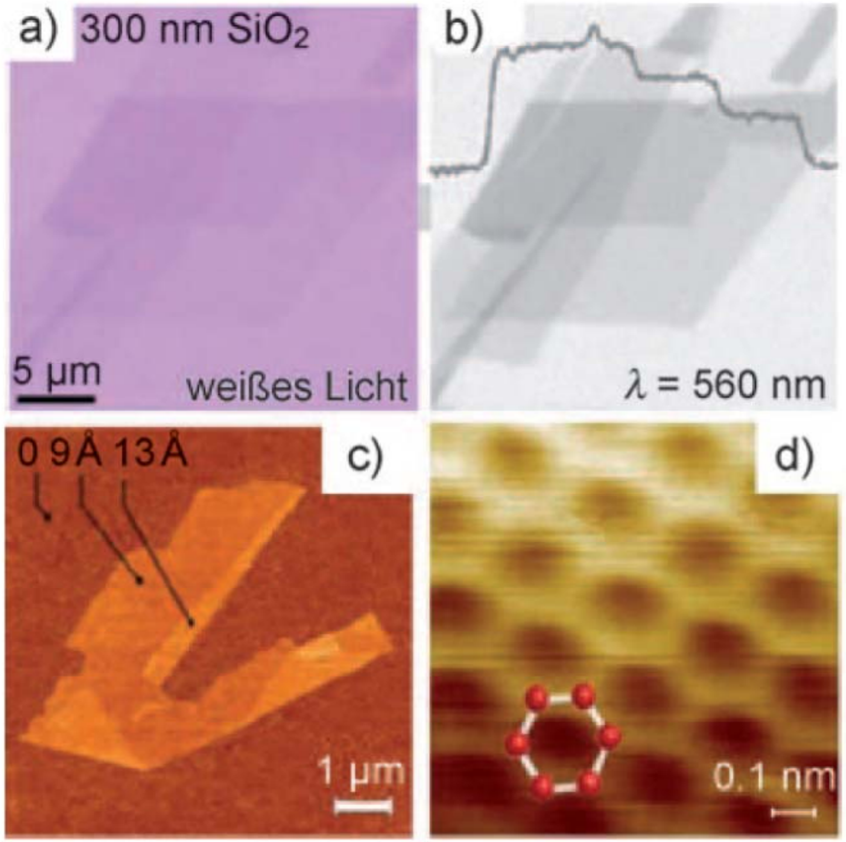
The properties of graphene

- The atomic structure, two-dimensional crystals
- The thinnest Materials



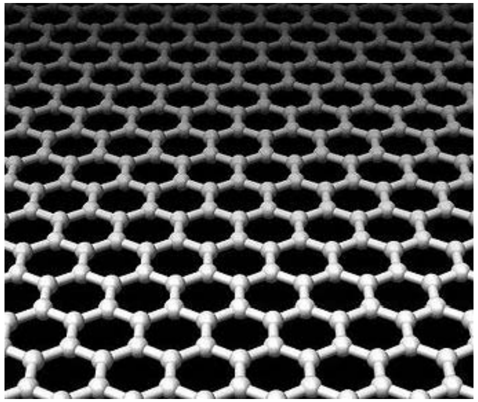


Kraner et al. Chem. Rev. 2010,110,132

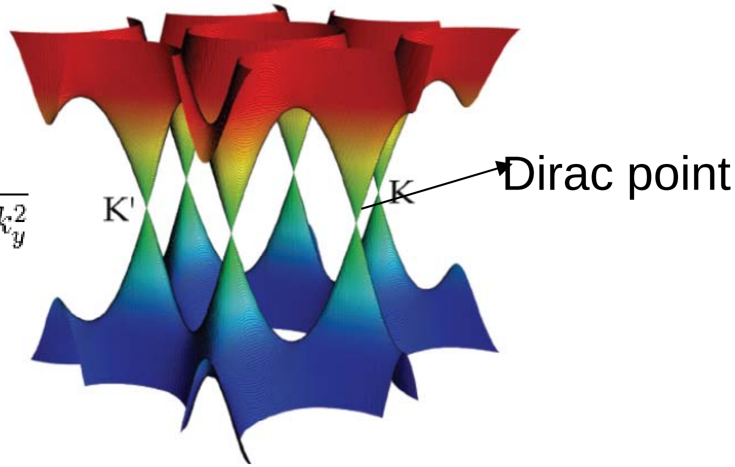


Rao et al, Angew. Chem., 2009,48,7752

Graphene

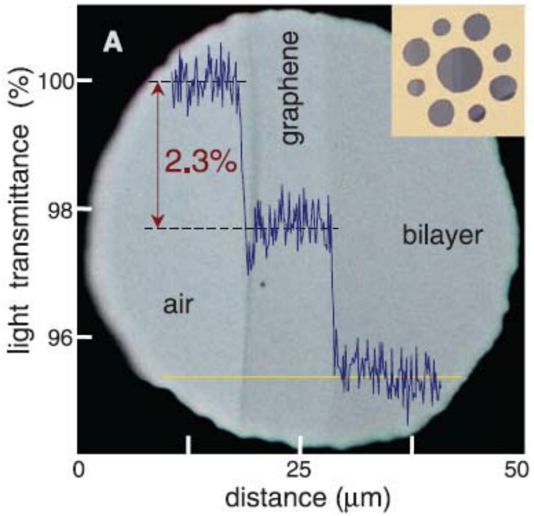


$$E = \hbar v_F \sqrt{k_x^2 + k_y^2}$$



Electronics

- **Zero effective mass near the Dirac point**
- **High carrier mobility >15,000 cm^2/ V^{-1}s^{-1}**
- **Low Resistivity about 10^{-6} Ω·cm, (< siliver)**
- **etc...**



Nair et al., Science, (2008)

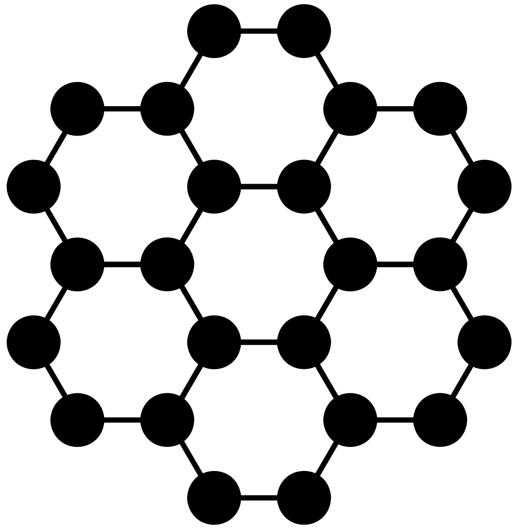
Optics

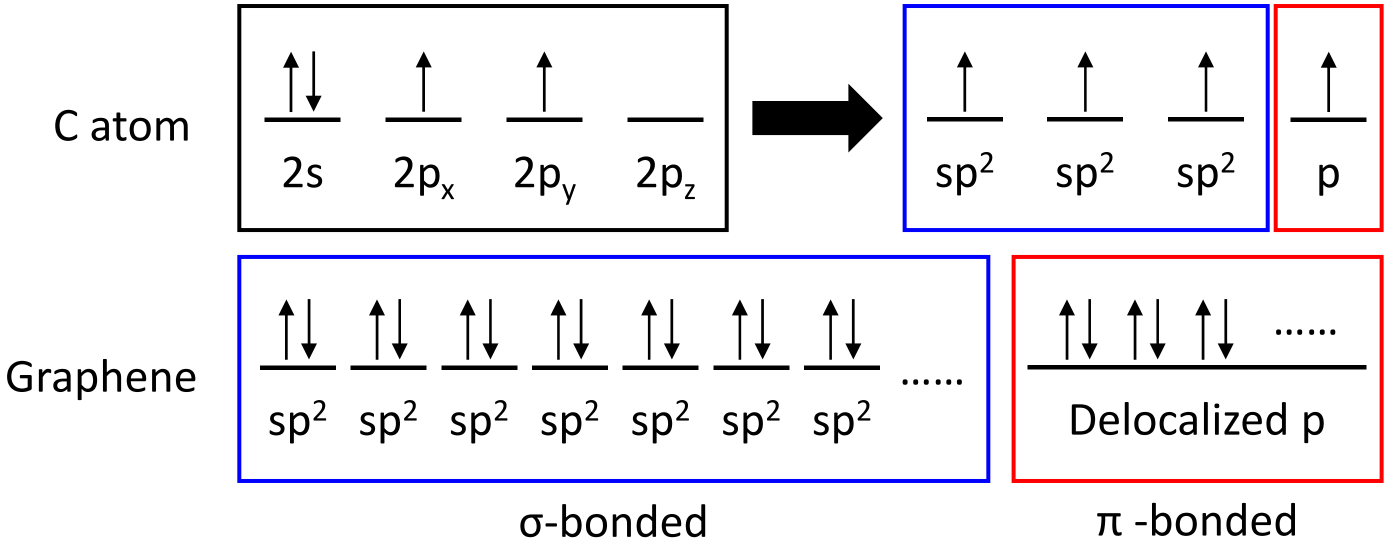
1. **One atomic layer absorption** $\frac{\pi e^2}{\hbar c} = \pi\alpha = 2.3\%$
2. **High transparency**

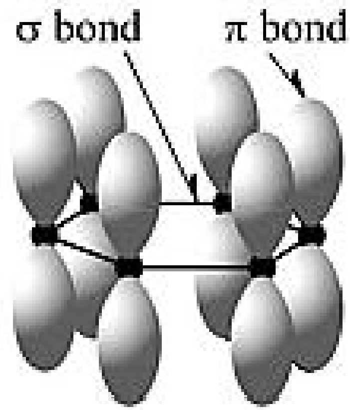
2010 Nobel prize award in Physics

Electronic Structure of Graphene

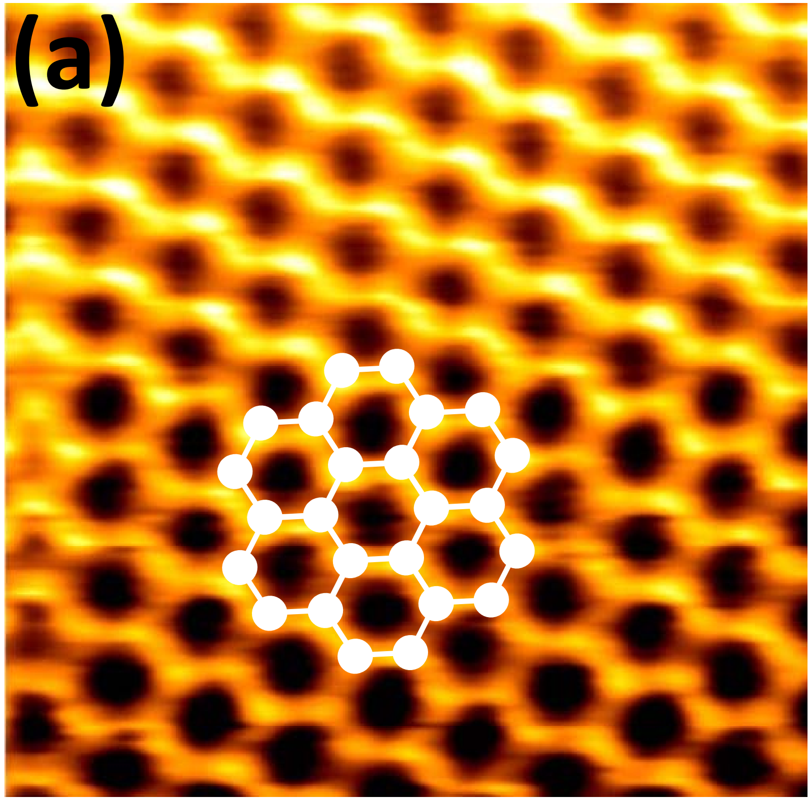
- All C atoms are sp^2-bonded to adjoining C atoms
  - sp^2 electrons form σ bonds
    - Form the honeycomb net of C atoms
  - Delocalized p electrons form π bonds



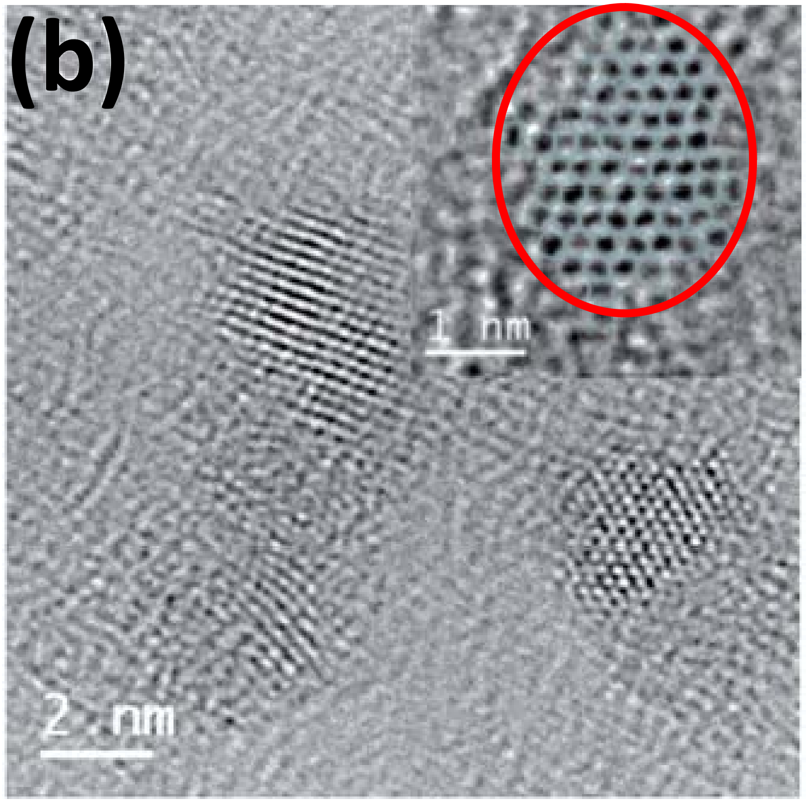




Electronic Structure of Graphene

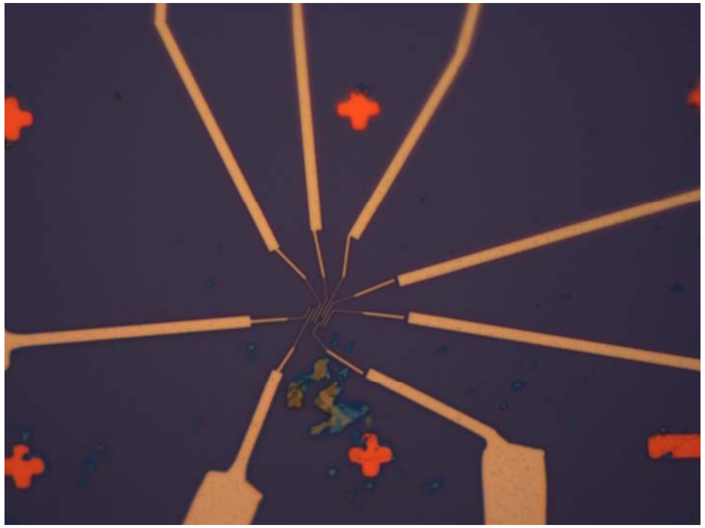


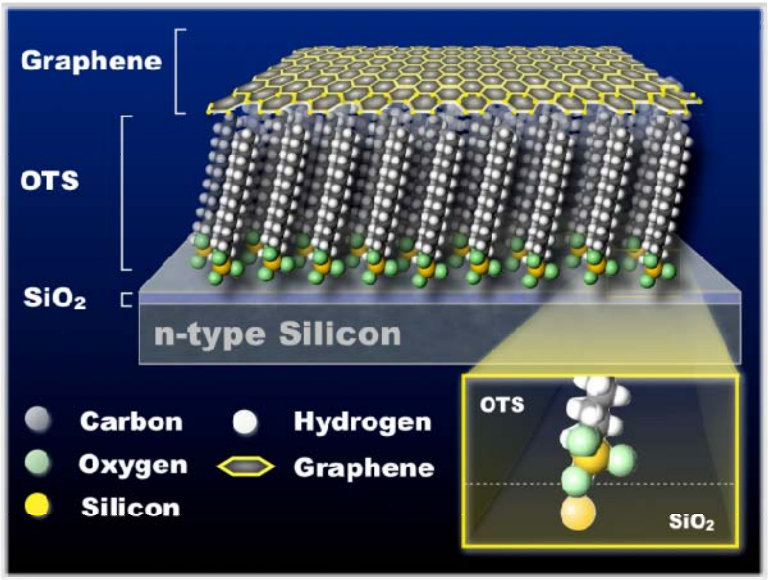
(a) STM image of graphene

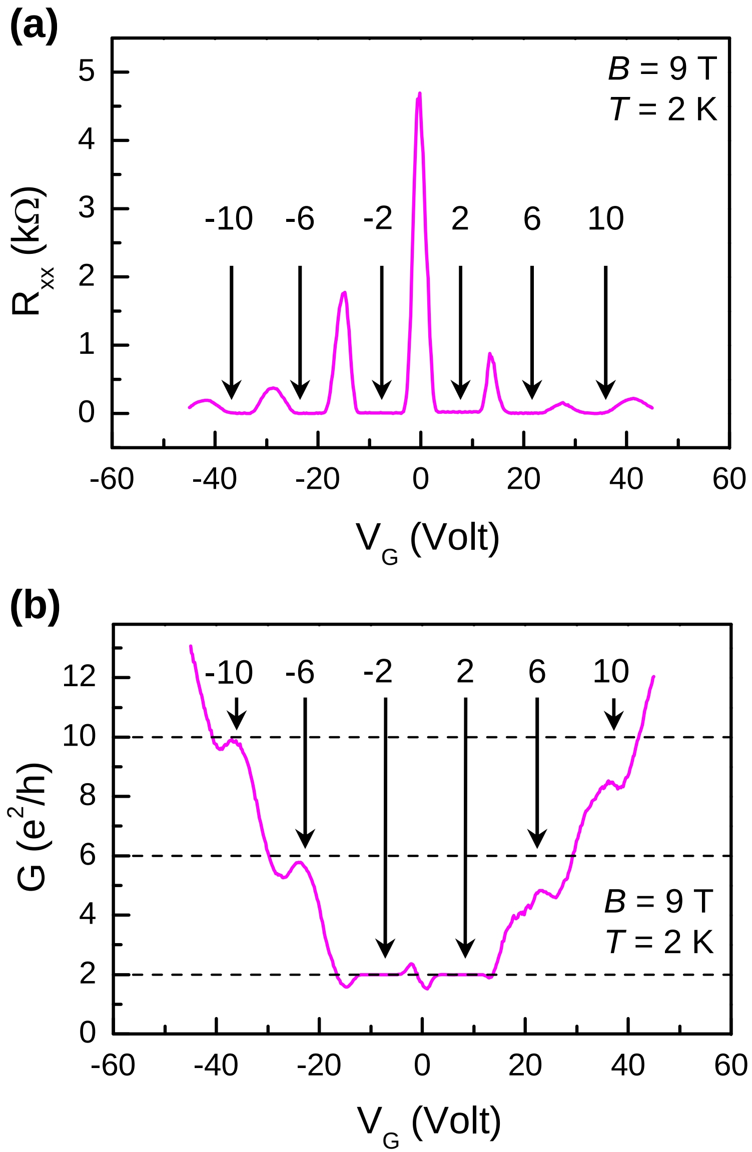


(b) TEM image of graphene clusters within graphene oxide

Graphene transistor device with high mobility







***Nano Letters*, 12, 964-969 ,(2012)**

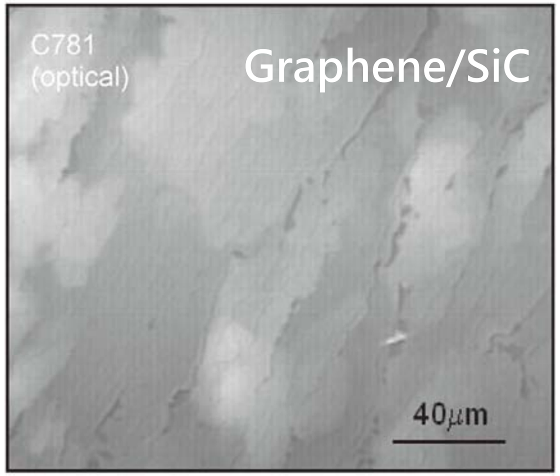
1-2. Synthesis of Graphene

Synthesis of Graphene

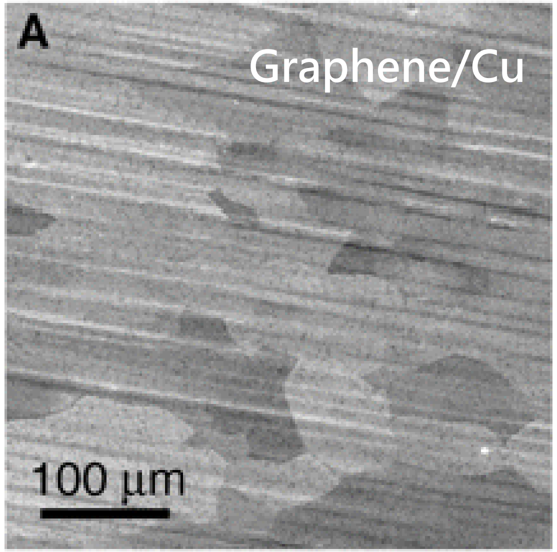
- **Mechanical exfoliation**
- **Epitaxial growth on silicon carbide**
- **Epitaxial growth on metal substrates**
- **Reduction of graphene oxide**

=> solution processible, mass producible, simple and cheap

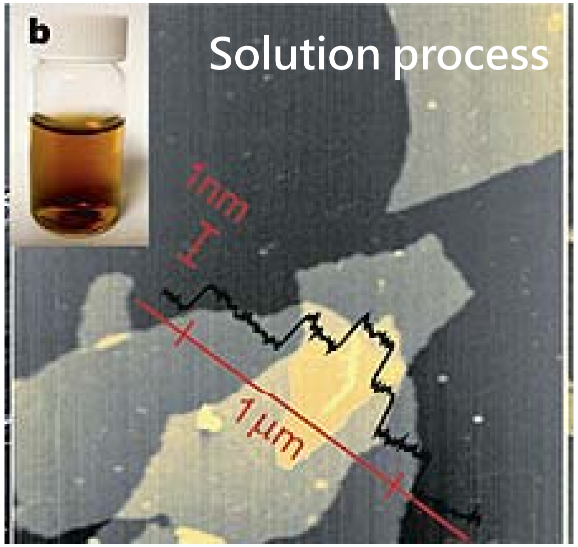
Novoselov et al., *Science* (2004)



de Heer et al, *Science* (2006)



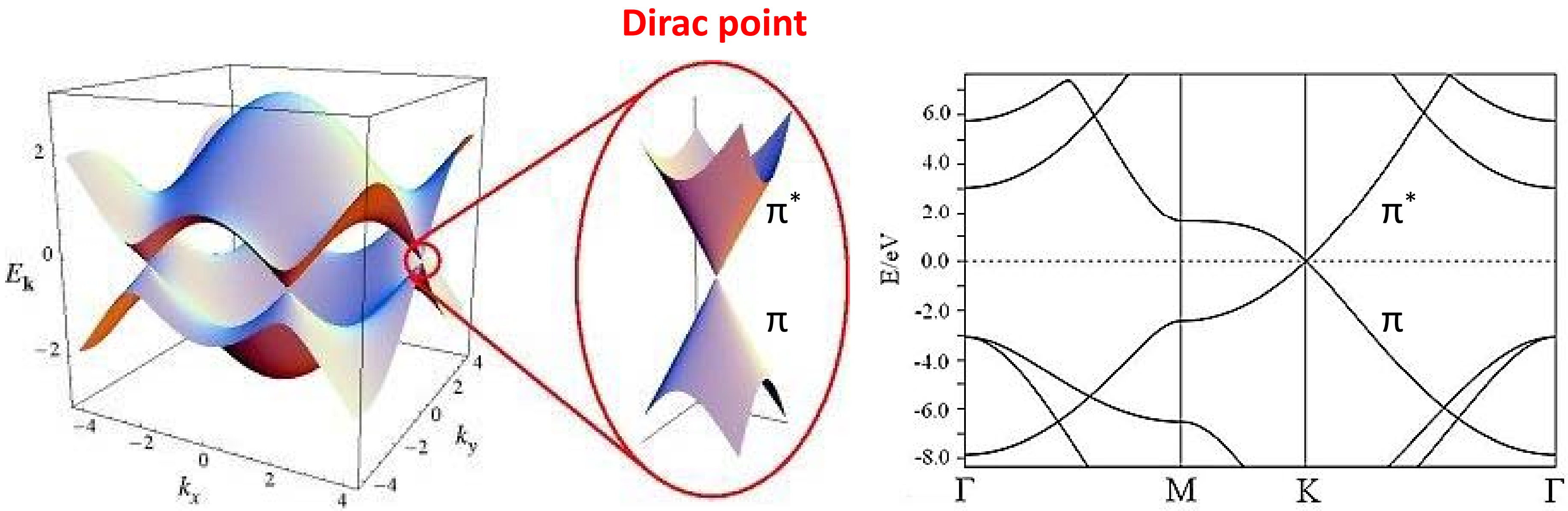
Ruoff et al., *Science*, vol. 324, pp1312-1314, **2009**



Sasha Stankovich, et al., *Nature* 442, 282-286, **2006**

1-3. Properties of Graphene

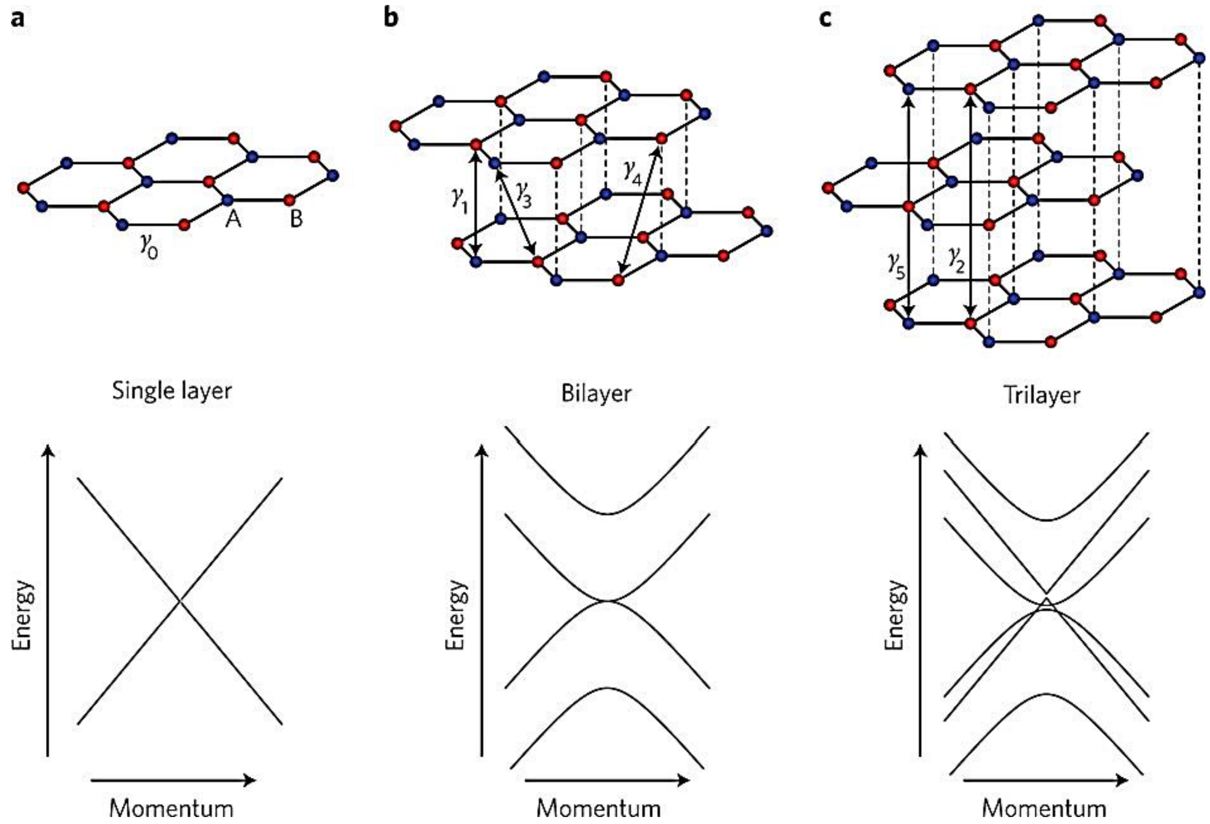
Band Structure of Graphene



- The valence band and the conduction band meet at Dirac point
  - Metallic behavior
  - “Semi-metal” or “zero-bandgap semiconductor”
- Linear E-k dispersion near Dirac point
  - “Massless” electrons and holes

Band Structure of Graphene

- How about multi-layered graphene?

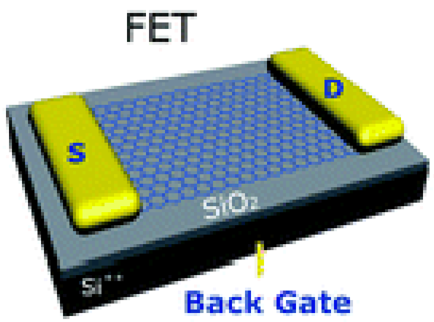


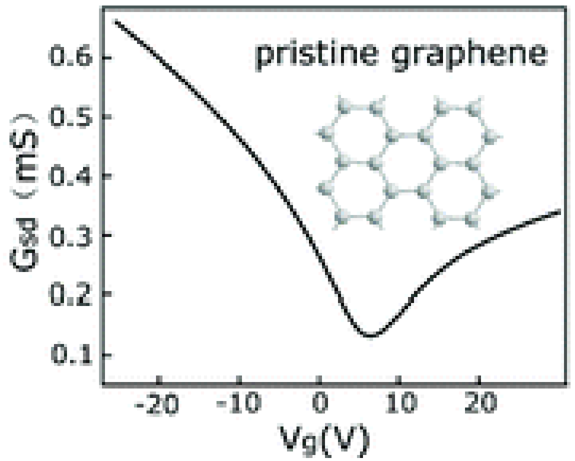
[8] Marcus Freitag, *Nature Physics* **7**, 596 (2011)

Electronic Properties

- Semi-metal
  - Zero bandgap
- High electron mobility at room temperature
  - Excess of 15,000 $cm^2V^{-1}s^{-1}$
- Can be doped
  - In order to increase the carrier concentration

Graphene transistor

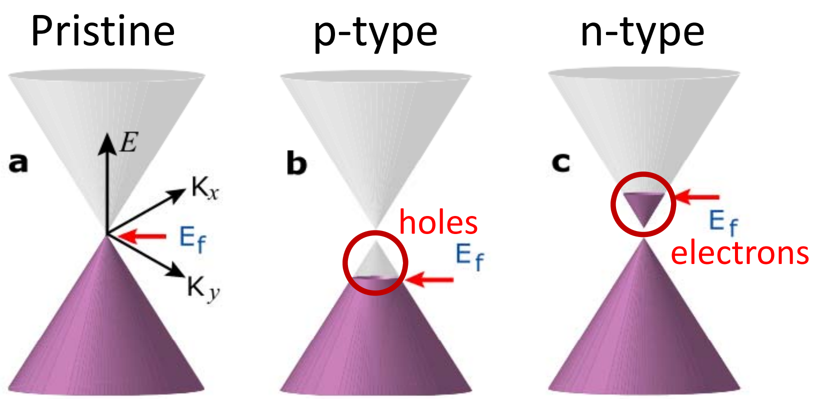




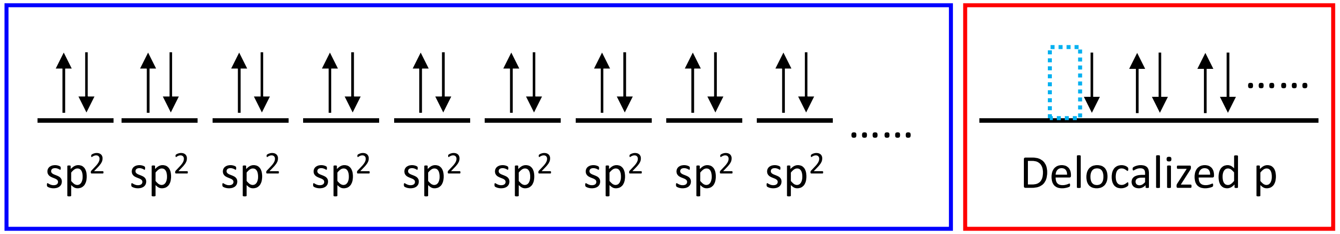
Nano Lett., **2010**, *10* (12), pp 4975–4980

Doped Graphene by heteroatoms

- Doping by heteroatoms
  - p-type doping
    - Group IIIA, such as B
  - n-type doping
    - Group VA, such as N and P

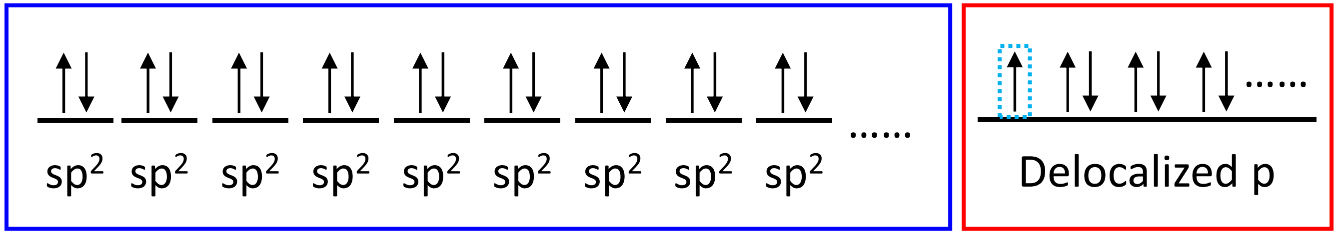


p-type:



Create holes

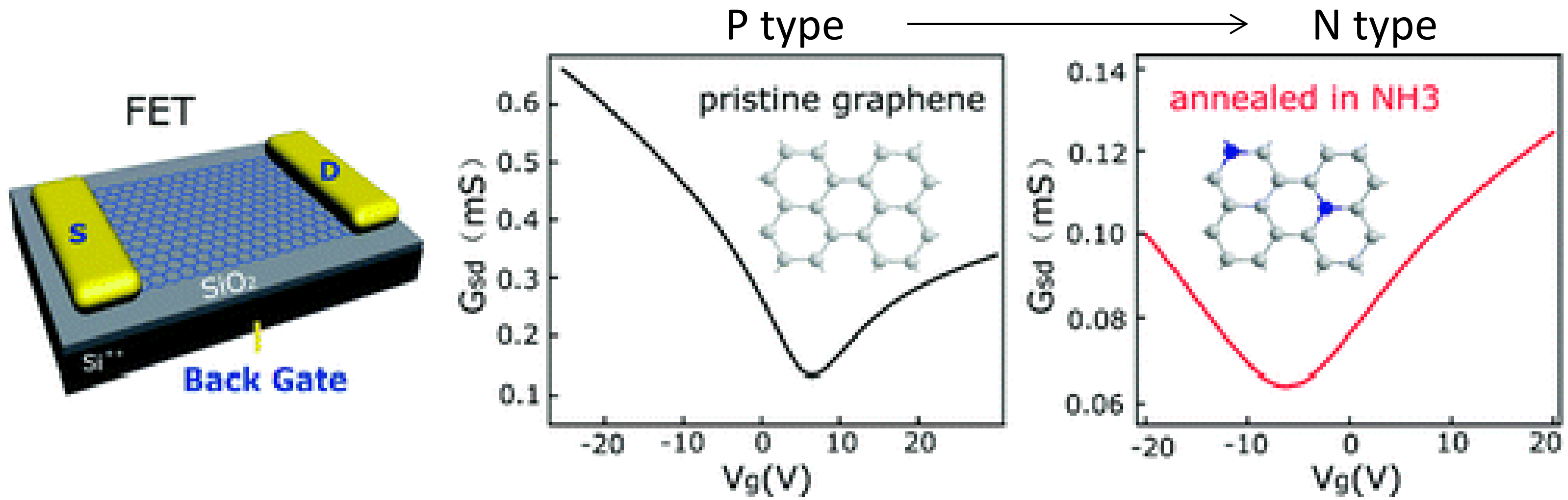
n-type:



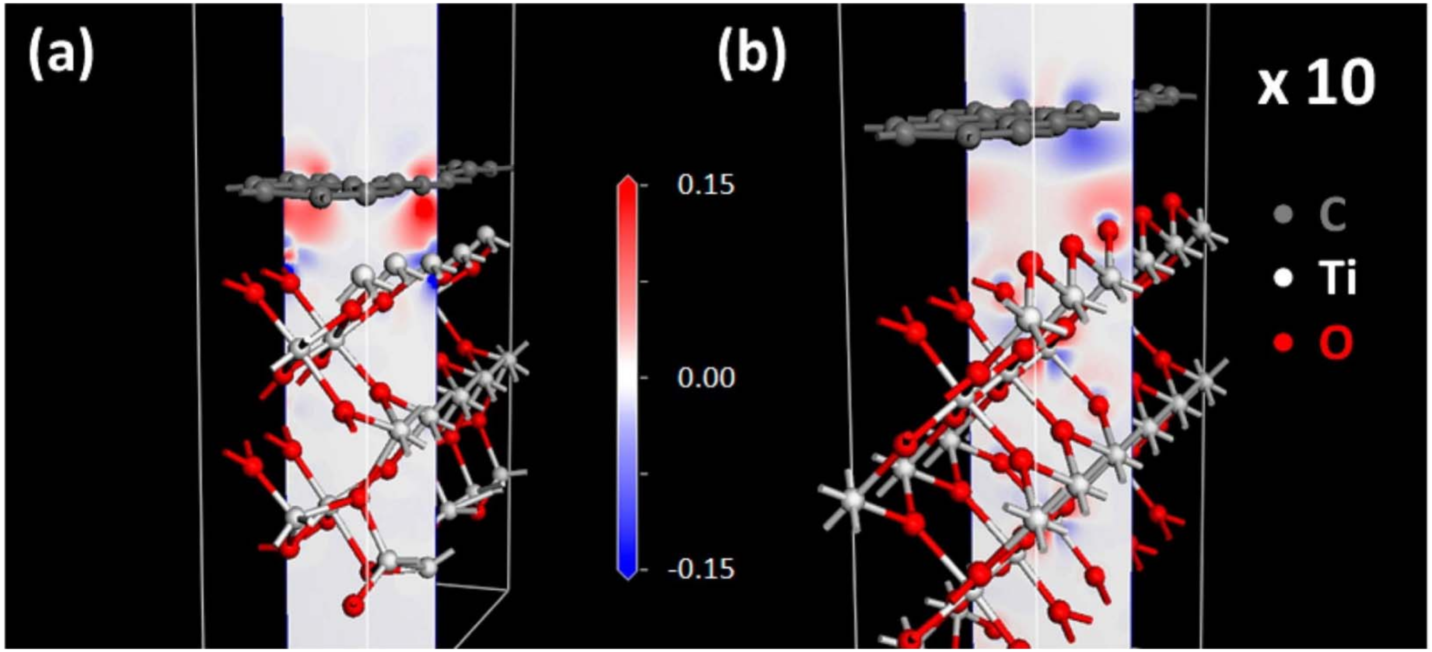
Create electrons

Doped Graphene by chemical modification

- Doping by chemical modification
  - Charge transfer
  - Molecules adsorb on graphene, acting as donors or acceptors
  - Epitaxial graphene can be doped by the substrate



Substrate Doping of Graphene

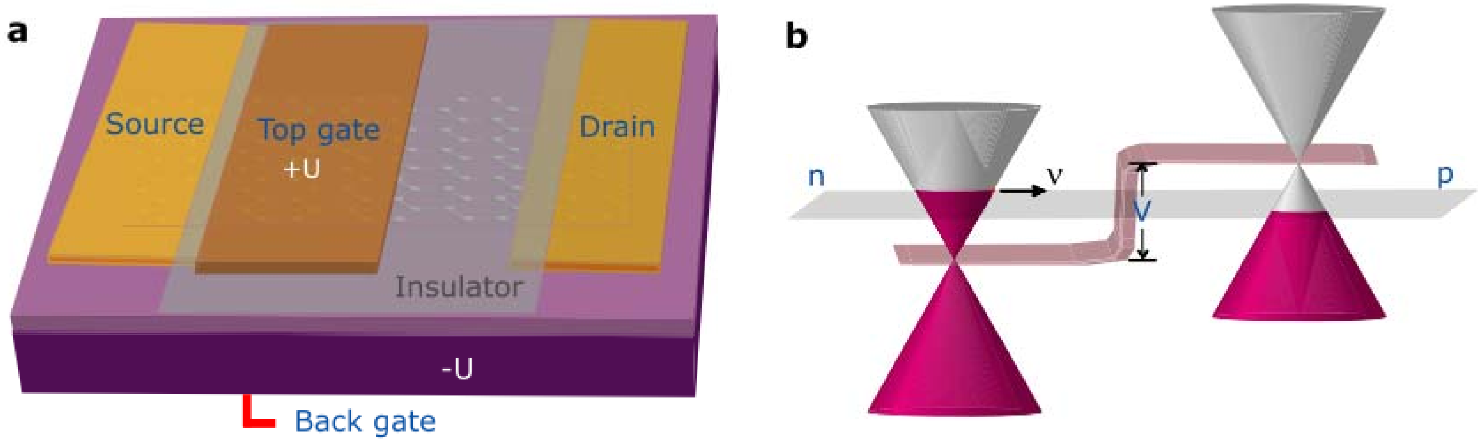


(a) Graphene is n-type doped by Ti-rich TiO_2 surface
(b) Graphene is p-type doped by O-rich TiO_2 surface

PH Ho, CW Chen et al., *ACS Nano* **6** (7), 6215 (2012)

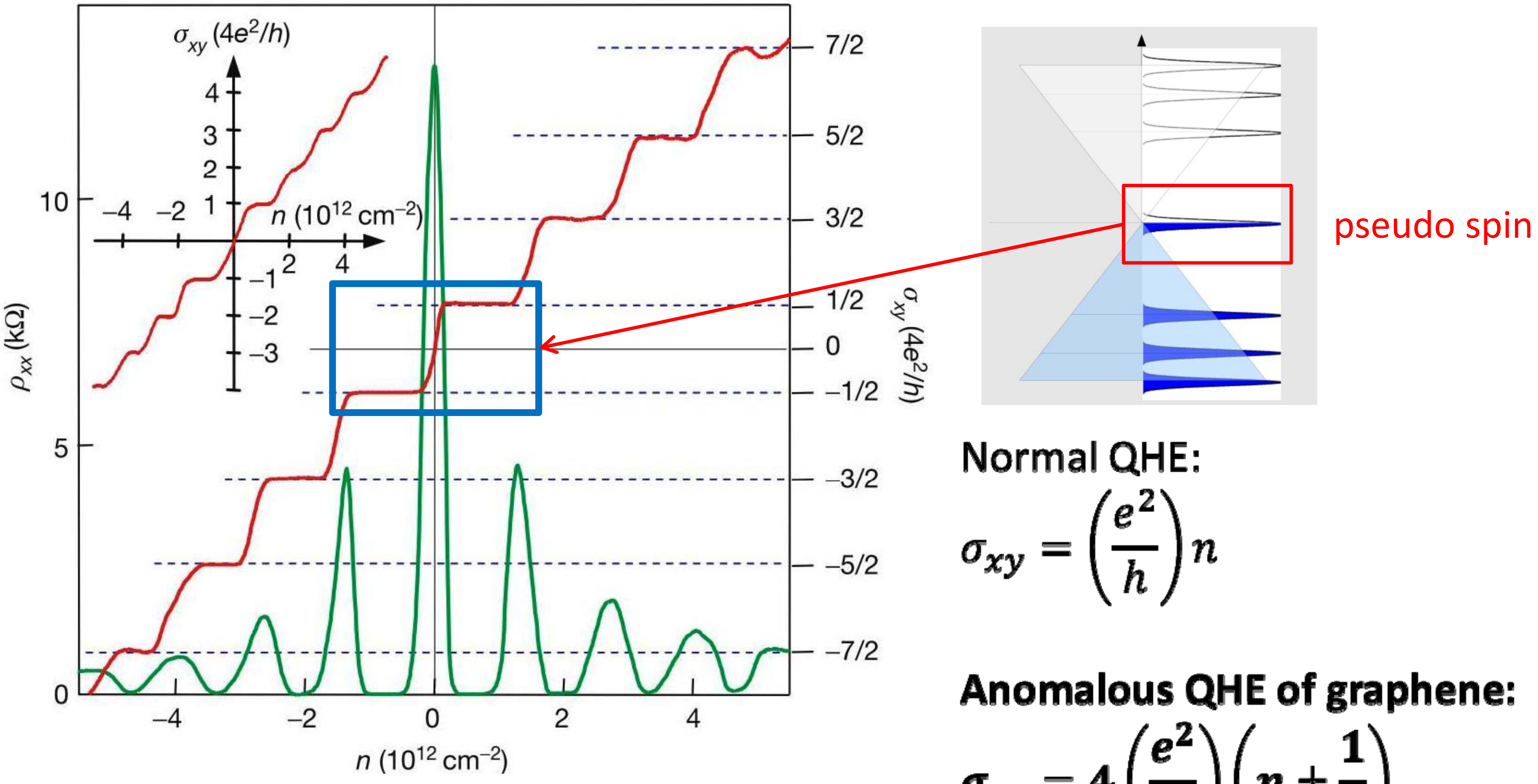
Doped Graphene by electric field

- Doping by electric field
  - Use electric field to shift the Fermi level of graphene



B. Guo et al., *Insciences J.* **1** (2), 80 (2011)

Anomalous Quantum Hall Effect



Novoselov, K. S et al., *Nature* **438**, 197 (2005)

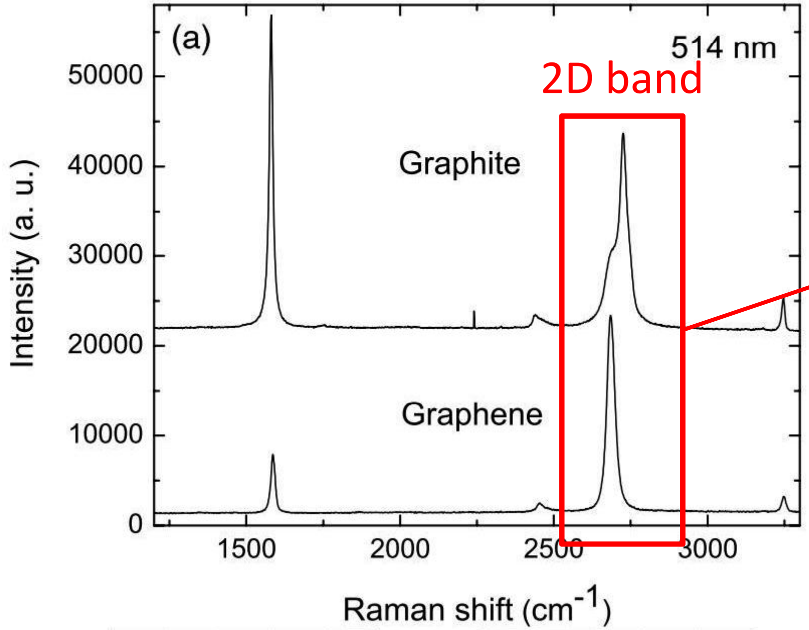
Normal QHE:

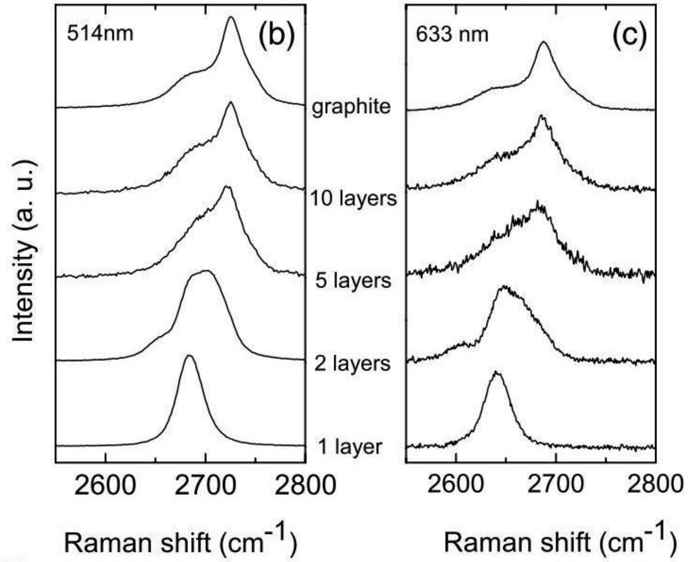
$$\sigma_{xy} = \left(\frac{e^2}{h}\right) n$$

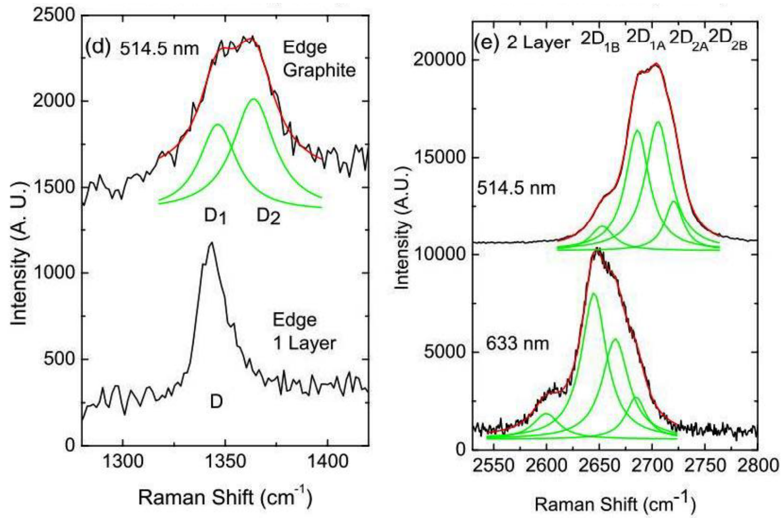
Anomalous QHE of graphene:

$$\sigma_{xy} = 4\left(\frac{e^2}{h}\right)\left(n \pm \frac{1}{2}\right)$$

Raman Spectra of graphene





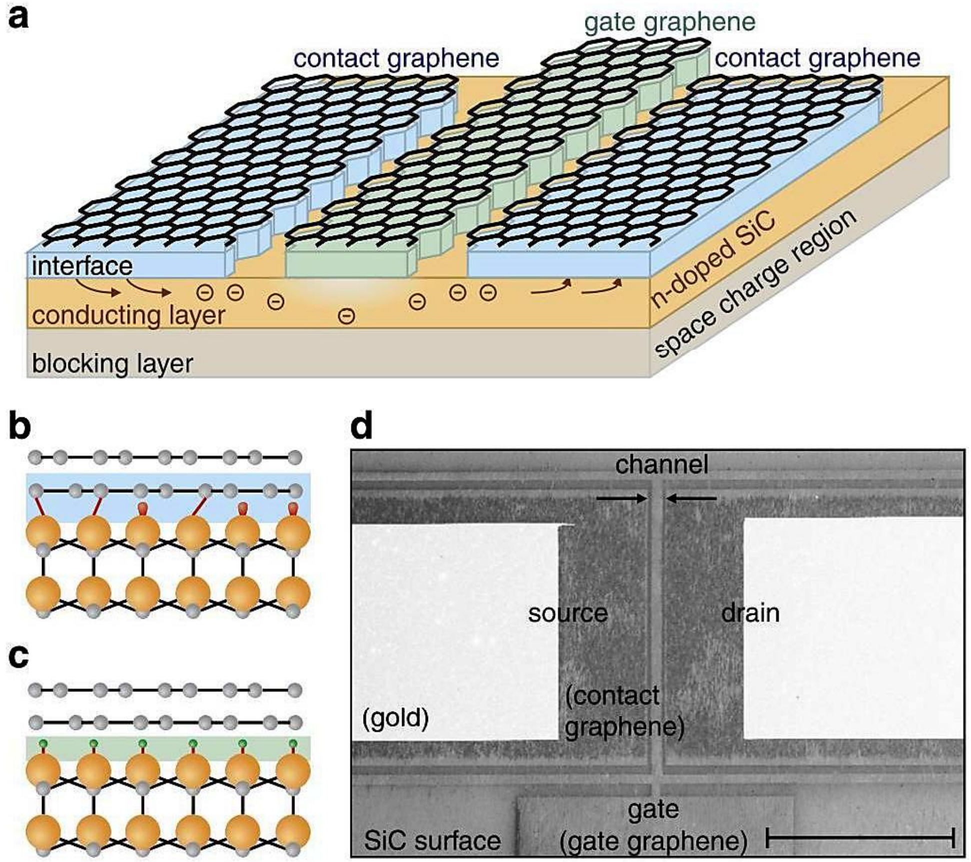


- Identify the layers of graphene

A. C. Ferrari et al., *PRL* **97**, 187401 (2006)

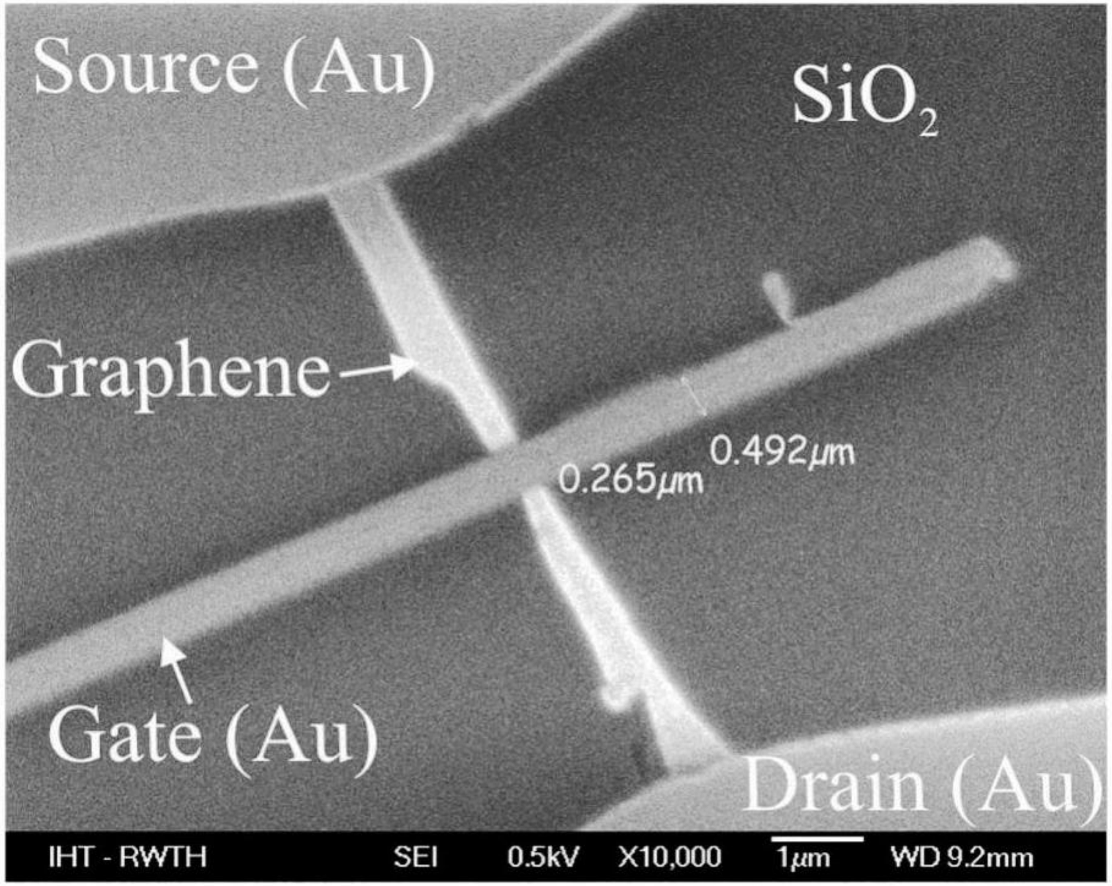
1-4. Applications of Graphene

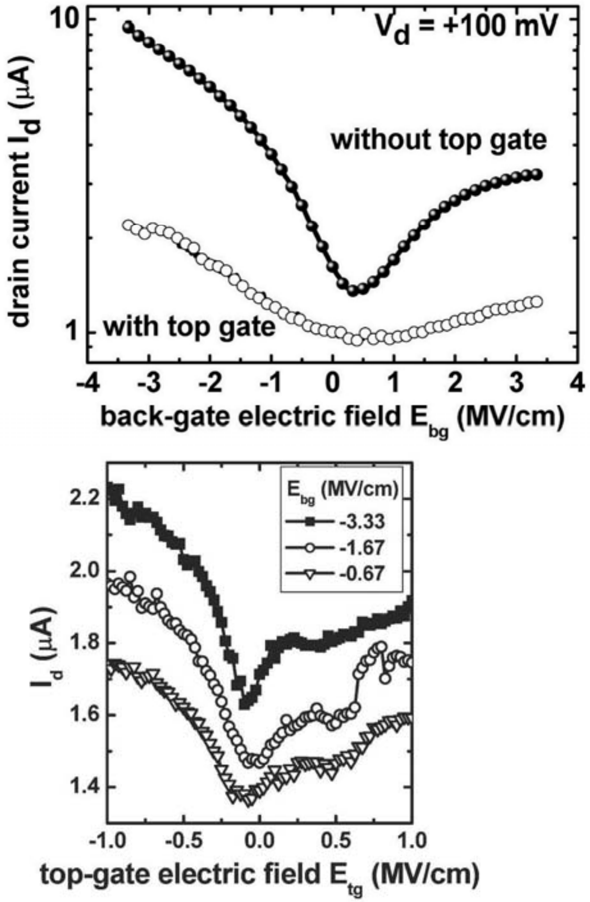
Graphene Transistor



[20] S. Hertel et al., *Nat. Commun.* **3**, 957 (2012)

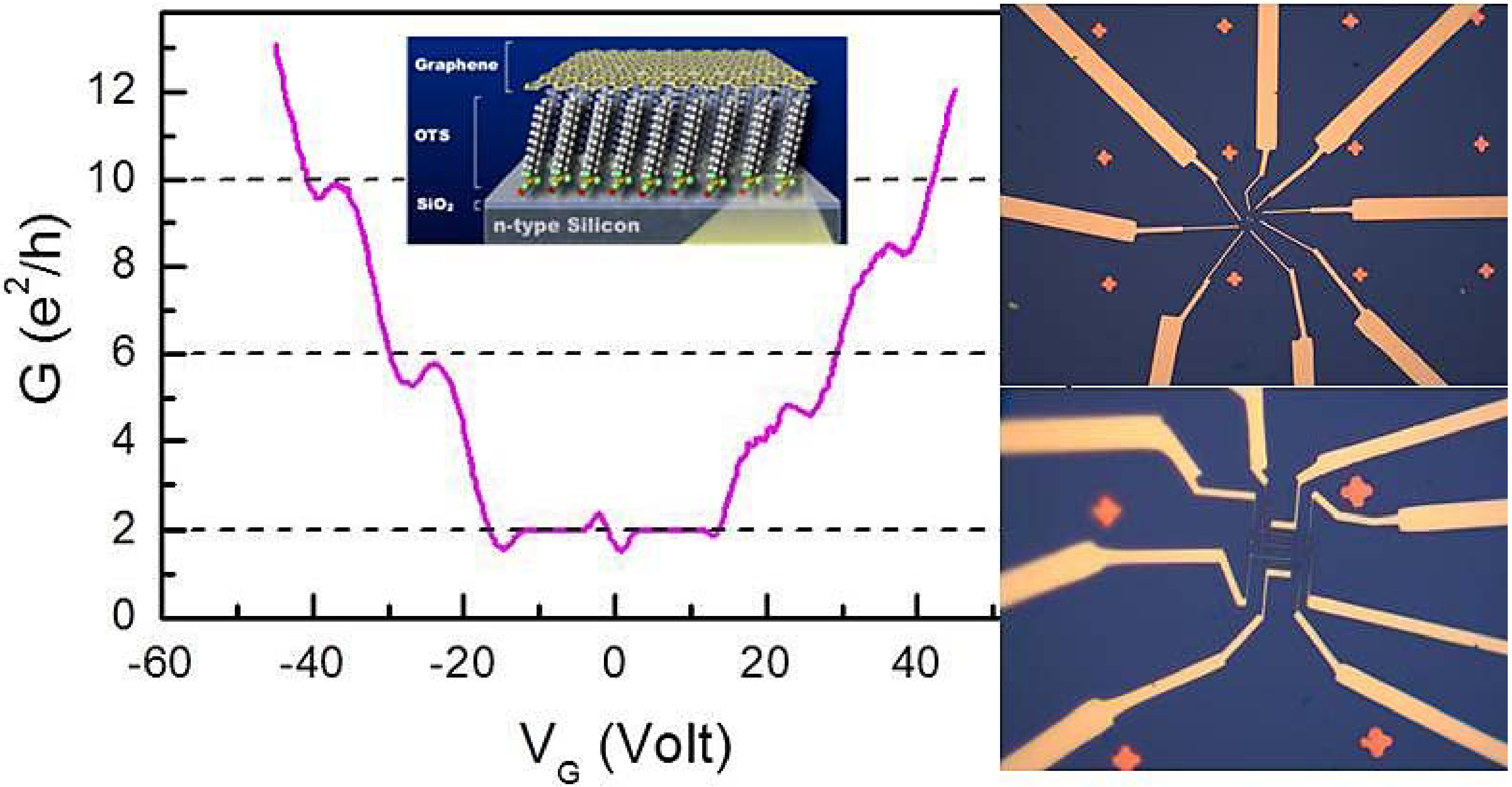
Graphene Transistor





Max C. Lemme et al., *EDL* **28** (4), 282 (2007)

Graphene Transistor



[22] *Nano Lett.* **12** (2), 964 (2012)

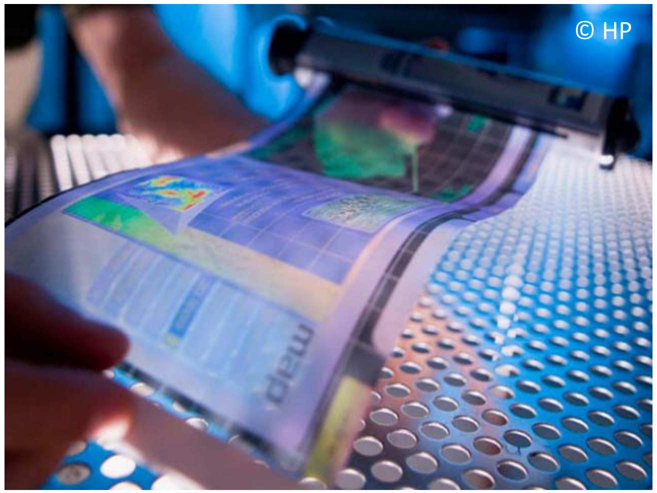
Next generation production ?

Household appliances

- High conductivity
- High transparency
- Good mechanical property
- Flexible
- Good thermal conductivity
- etc.

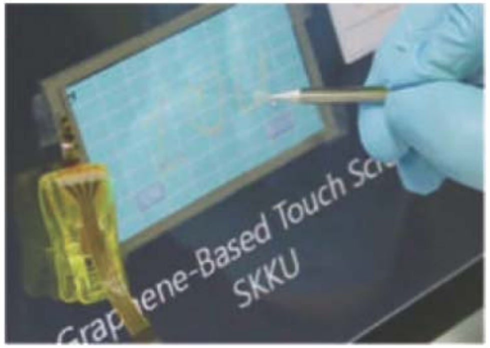
Communication production

E-paper



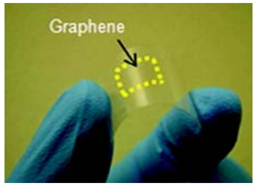
- **Transparent conducting electrode**

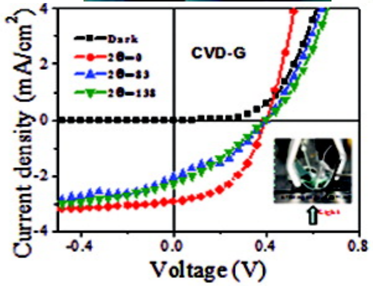
Touch Panel

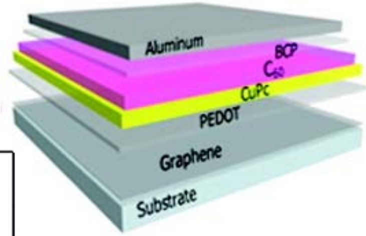


Bae, S. *et al.*
Nature Nanotech. ***4, 574–578 (2010).***

Solar Cell

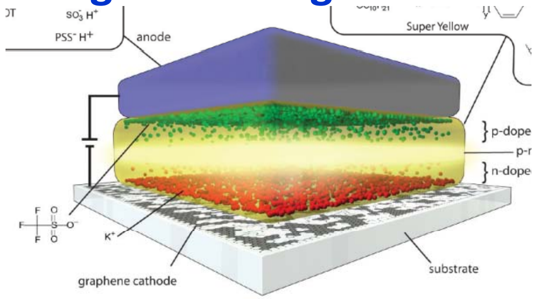


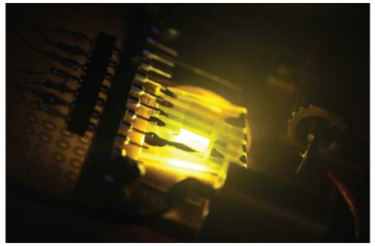




De Arco, L. G. *et al*
ACS Nano ***4,*** **2865–2873 (2010)**

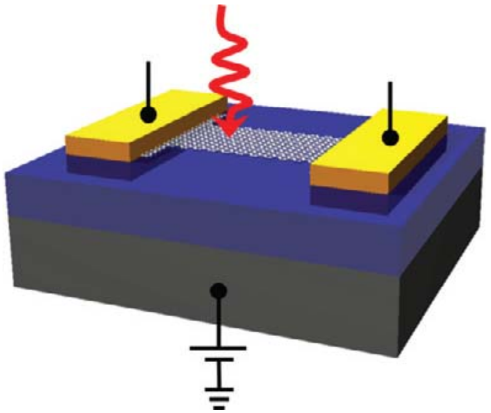
Light Emitting Diode

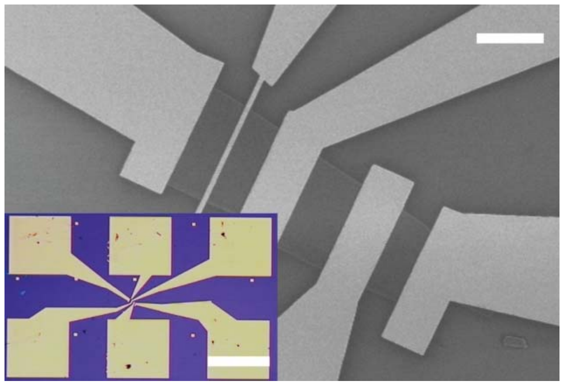


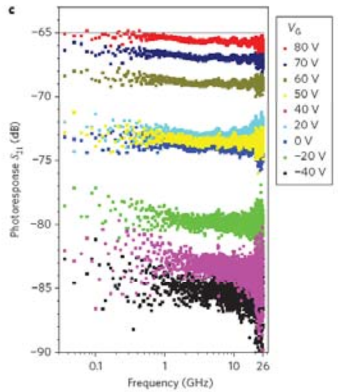


Matyba, P. *et al.*
ACS Nano ***4, 637–642 (2010).***

- **Ultra fast Photodetector**







Xia, F. *et al. Nature Nanotech.* ***4, 839–843 (2009).***

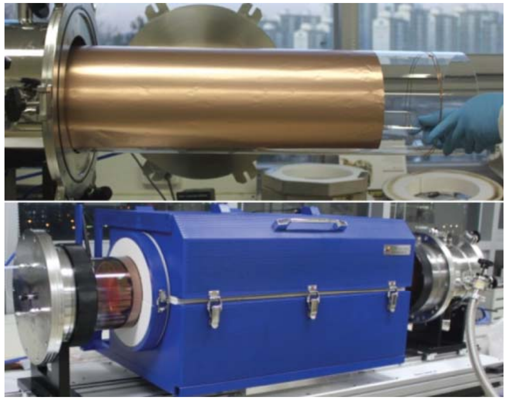
Large area CVD grown graphene for optoelectonic applications

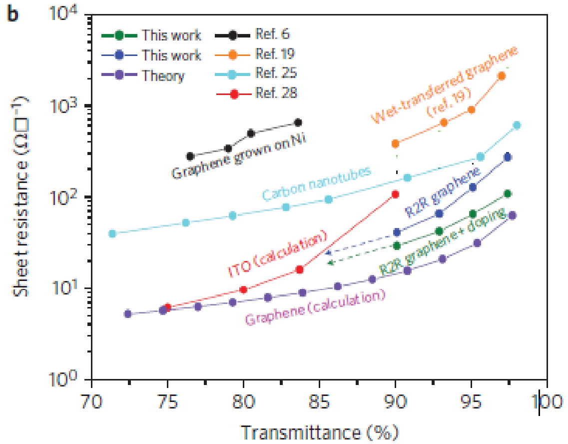
nature nanotechnology | LETTERS

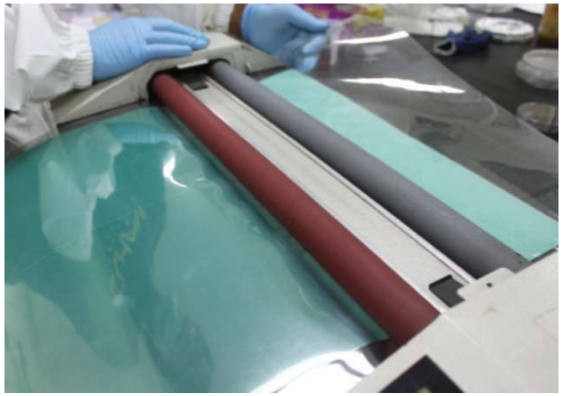
PUBLISHED ONLINE: 20 JUNE 2010 | DOI: 10.1038/NNANO.2010.132

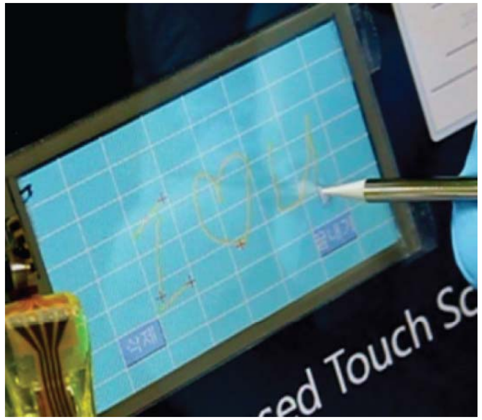
Roll-to-roll production of 30-inch graphene films for transparent electrodes

Jong-Hyun Ahn and Byung Hee Hong *et al.**









Roller printing

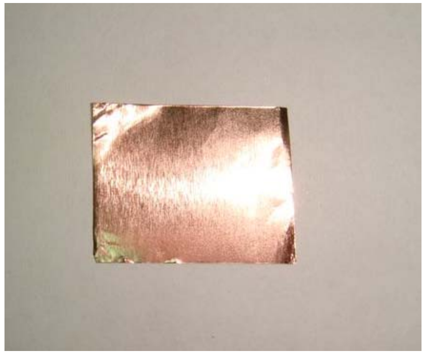
Scale up

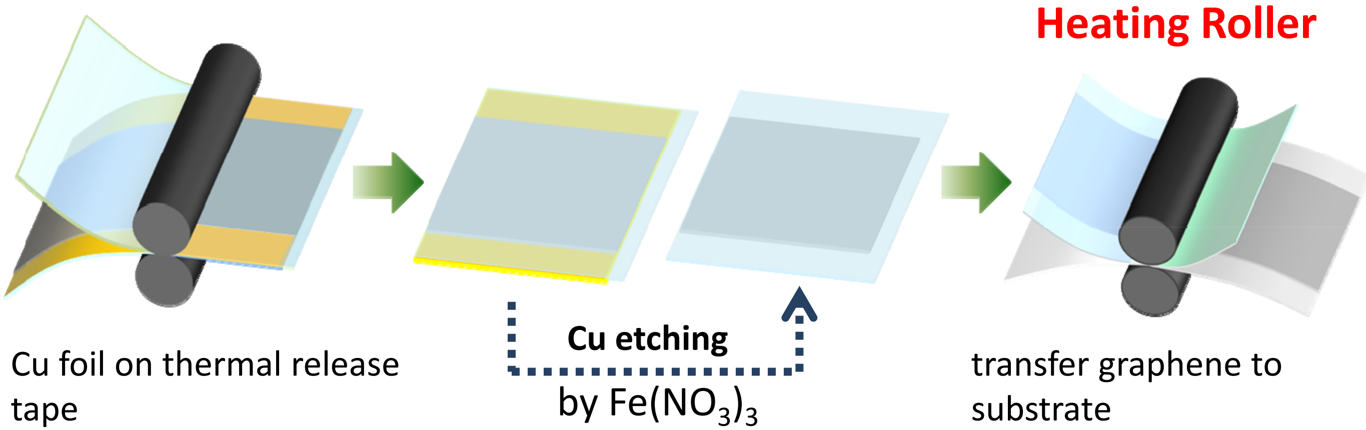
Touch panel

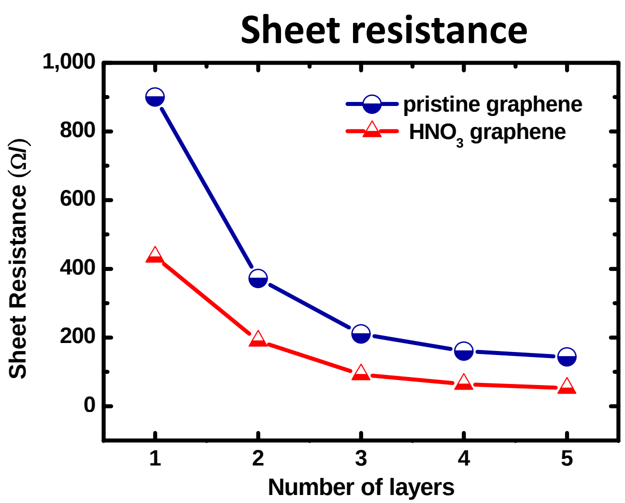
Bae et al. Nature Nanotechnology 5, 574–578 (2010)

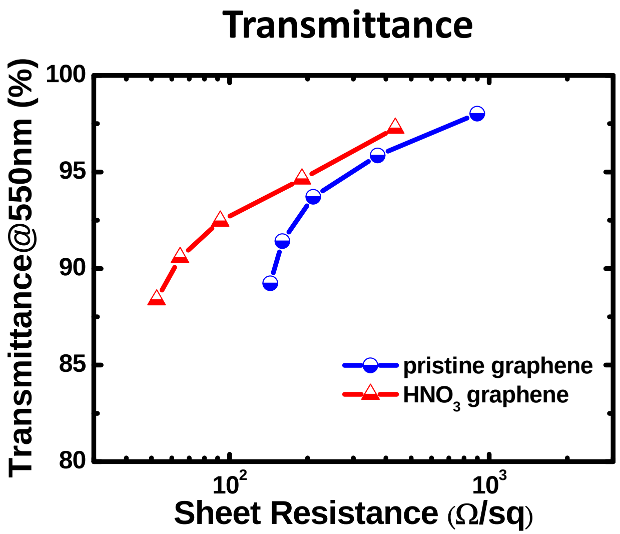
Fabrication of CVD Graphene Electrode on PET

Graphene on Cu foil by CVD

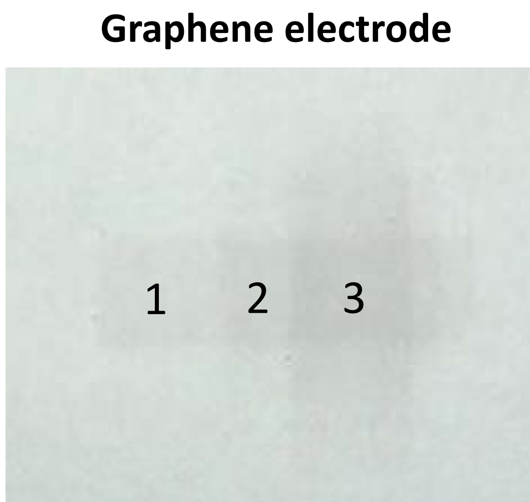






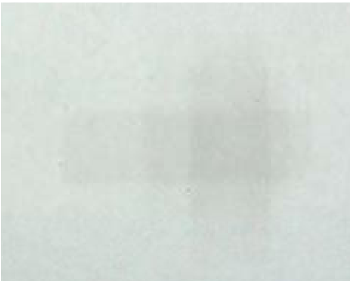


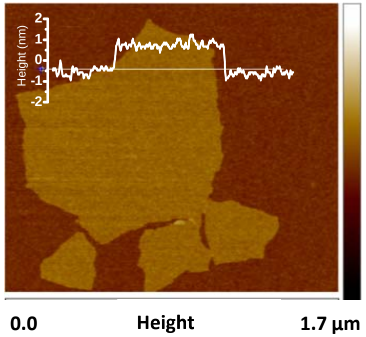
(~55Ω/sq) at a transparency. (~90%)



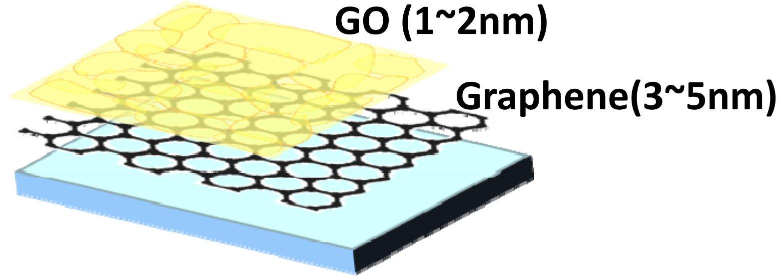
Polymer solar cells based on "Ultra thin" Graphene/GO anode by Roll-to-roll technology on PET

graphene + **graphene oxide**





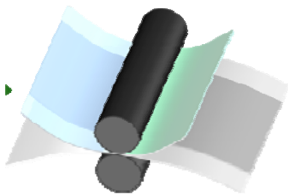
"Ultra thin anode"

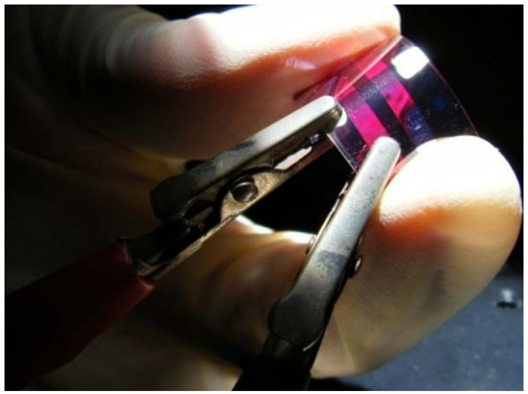


Graphene(3nm)/GO(2nm)

ITO(100nm)/PEDOT:PSS(30nm)

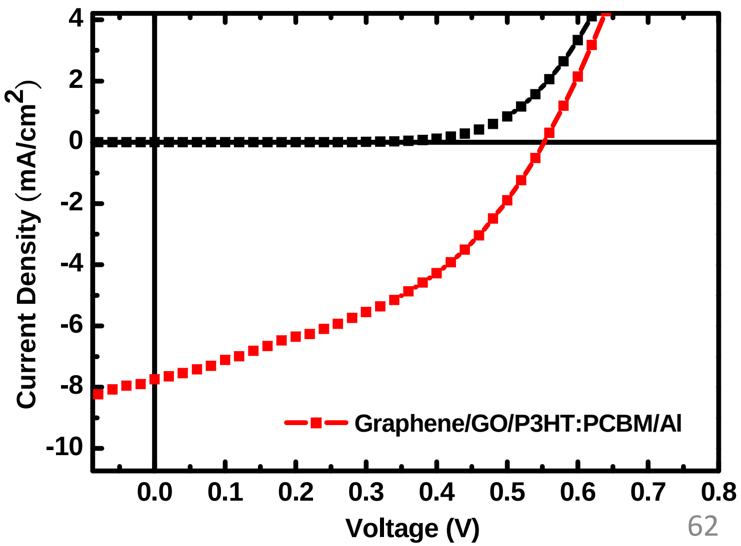
Polymer solar cell based on "graphene" platform !



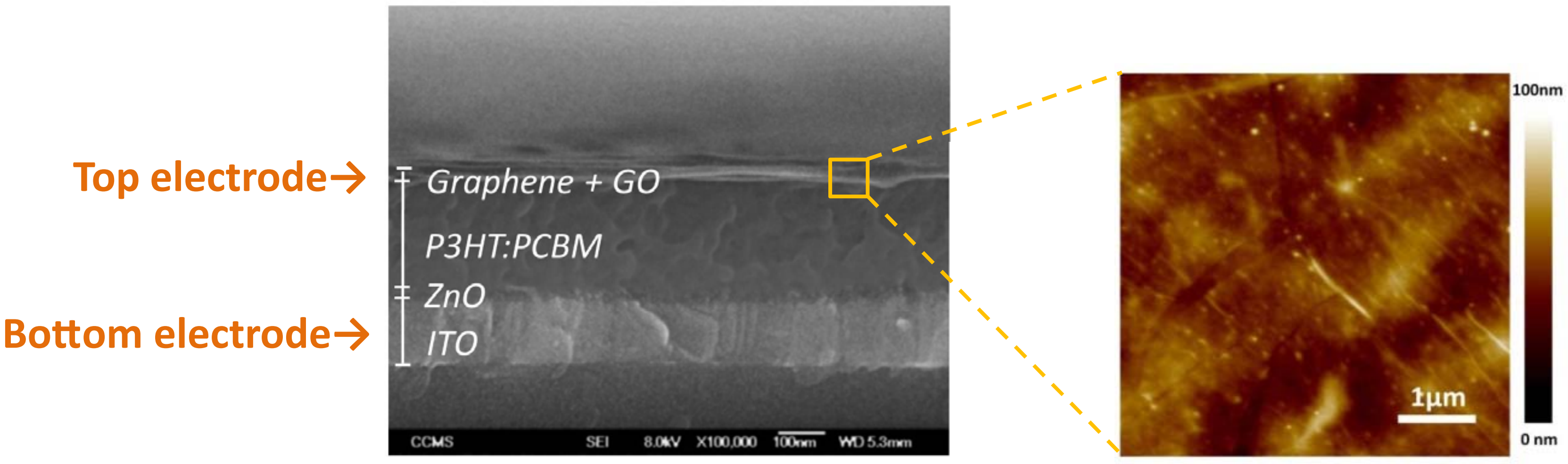


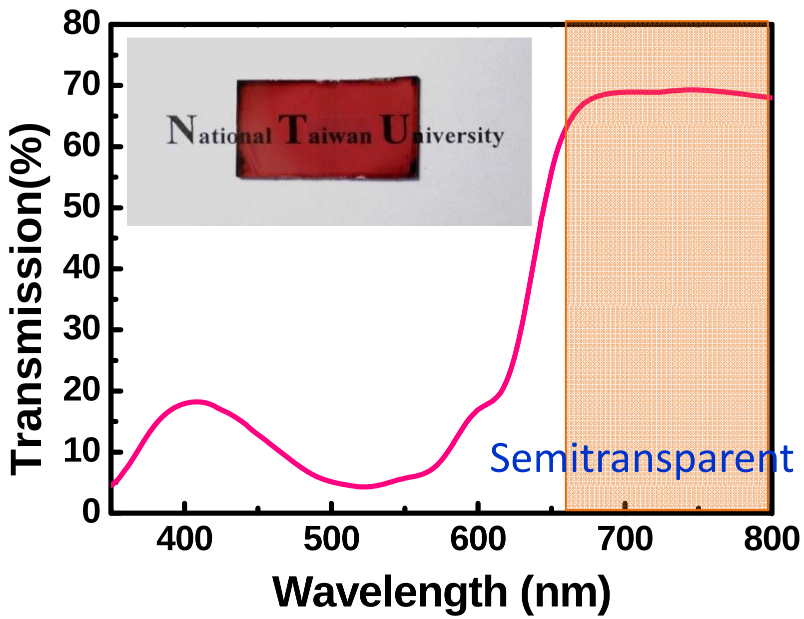
Graphene/GO/P3HT:PCBM/Al

Device performance



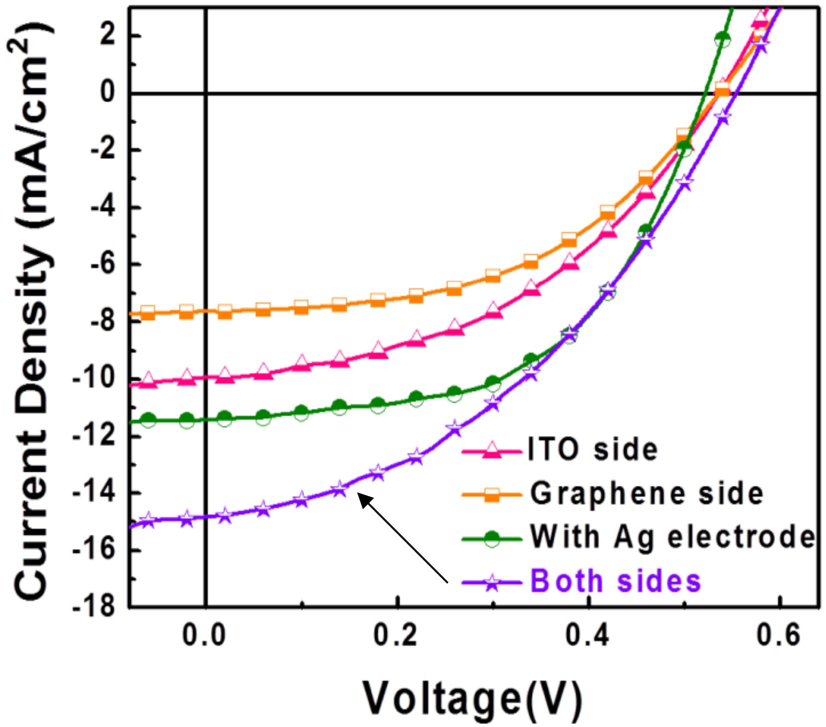
Top laminated graphene electrode in a semitransparent polymer solar cell

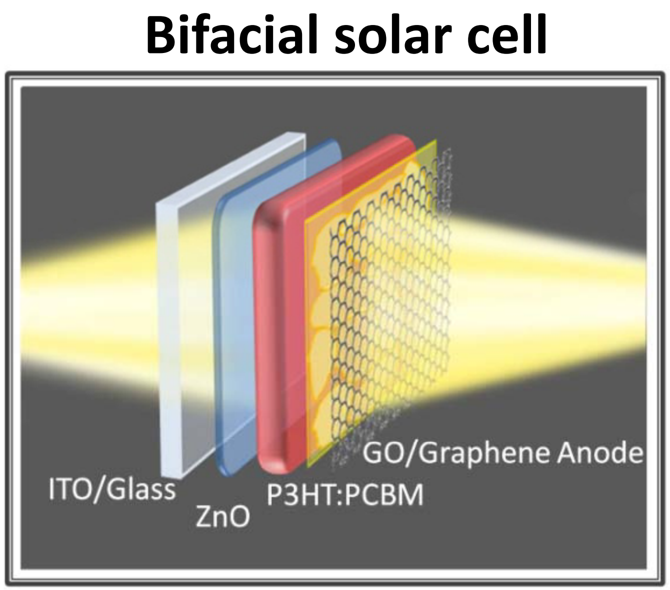




ACS Nano ,Vol.5, 6564, (2011)

Device performance of a bifacial polymer solar cell using graphene top electrode



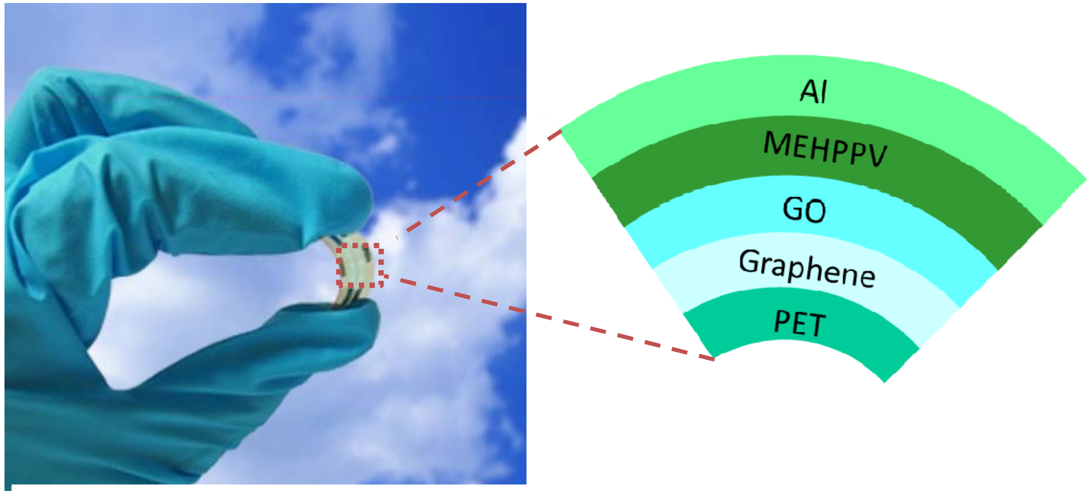


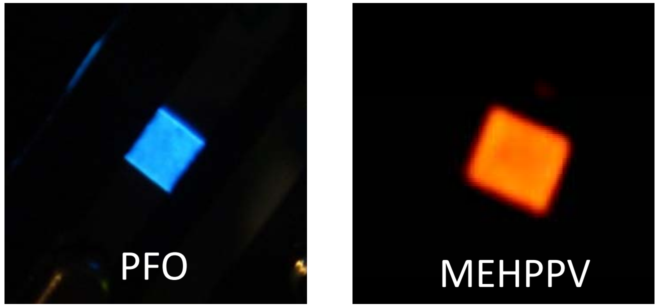
ACS Nano ,5,6564, (2011)

	V_{oc}(V)	J_{sc}(mA/cm^2)	FF	PCE(%)
Graphene side	0.54	7.7	0.49	2.04
ITO side	0.54	10.1	0.44	2.50
Ag electrode	0.52	11.5	0.55	3.30

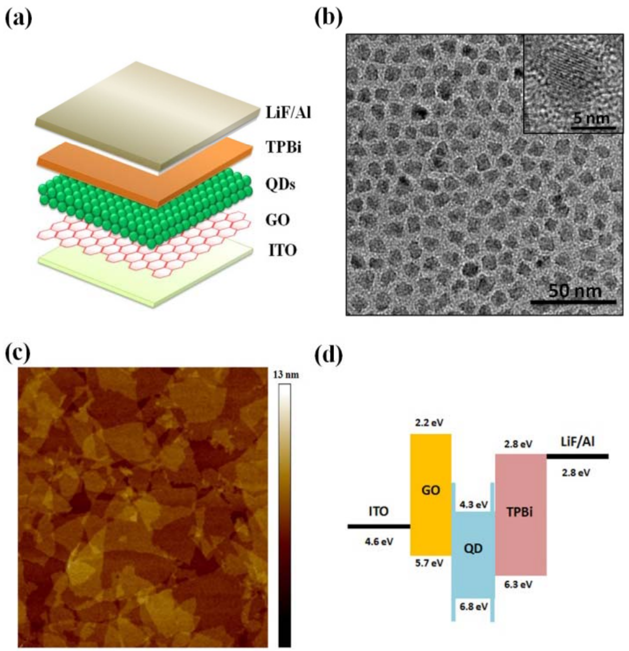
~75% of a standard opaque device

Graphene-based materials for Polymer and QD LED

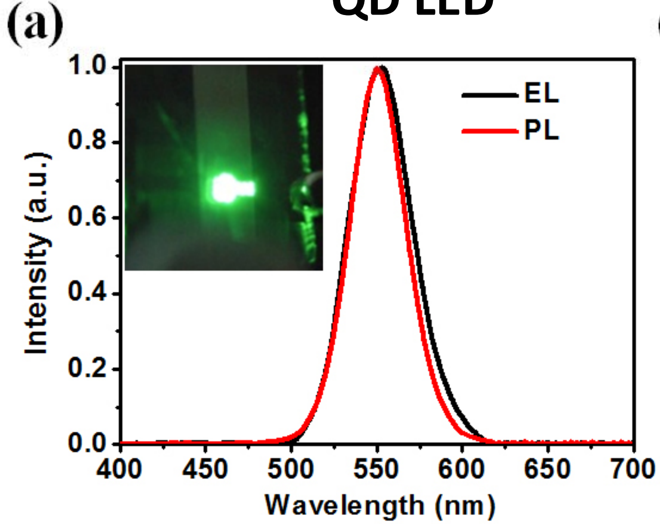




Polymer LED



QD LED

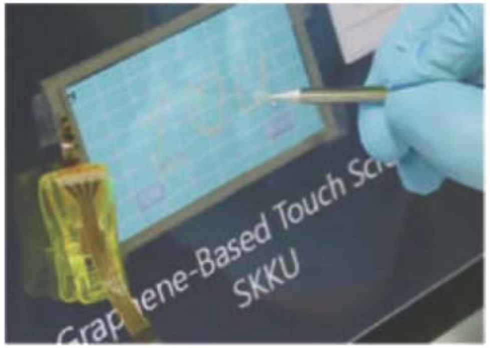


Journal of Physical Chemistry C,116, 10181, (2012)

Other optoelectronics application of Graphene

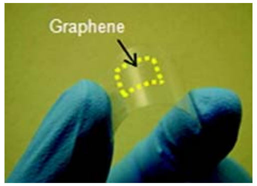
- **Transparent conducting electrode**

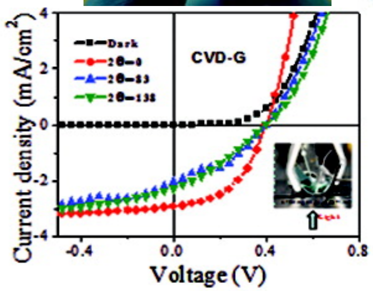
TOUCH PANEL

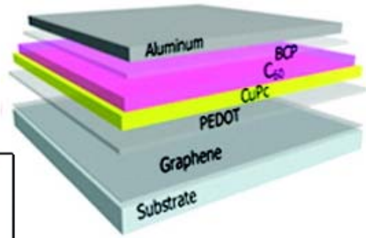


Bae, S. *et al.*
Nature Nanotech. ***4, 574–578 (2010).***

SOLAR CELL

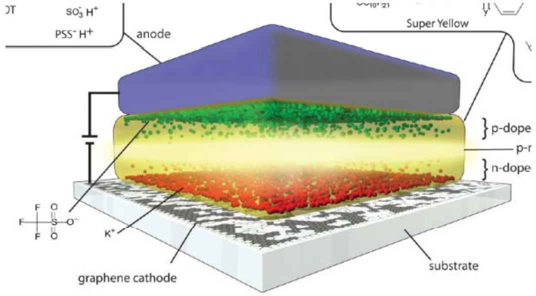


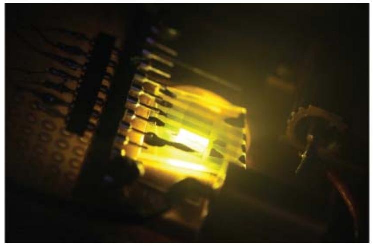




De Arco, L. G. *et al*
ACS Nano ***4,*** **2865–2873 (2010)**

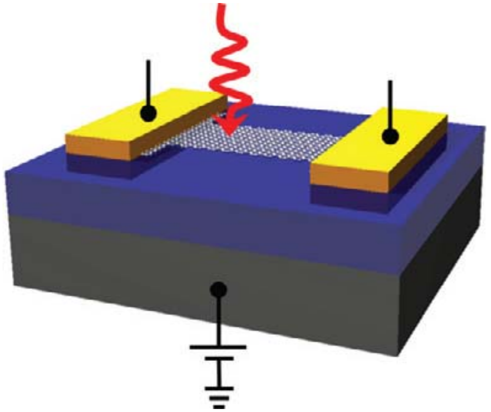
Light emitting diode

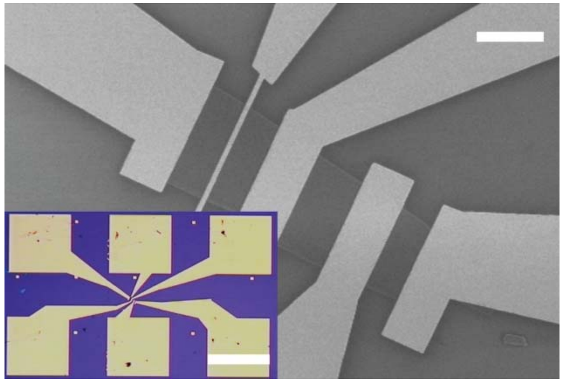


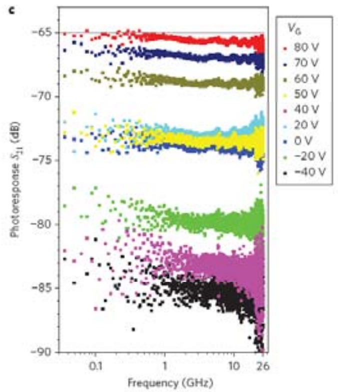


Matyba, P. *et al.*
ACS Nano ***4, 637–642 (2010).***

- **Ultra fast Photodetector**

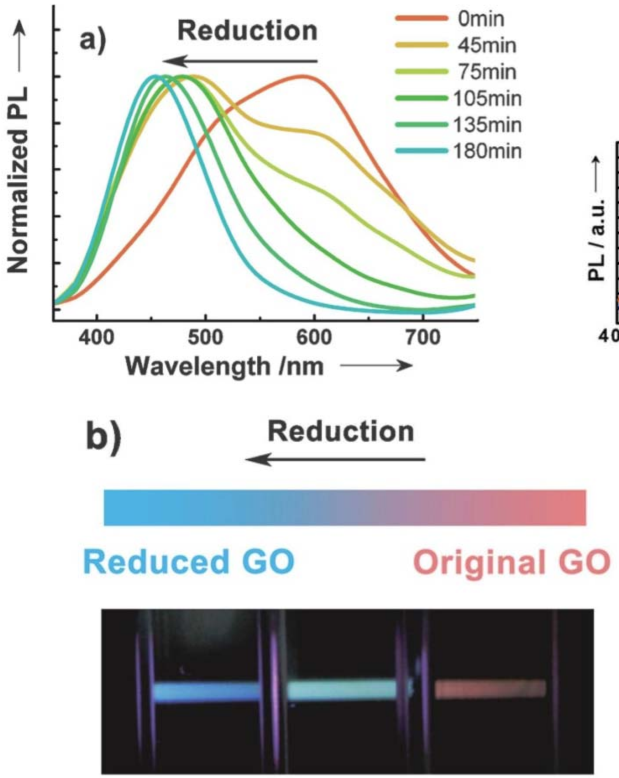


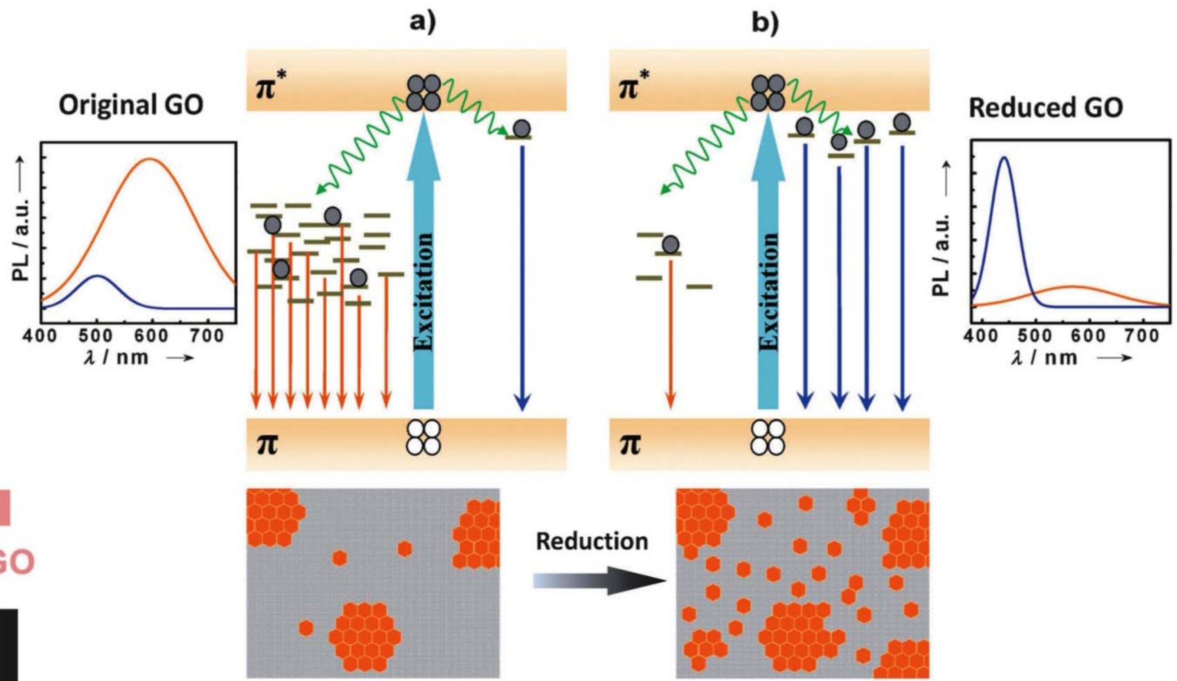




Xia, F. *et al. Nature Nanotech.* ***4, 839–843 (2009).***

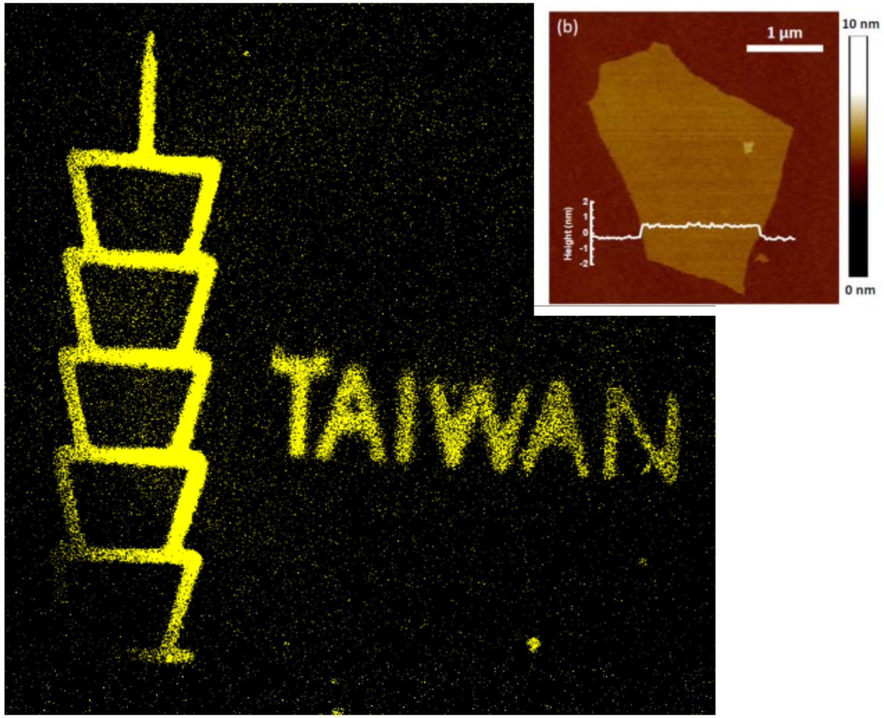
Tunable PL of Graphene /GO





CT Chien, CW Chen et al., *Angew. Chem. Int. Ed.* **51** (27), 6662 (2012)

石墨烯氧化物之發光



Advanced Materials,22,505, (2010)
Angewandte Chemie, (2012)

End of Part II