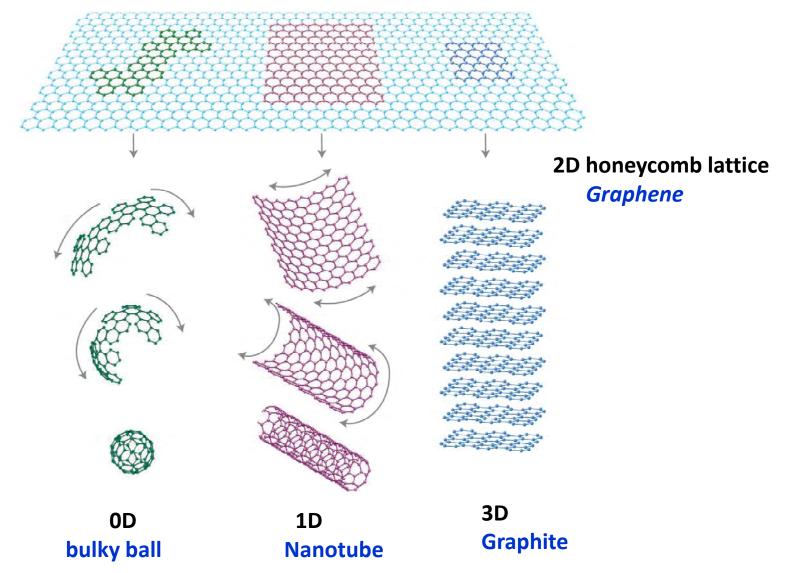
Part II. Introduction of Graphene

Graphene (Mother of all-graphitic form)



History of Graphene

Early: Theoretical description

1962: Named by Hanns-Peter Boehm (Graphite + -ene)

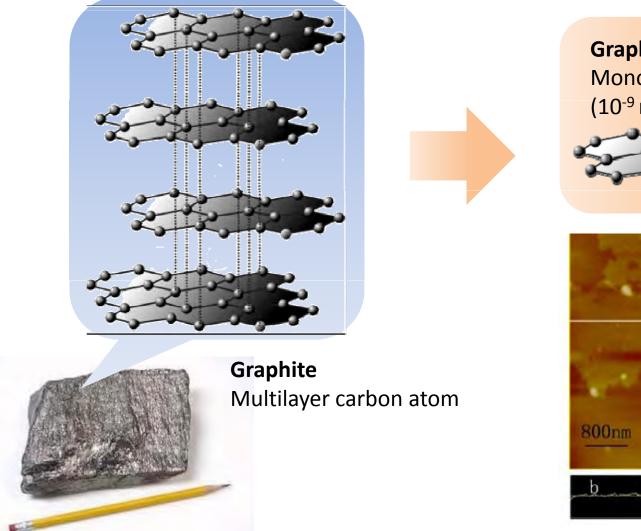
• 2004: Single-atom-thick, free-standing graphene is extracted (by Andre Geim and Konstantin Novoselov, Manchester University, U.K.)

2005: Anomalous quantum Hall effect was observed

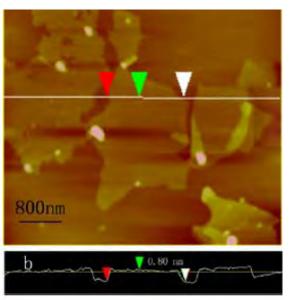
 2010: Nobel prize in Physics for Andre Geim and Konstantin Novoselov

Now: Stimulate wide researches and be applied to various fields

From graphite to graphene







2010 The Nobel Prize in Physics





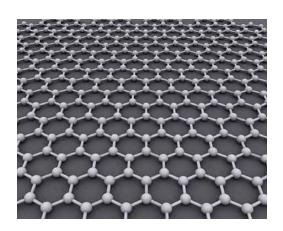
Prof. Andre Geim and Konstantin Novoselov at the U. Manchester for groundbreaking experiments regarding the 2-D material graphene

Andre Geim

Konstantin Novoselov

Graphite Graphene

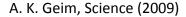
20 um

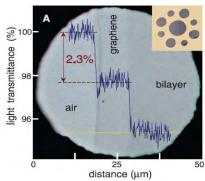


Graphene

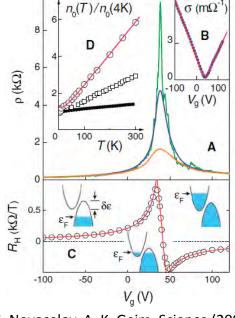
- Atomic-thick layer of carbon atom
- Zero bandgap
- Massless Dirac fermions
- High transparency and Flexible
- Low Resistivity about 10⁻⁶ Ω·cm, (< siliver)
- Ultrahigh high mobility (1000~300000cm²V-¹S-¹)
 - etc...

$$\hat{H} = v_F \vec{\sigma} \cdot \hat{p}$$

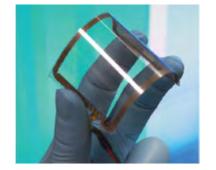




Nair et al., Science, (2008)



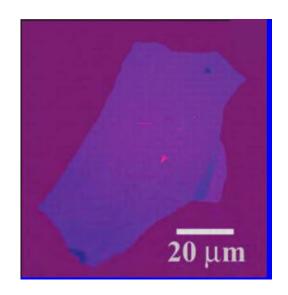
K. S. Novoselov, A. K. Geim. Science (2004)

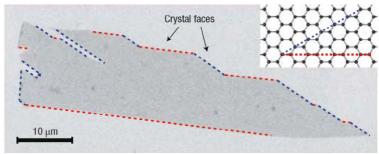


Bae. S et al. Nat. Nanotechnol. (2011)

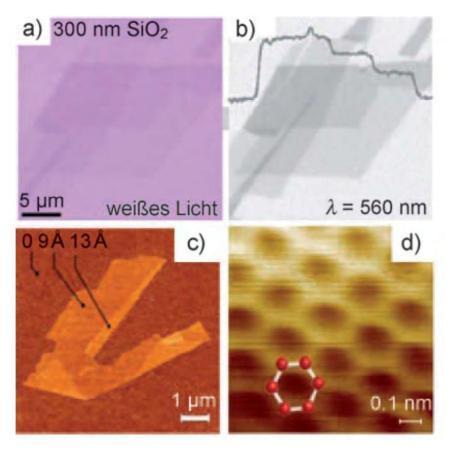
Atomic structure of graphene

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





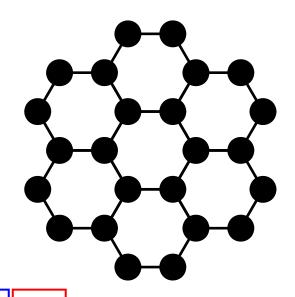
Kraner et al. Chem. Rev. 2010,110,132



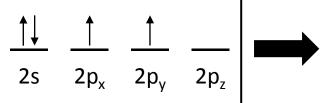
Rao et al, Angew. Chem., 2009,48,7752

Electronic Structure of Graphene

- All C atoms are sp²-bonded to adjoining C atoms
 - sp^2 electrons form σ bonds
 - Form the honeycomb net of C atoms
 - Delocalized p electrons form π bonds



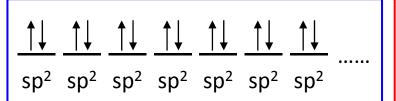
C atom



sp² sp² sp^2

o bond π bond

Graphene

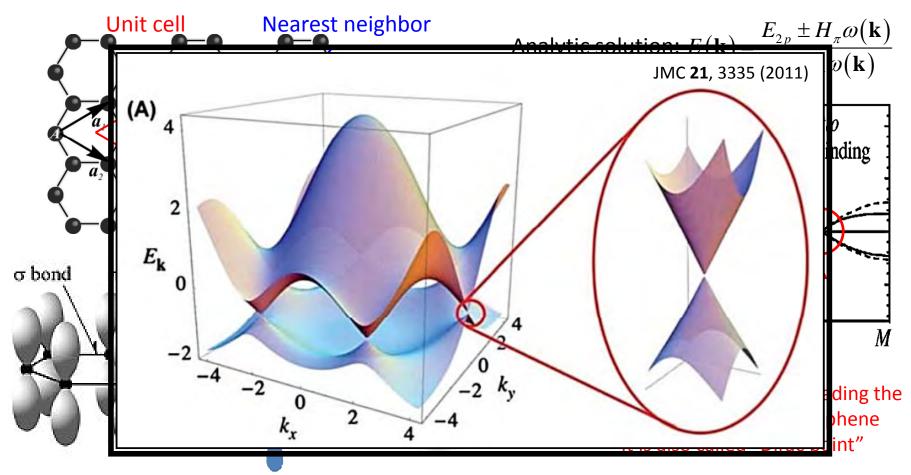


σ-bonded

 π -bonded

Delocalized p

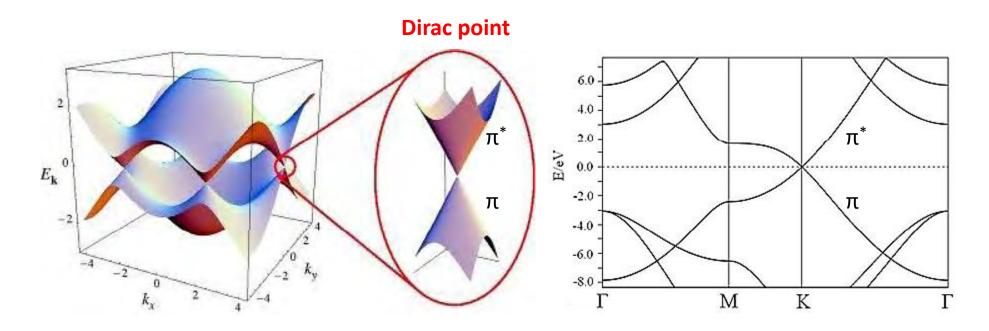
Tight-binding



 Bonds with adjacent atoms are most important, therefore the "nearest-neighbor tight-binding description" is usually used

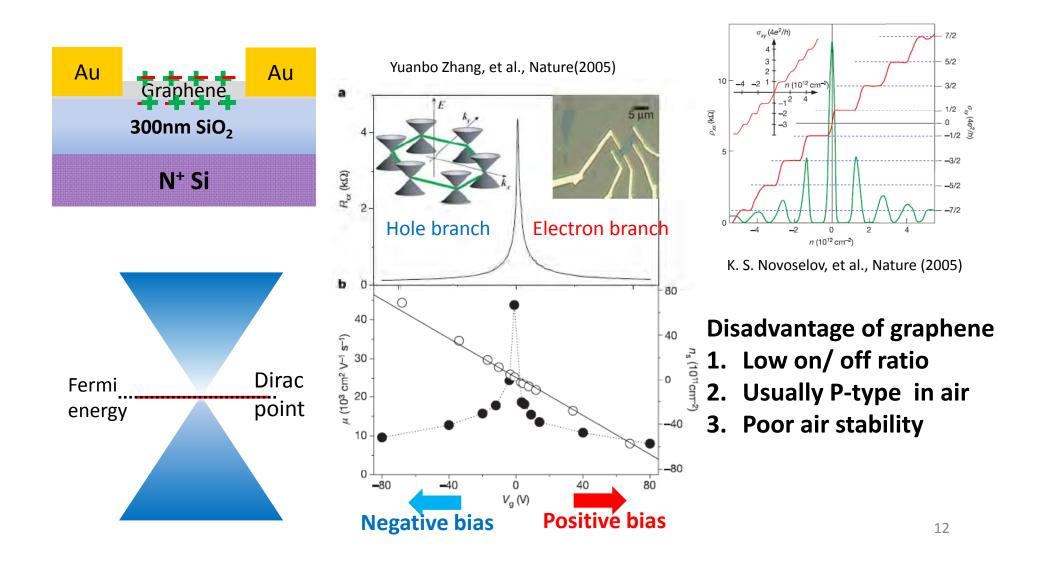
1-2. Fundamental Properties of Graphene

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

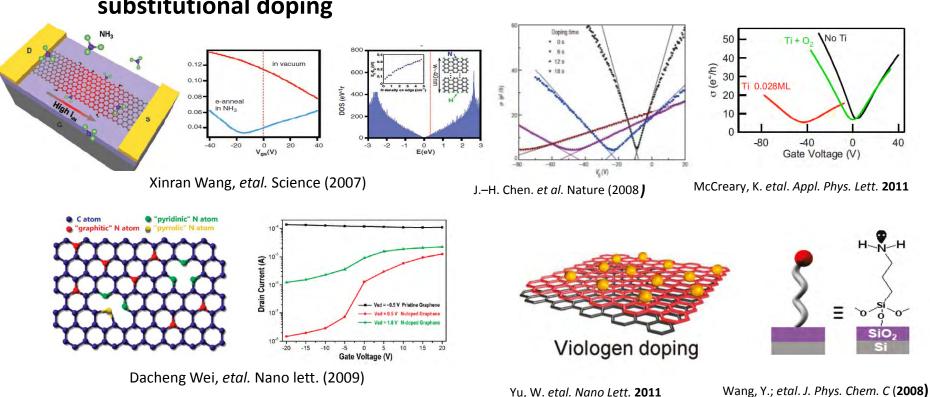
Graphene Ambipolar transport



Doped graphene

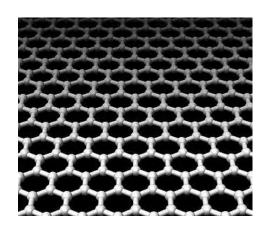
2. Surface charge transferred doping

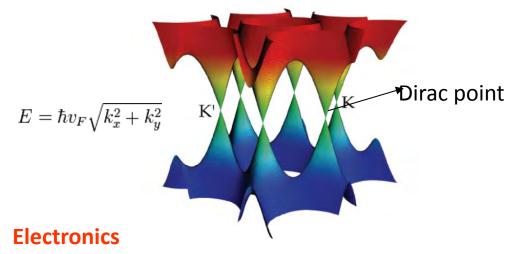
Covalent functionalized or substitutional doping

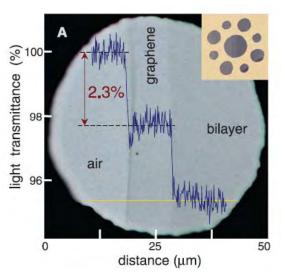


- Most of doping methods could considerably damage carrier mobilities of graphene.
- The doping level could not easily be easily controlled.
- The doping devices are very vulnerable to environment, especially for n-type doping.

High transparency of Graphene







Nair et al., Science, (2008)

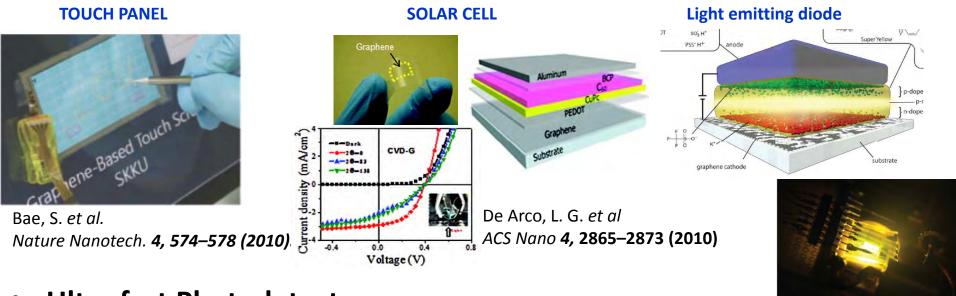
- Zero effective mass near the Dirac point
- High carrier mobility >15,000 cm²/ V⁻¹s⁻¹
- Low Resistivity about $10^{-6} \Omega \cdot \text{cm}$, (< siliver)
- etc...

Optics

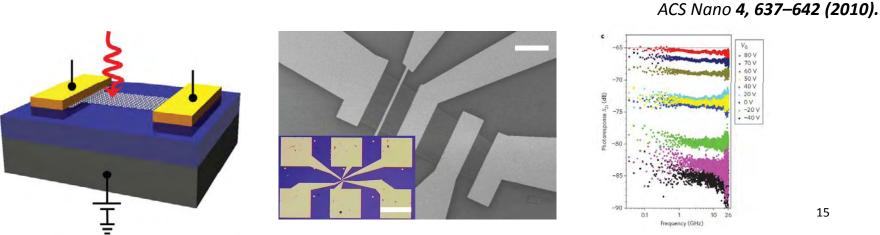
- Optics
 1. One atomic layer absorption $\frac{\pi e^2}{\hbar c} = \pi \alpha = 2.3\%$
- 2. High transparency

Optoelectronics application of Graphene

Transparent conducting electrode



Ultra fast Photodetector



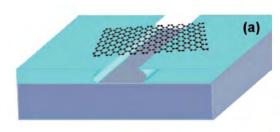
Xia, F. et al. Nature Nanotech. 4, 839-843 (2009).

Matyba, P. et al.

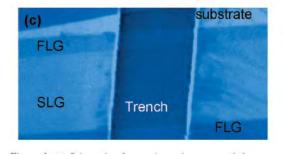
Thermal conductivity of graphene

Table 1. Room Temperature Thermal Conductivity in Graphene and CNTs

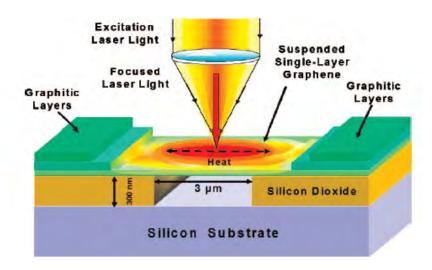
sample type	K (W/mK)	method	comments	ref
SLG	~4840–5300	optical	individual; suspended	this work
MW-CNT	>3000	electrical	individual; suspended	Kim et al. 15
SW-CNT	$\sim \! \! 3500$	electrical	individual; suspended	Pop et al. 16
SW-CNT	1750-5800	thermocouples	bundles	Hone et al. 17



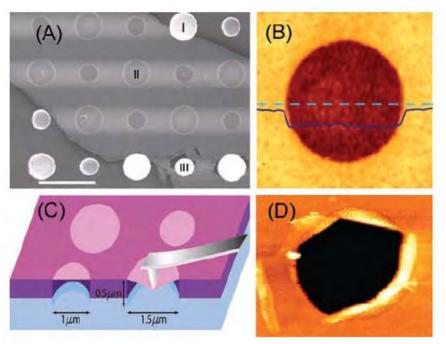




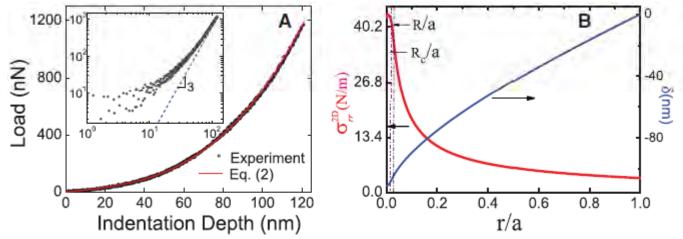
The extremely high value of the thermal conductivity suggests that graphene can outperform carbon nanotubes in heat conduction.



Mechanical properties of graphene



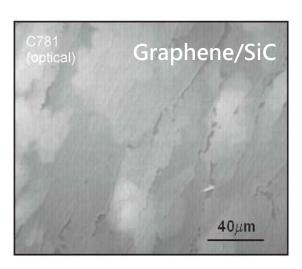
- 1. These experiments establish graphene as the strongest material ever measured.
- 2. The results show that atomically perfect nanoscale materials can be mechanically tested to deformations well beyond the linear regime.



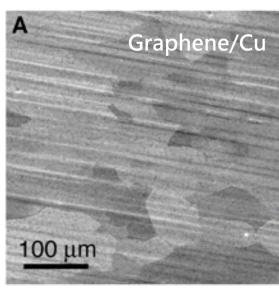
Hones et al, Science, Vol. 321, p385, 2008

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



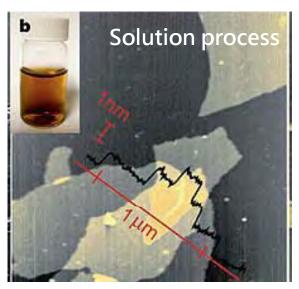
de Heer et al, Science (2006)



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



Novoselov et al., *Science* (2004)

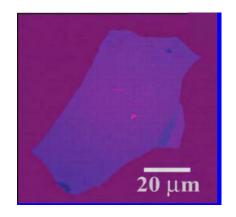


Sasha Stankovich, et al., *Nature* 442, 282-286, **2006**

Exfoliation process

- In 2004, Andre Geim and Konstantin Novoselov suggest this method^[4]
- Use tapes to split one layer of C atoms from graphite and form graphene flake
- Free-standing graphene
- Demonstrate the first graphene transistor
- 2010 Nobel Prize in Physics

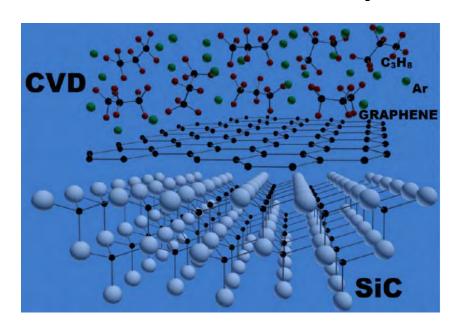




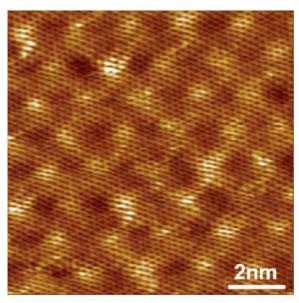
How to find the atomic layer "graphene" from repeatedly split graphite crystals by adhesive tape



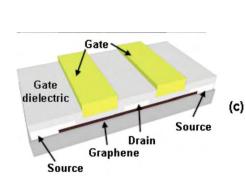
Epitaxial Graphene on SiC substrate by Chemical Vapor Deposition

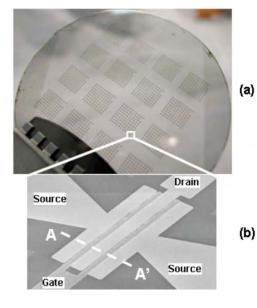


STM image of a CVD-EG layer grown on a 4HSiC(0001) substrate



Strupinski, W. et. al., Nano Lett. 2011, 11, 1786-1791

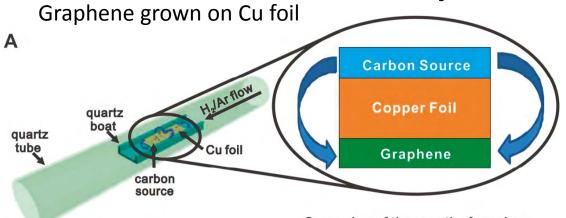




IBM wafer-scale epitaxial graphene

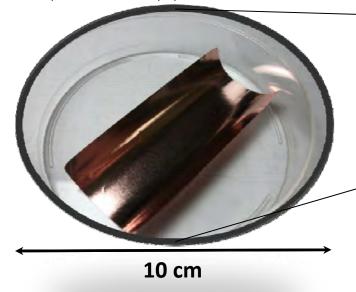
J. Vac. Sci., B. 28, 985,2010

Large area fabrication of graphene on Cu by using CVD processes



Cross view of the growth of graphene on the backside of the Cu foil

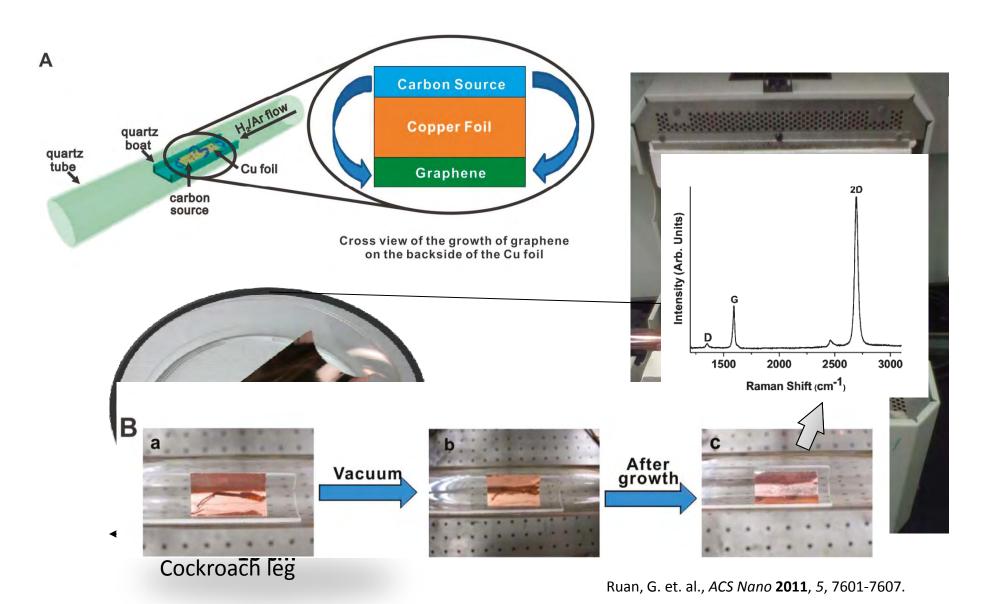
Ruan, G. et. al., ACS Nano 2011, 5, 7601-7607.



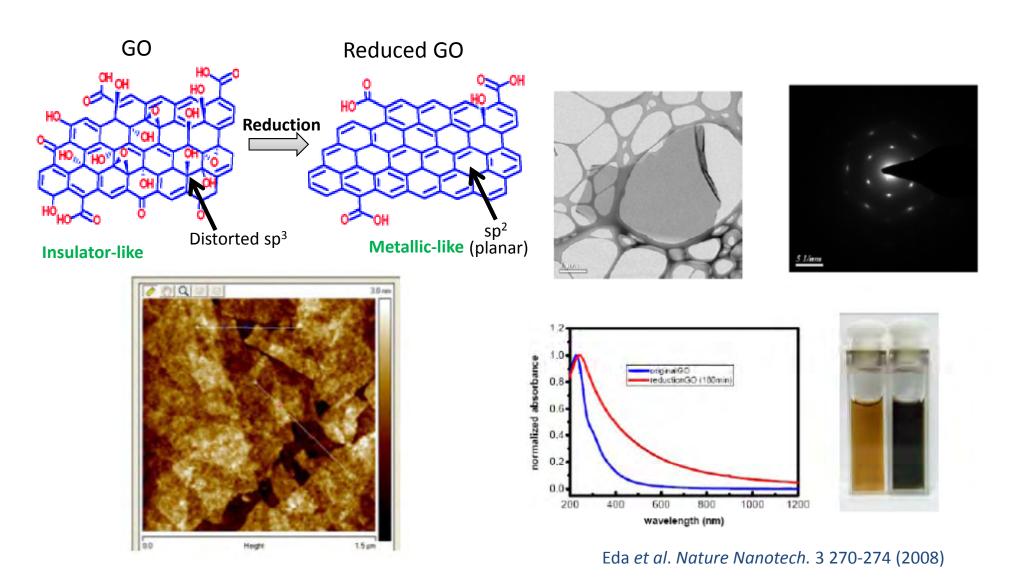


Ruoff et al., *Science*, vol. 324, pp1312-1314, **2009**

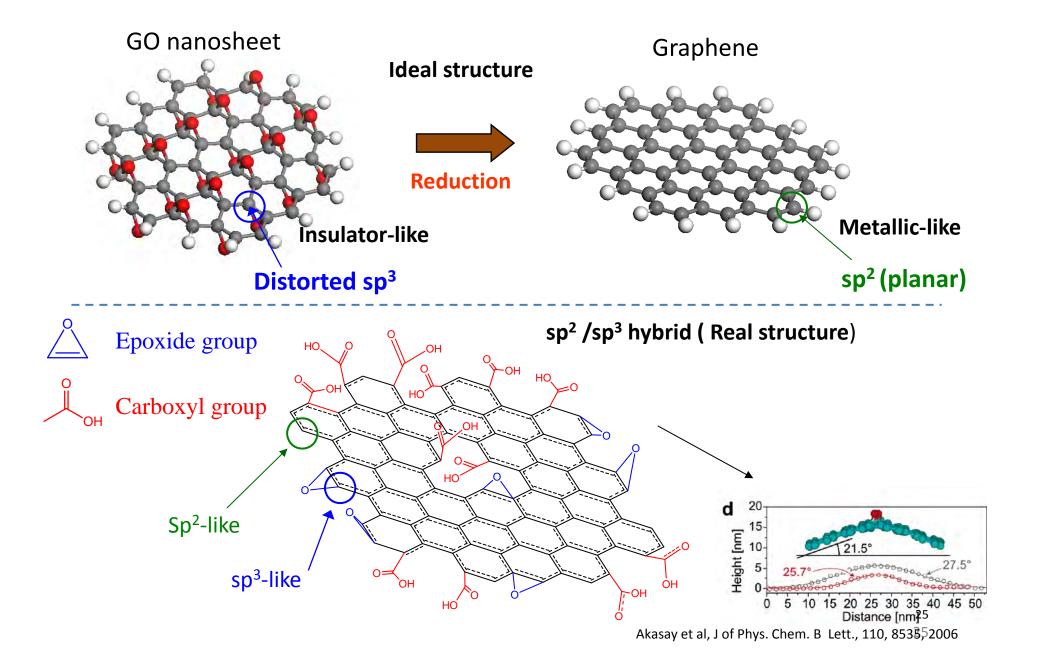
Fabrication process of CVD graphene



Chemical exfoliation of graphene from reduced graphene oxide



Atomic and electronic structure of GO/Graphene



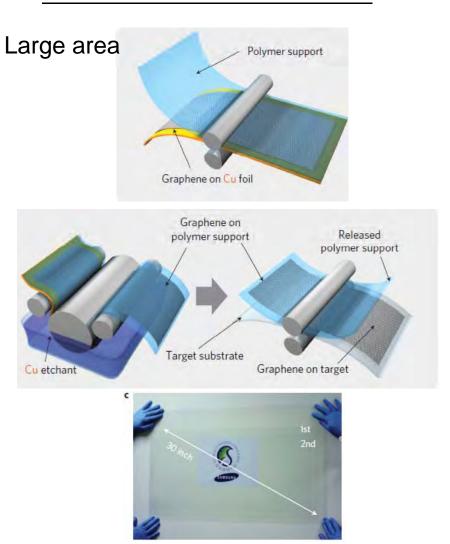
Transfer of graphene

Two Traditional Transfer Methods for CVD Graphene in the World

PMMA Transfer Method

Small area Graphene Graphene PMMA coating Cu foil Cu foil Floating Cu etching Transferring **PMMA** etching SiO₂/Si Graphene PMMA residue Quartz MM 1CM 2 a 4 s

Roll to Roll Transfer Method

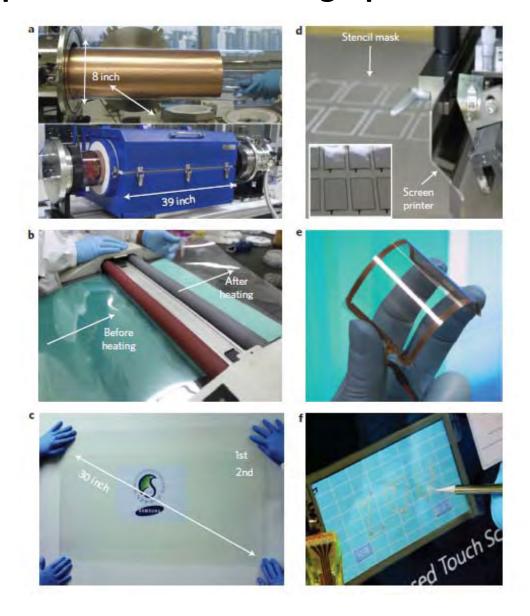


Lee, W. H., et. al, J. Am. Chem. Soc., 2010, 133, 4447

Bae, S., et. al., Nat. Nanotech., 2010, 5, 574

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

electrodes

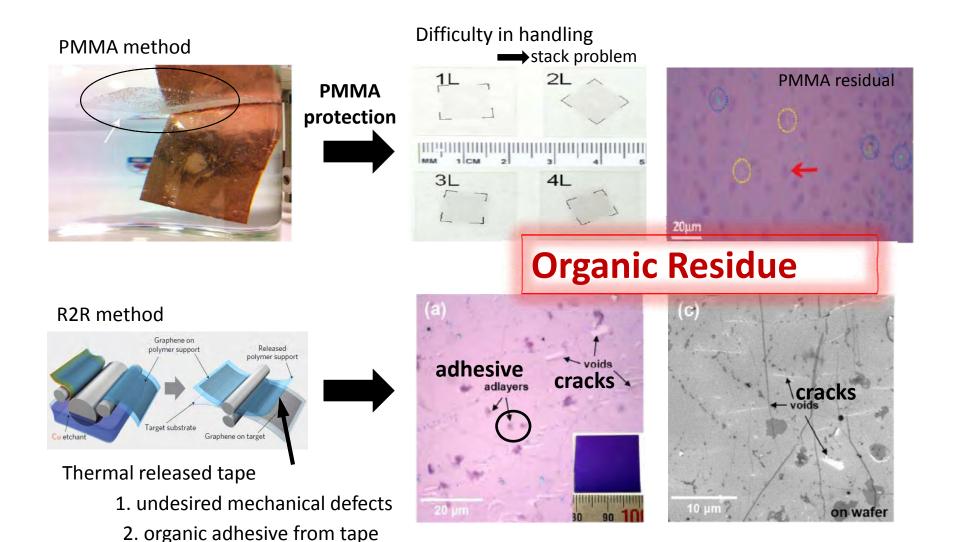


Processes of large-area CVD graphene film transferred onto arbitrary substrate

Graphene Transfer Graphene Film Graphene Growth PMMA method Cu foil Etching **Organic support protection** Graphene Graphene on on Cu foil Target substrate R2R method A critical step

Yu Wang et al, ACS Nano, **2011**, 5, 9227–9937 Bae, S., et. al., Nat. Nanotech., **2010**, 5, 574

Problems of PMMA and R2R Transfer Methods

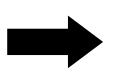


Junmo Kang et al, ACS Nano, 2012, 6, 5360. Xuesong Li et al, Nano Lett., 2009, 9, 4359 34363

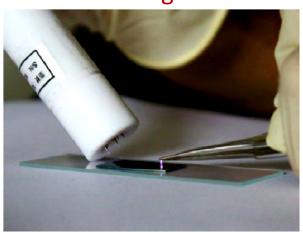
Can we transfer graphene with no organic residue ???

Using electrostatic attraction



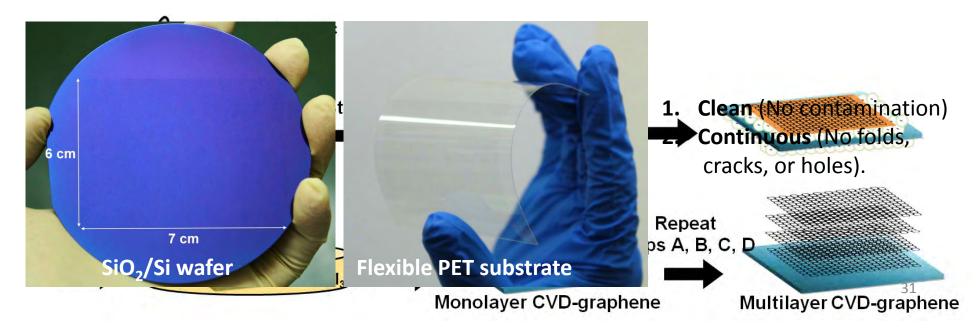


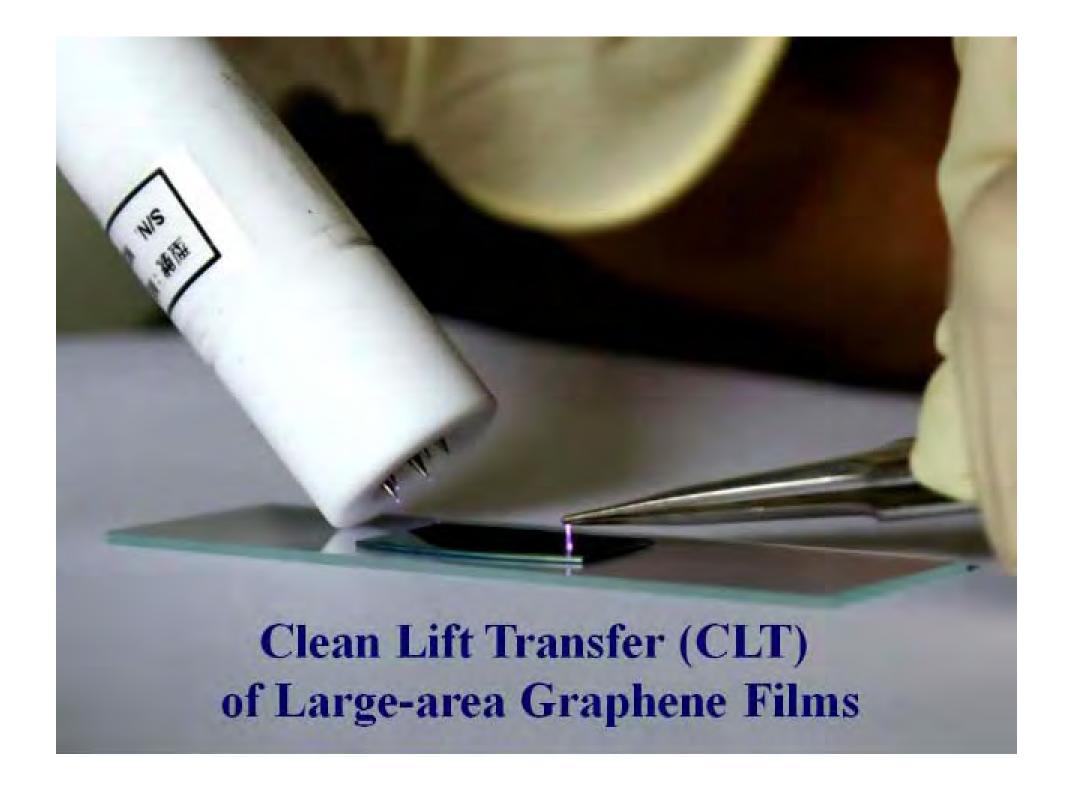
Electrostatic generator



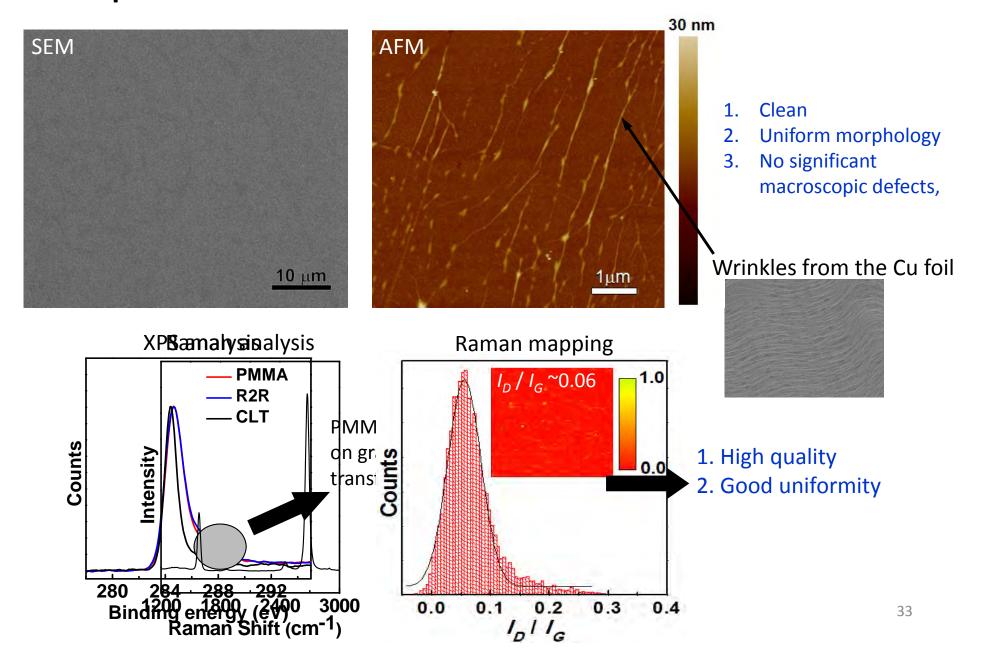
Clean-Lifting Transfer (CLT) Technique

Adv. Mater. 25, 4521, (2013) Adv. Mater. 25, 4521, (2013)





High quality CVD graphene of transferred by the CLT technique



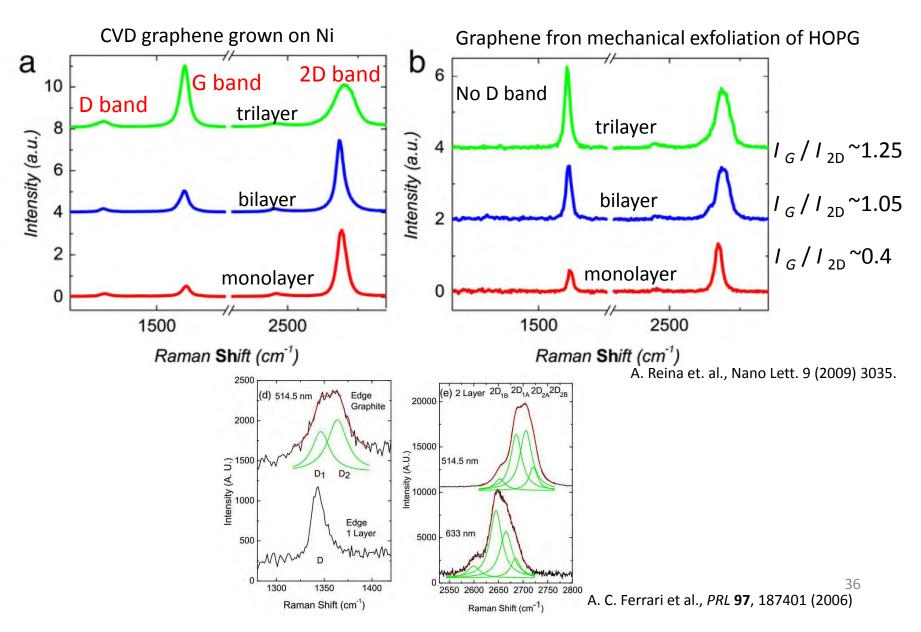
CLT of graphene by a screen protector



Characterizations of garphene

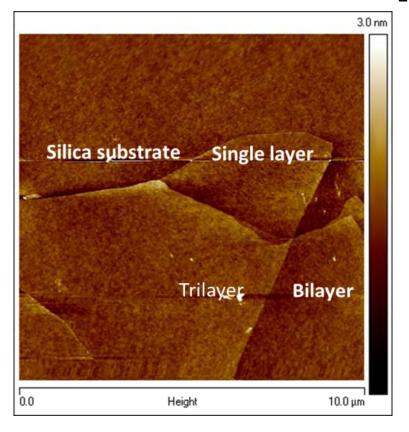
Raman Spectra of graphene

Identification of the layer number of graphene

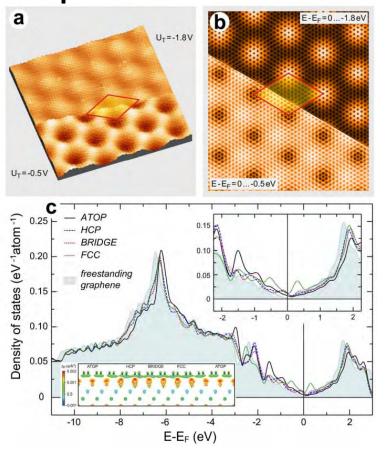


AFM and STM image of graphene

AFM images of graphene on SiO₂

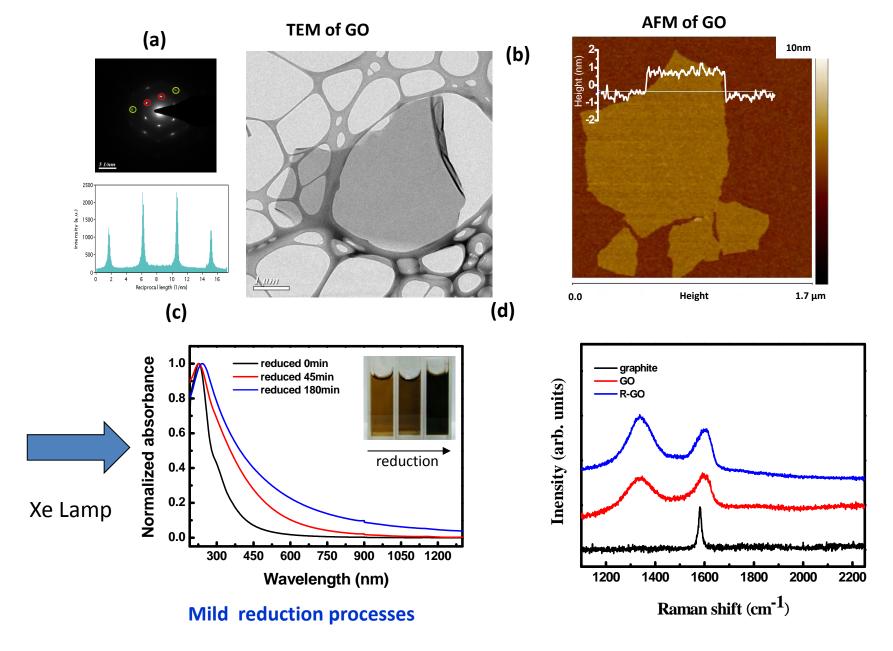


STM images of graphene/Ir(111) Experimental calculated



Voloshina, E. N. Science Report, 2013, 3, 1

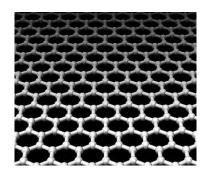
Photothermal reduction method for GO and r-GO



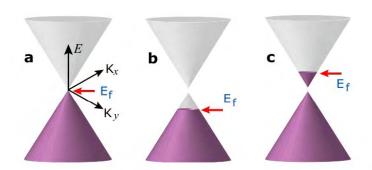
Electrical properties of graphene

Tunable electrical and optical platform of graphene

Atomically thin structure



Tunable electronic structure



Easily modulated by electrical, or chemical, optical and mechanical methods

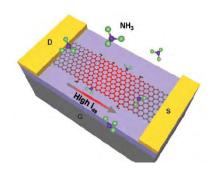
Source Top gote Drain
Insulator

Back gate

Electrical gating

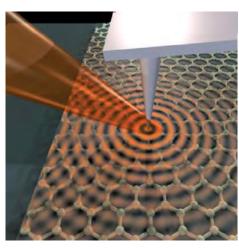
B. Guo et al., *Insciences J.* **1** (2), 80 (2011)

Chemical Doping



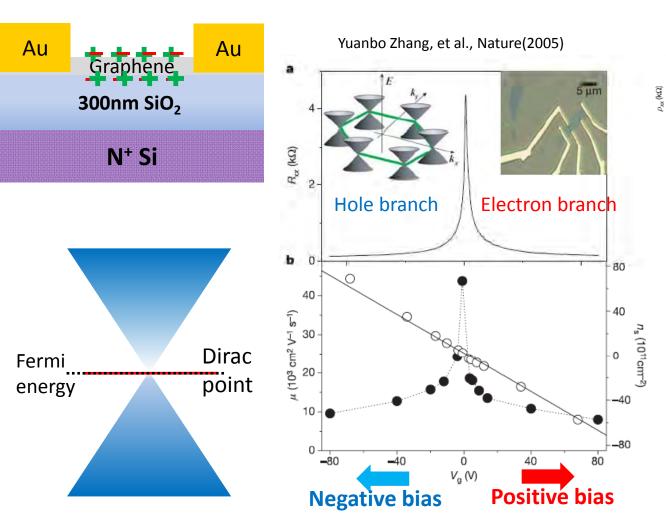
Xinran Wang, et al. Science (2007)

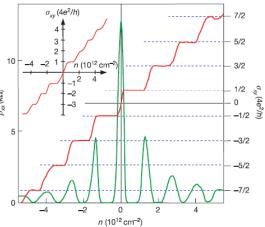
IR Nano imaging



Fei. Etal, Nature, 82, V 487, 2012

Graphene Ambipolar transport property



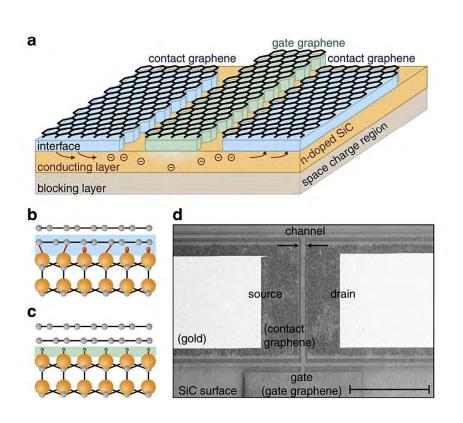


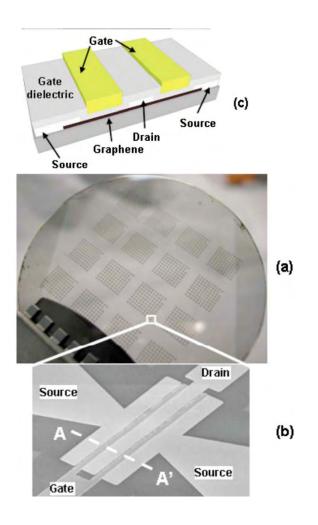
K. S. Novoselov, et al., Nature (2005)

Disadvantage of graphene

- Low on/ off ratio
- 2. Usually P-type in air
- 3. Bad air stability

Graphene Transistor (on SiC) top-gated

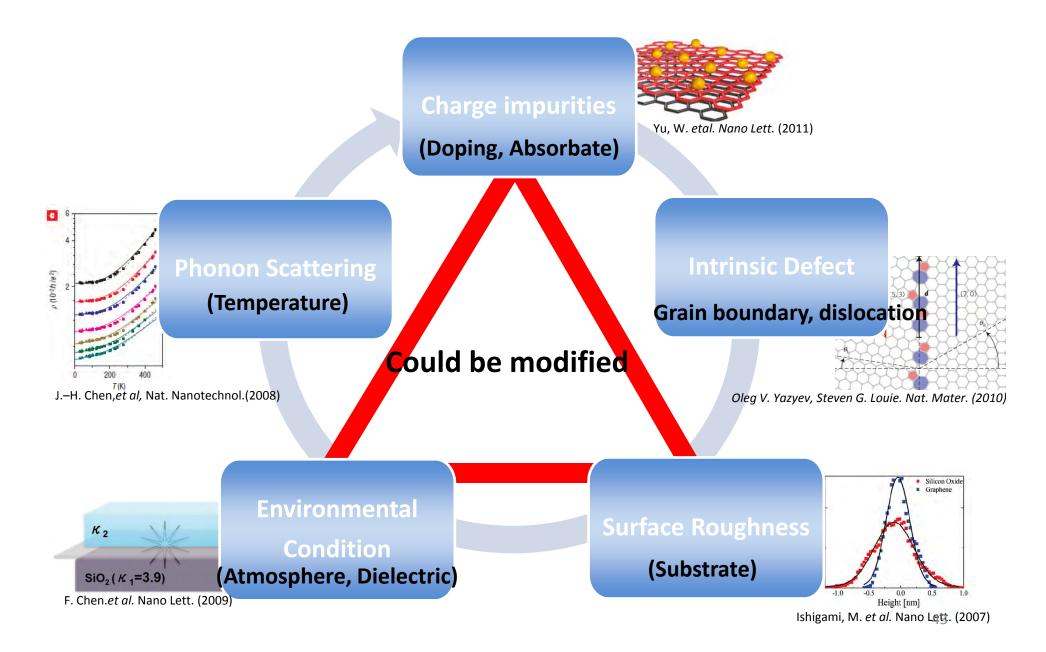




[20] S. Hertel et al., Nat. Commun. 3, 957 (2012)

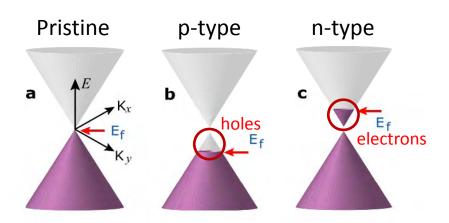
IBM wafer-scale epitaxial graphene

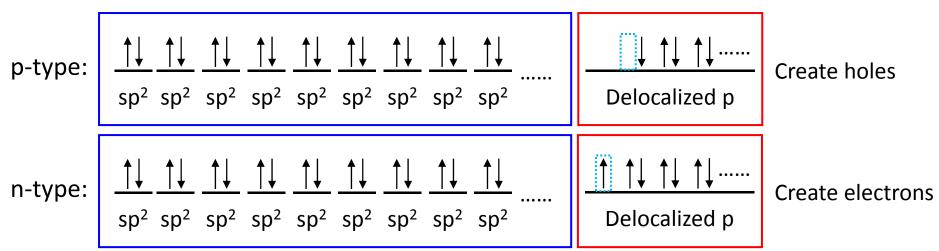
Effects on Transport Properties



Doped Graphene by heteroatoms

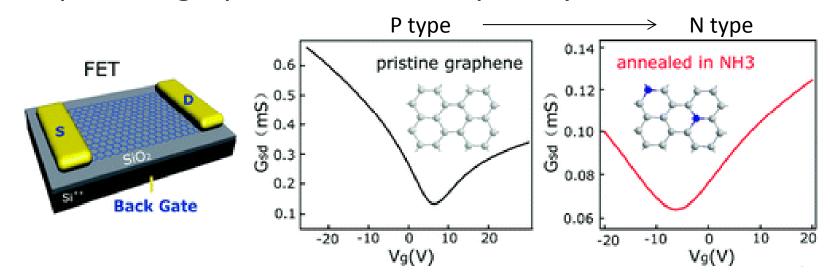
- Doping by heteroatoms
 - p-type doping
 - n-type doping





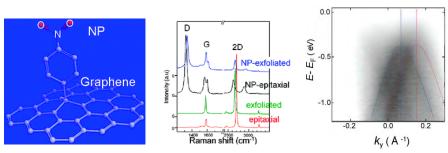
Doped Graphene by chemical modification

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

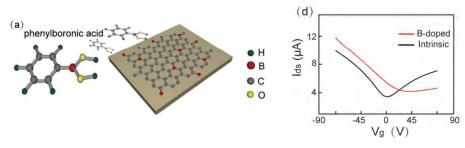


p-type doped graphene

Covalent functionalized or substitutional doping

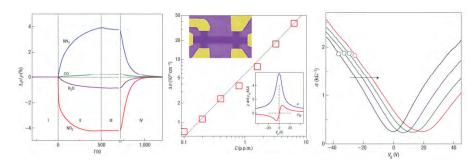


Nano Lett. 10, 4061-4066 (2010)

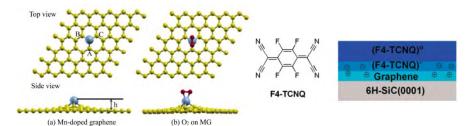


Small, 9, No. 8, 1316-1320 (2013)

2. Surface charge transferred doping



Nat. Mater. 6, 652 - 655 (2007)



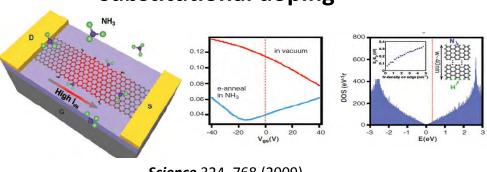
Phy. Rev. B, 81, 165414 (2010)

J. Am. Chem. Soc. 129, 10418-10422 (2009)

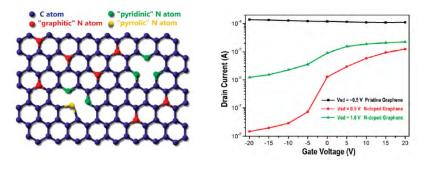
- Covalent functionalized and substitutional doping => destruction of sp2, low mobility
- Surface charge transfer => Graphene is vulnerable to atmosphere

n-type doped graphene

Covalent functionalized or substitutional doping

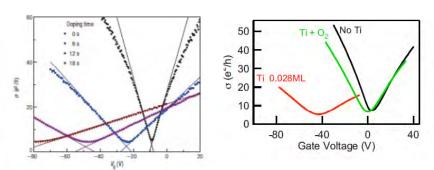


Science 324, 768 (2009)



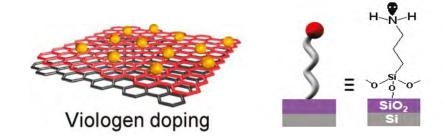
Nano Lett. 9, 1752 (2009)

2. Surface charge transferred doping



Nat. Phys. 4, 377 - 381 (2008)

Appl. Phys. Lett. 98, 192101 (2011)

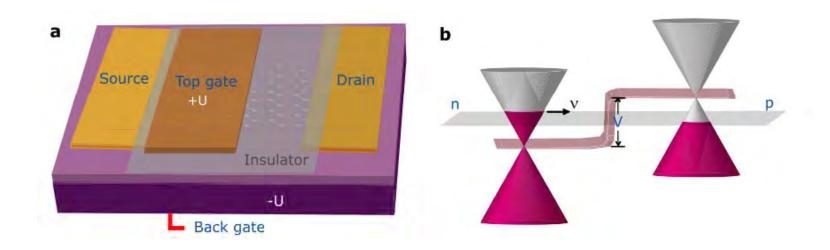


Nano Lett. 11, 4759–4763 (2011) J. Phys. Chem. Lett. 2011, 2, 841–845

- Most of doping methods could considerably damage carrier mobilities of graphene.
- The doping level could not easily be easily controlled.
- The doping devices are very vulnerable to environment, especially for n-type doping.

Doped Graphene by electric field

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

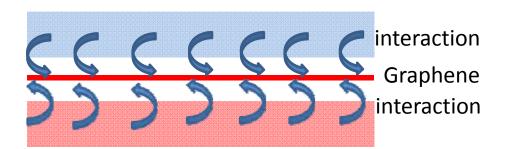


How to improve mobility or control the carrier types in graphene?

Graphene encapsulated by doping layer

Suspended Graphene

Graphene on substrate



Bottom layer - Substrate

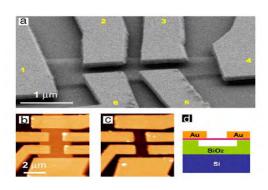
- 1. Charge impurity
- 2. Surface Roughness

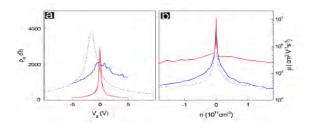
Top layer - Encapsulated layer

- 1. Charge transfer (doping)
- 2. Preventing from atmosphere

Substrate-dependet transport

1. Suspended Graphene

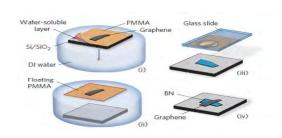


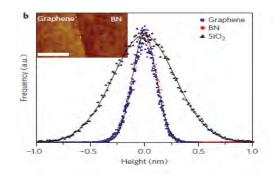


Solid State Commun. 146, 351-355 (2008)

- Suspended Graphene
- 1. highest mobility
- 2. nearly ballistic transport
- 3. difficult to fabricate
- 4. Can not scale to large area

2. Graphene on Boron Nitride

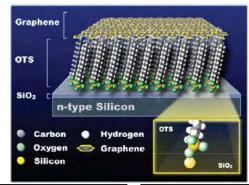


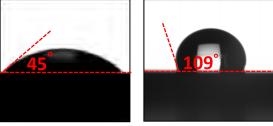


Nat. Nanotechnol. 5, 722-726 (2010)

- Graphene on h-BN
- 1. high mobility
- 2. Difficult to fabricate
- 3. Can not scale to large area

3. Graphene on organic functionalized substrate



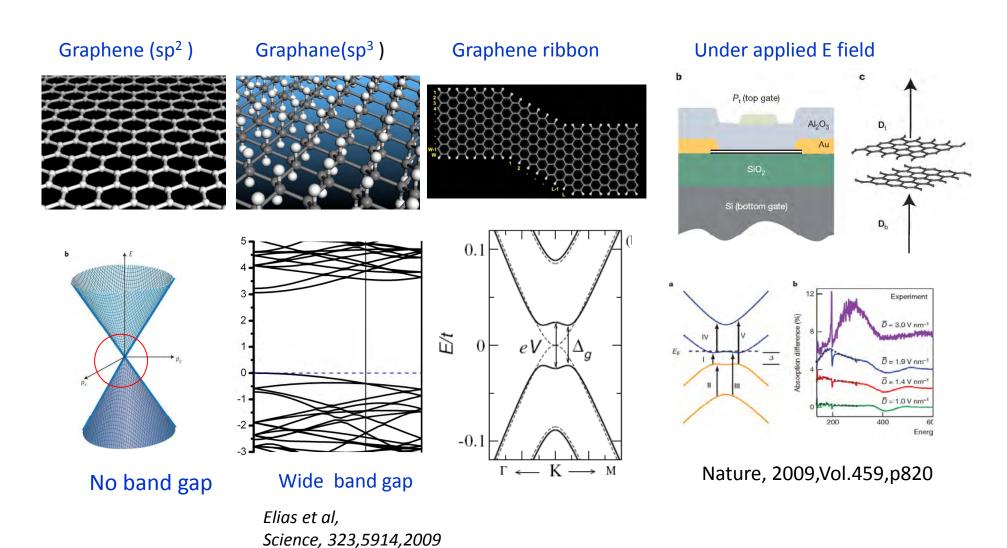


Nano Lett. 2012, 12, 964-969

- Graphene on organic functionalized substrate
- 1. high mobility
- 2. Easy to fabricate
- 3. Scalable

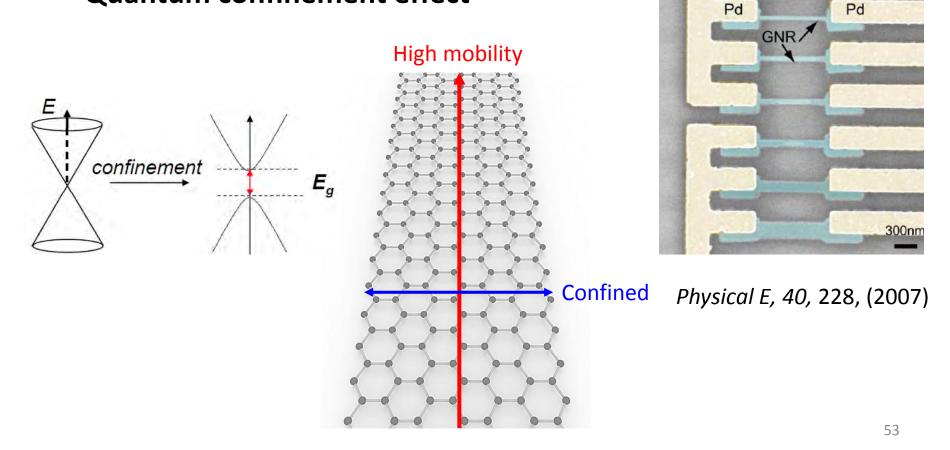
Bilayer graphene and Gap Opening

Gap opening



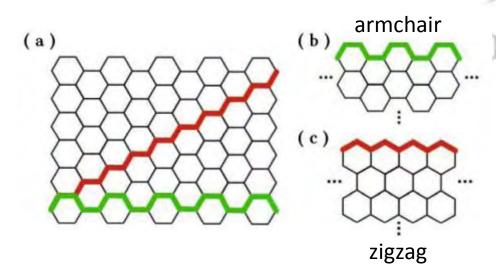
Electronic Structures of GNRs

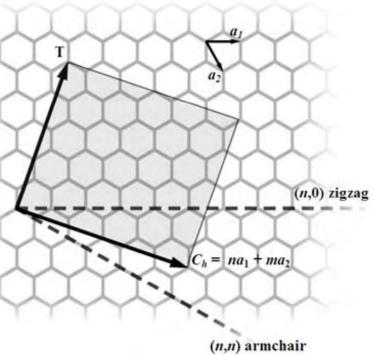
- Open a gap in graphene-graphene nanoribbon (GNR)
- High mobility along the specific direction
- Quantum confinement effect



Graphene Nanoribbon (GNR)

- Structure
 - Graphene strips
 - Charity
 - Two types of edge





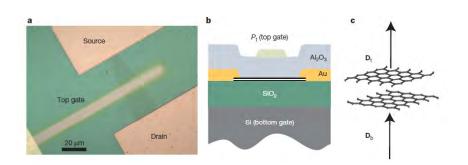
Some of armchair GNRs are semiconucting

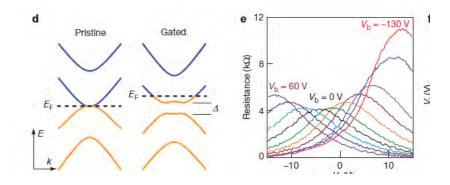
metallic: n = 3m+2

semiconducting: n = 3m or 3m+1

Gap-opening of Bilayered-graphene

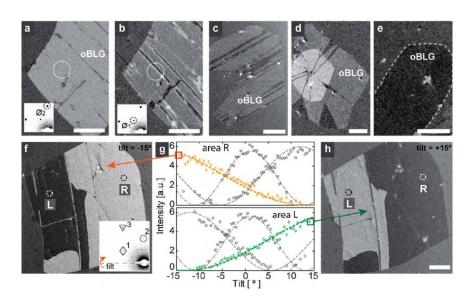
Mechanically exfoilated garpehene





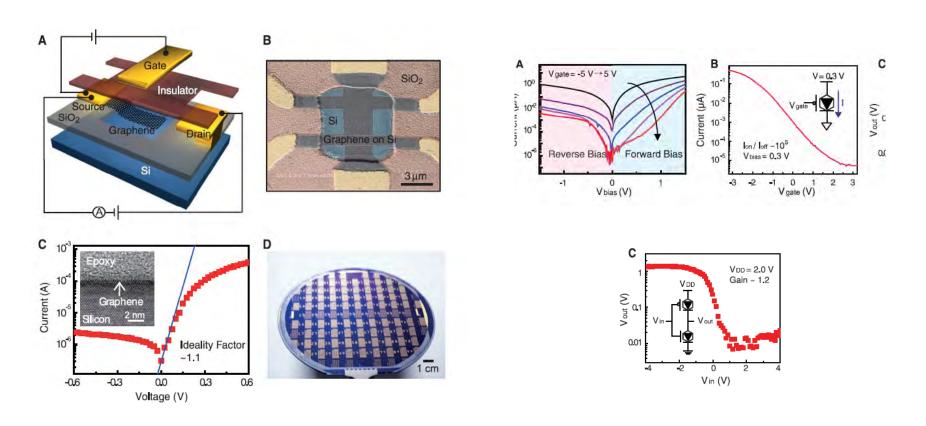
Nature, 2009, Vol. 459, p820

CVD-graphene



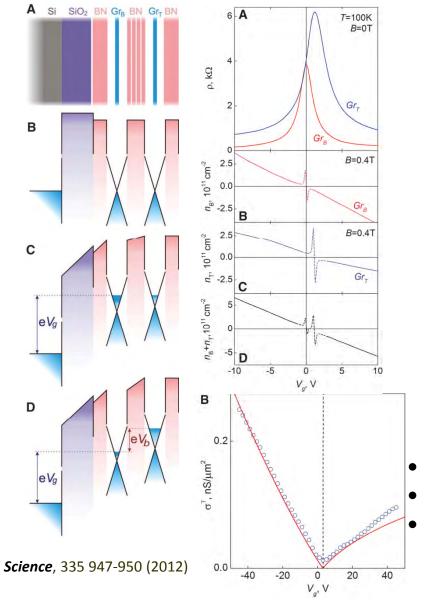
Nano Letters, 2012,12, 1609

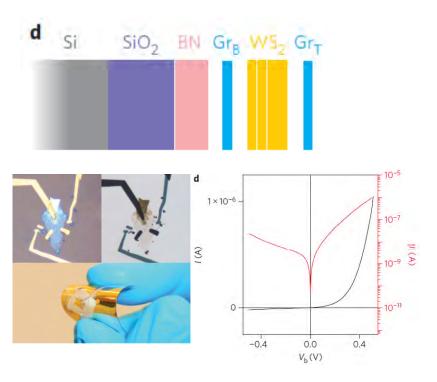
Graphene Barristor- a gate controlled Schottky barriar



Adjusting graphene workfunction High on/off ratio~ 10⁵

Vertical transnsitor

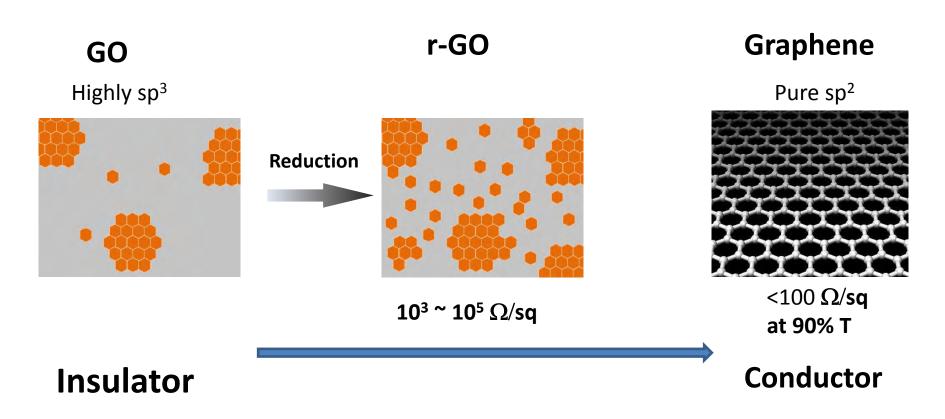




Nature Nanotechnol. 8, 100–103 (2013)

- Combine kinds of 2-D material
- Control tunneling barrier through ultra-thin barrier
- Very Difficult to fabricate

Tunable conduction in graphene based materials



Thin tunneling barrier

Transparent conducting electrode

Next generation production?



© NOKIA



Household appliances



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



© SAMSUNG

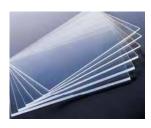
CO SAMS

Communication production

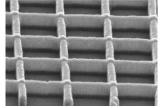
E-paper

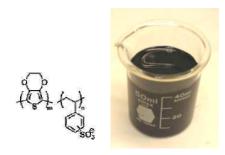
Conventional Transparent Electrode

- ITO (Indium Tin Oxide)
 - Scarcity of indium and high manufacturing cost
 - Vacuum process
 - Relatively brittle
- Alternative:
- Conducting oxides
 - Al doped ZnO
- Metal wire mesh
 - Ag nanowire, Cu grid
- Conductive polymer, PEDOT:PSS





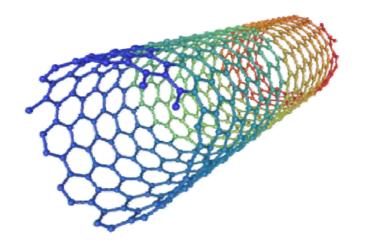




© SPI

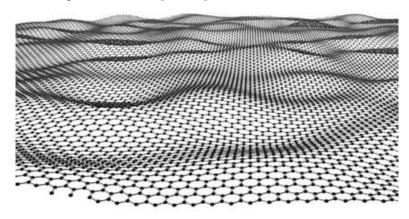
Low Dimensional Nanocarbon Materials

Single walled carbon nanotube (ID)



- 1-D material
- Metallic and semiconducting
- High carrier mobility (120,000 cm²V⁻¹s⁻¹)
- High current carrying capacity
- Excellent mechanical strength

Graphene (2D)



- sp² bonded carbon
- 2-D honeycomb crystal lattice
- High carrier mobility (200,000 cm²V⁻¹s⁻¹)
- Low electrical resistivity ($10^{-6} \Omega \cdot \text{cm}$) (< siliver)
- Good mechanical properties

List of various end applications, their key features, and the suitability of each material

Application	Key Features	Nanotube	Graphene	Metal Nanowires
Touch Panels	Flexibility	0	0	X
	Patterning	0	0	O
	Sheet resistance	0	-	0
	Transparency	-	-	0
LCD	Surface roughness	-	0	X
	Ionic impurities	×	x	X
	Conformal Coating	0	0	X
	Color/Haze	o	O	X
OLED/Solar Cell	Work Function	0	0	X
	Sheet resistance	x	x	0_
	Surface Roughness		O	X
	Stability	0	0	x

("o" = superior, "-" = good, "x" = poor).

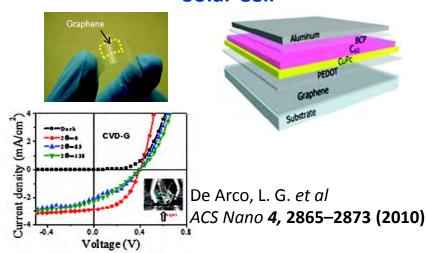
Transparent conducting electrode

Touch Panel

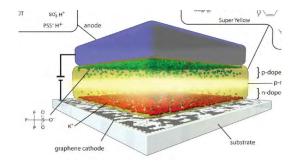


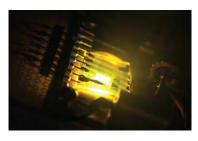
Bae, S. et al. Nature Nanotech. **4, 574–578 (2010).**

Solar Cell



Light Emitting Diode





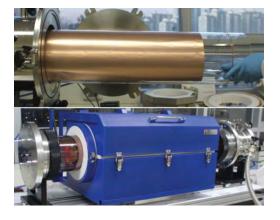
Matyba, P. et al. ACS Nano 4, 637–642 (2010).

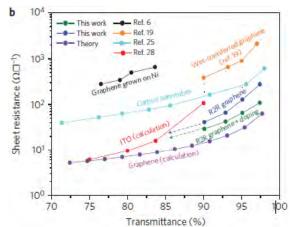
Large area CVD grown graphene for optoelectonic applications

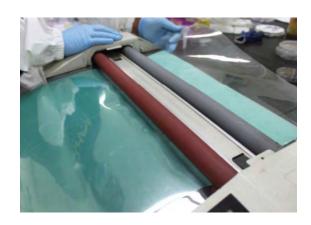


Roll-to-roll production of 30-inch graphene films for transparent electrodes

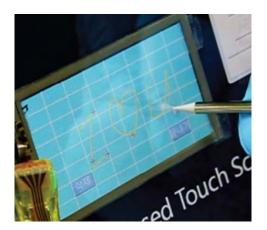
Jong-Hyun Ahn and Byung Hee Hong et al.*









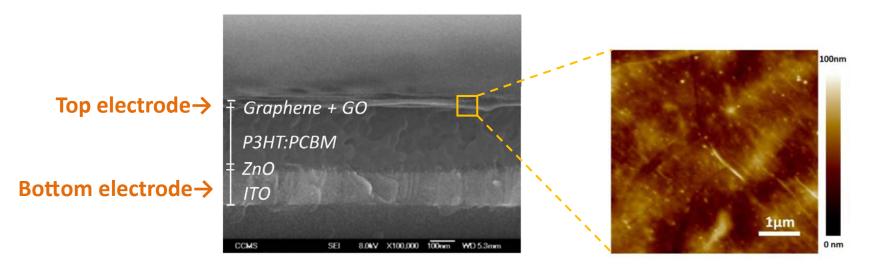


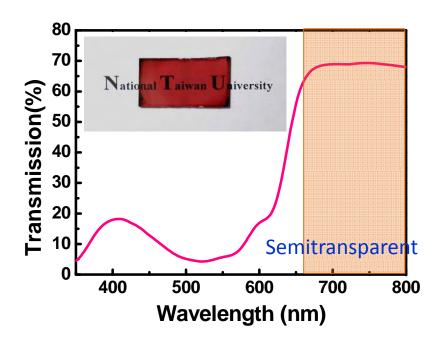
Roller printing

Scale up

Touch panel

Top laminated graphene electrode in a semitransparent polymer solar cell



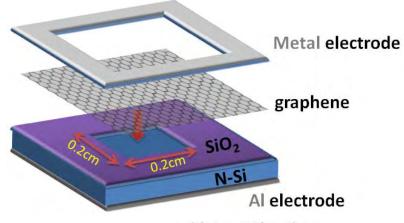


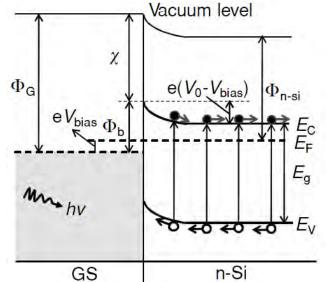


ACS Nano ,Vol.5, 6564, (2011)

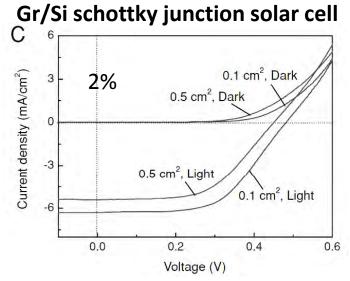
Si/Graphene junction solar cell

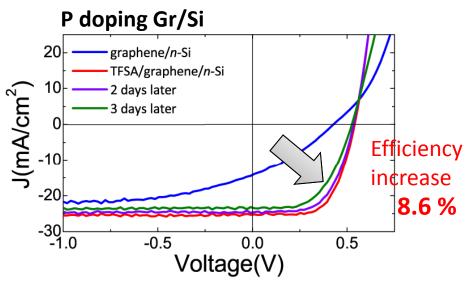
Device structure





Energy diagram of the forwardbiased GS/n-Si Schottky junction

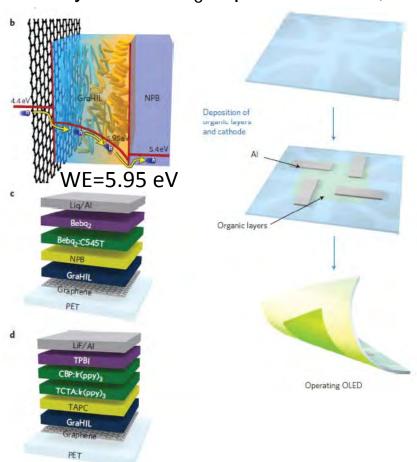




Li. X. et. al., Adv. Mater. **2010**, *22*, 2743–2748 Miao, X. Et. al., *Nano Lett.* **2012**, *12*, 2745–275(

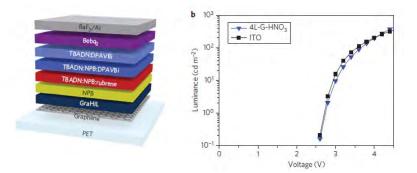
The Future development of large area CVD graphene in OLED applications

4-layered HNO₃ doped Gr~ 30 Ω/□

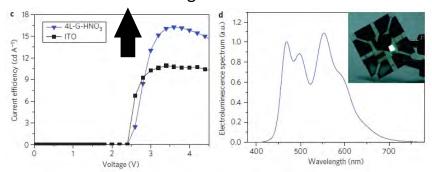


Gra HIL: Self-organized gradient hole injection layer

T.H. Han, et al., *Nature Photonics*, **6**, 105–110, (2012).



The white OLEDs with the graphene anode exhibited a much higher the ITO anode

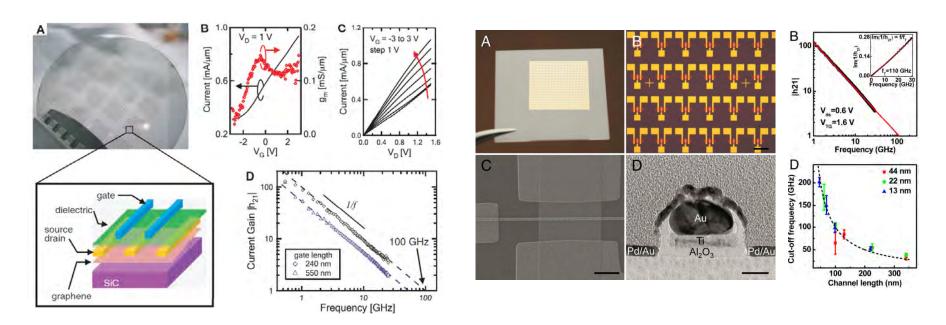






Graphene for other applications

Graphene for Radio Frequency (RF) Transistor



Science, 327, 662 (2010)

up to 100 GHz (cut-off frequency)

Proc. Natl. Acad. Sci. U.S.A. 109, 11588–11592 (2012)

up to 427 GHz

Why use graphene in RF-tech

- Low on-off ratio => fail in CMOS tech
- High mobility, carrier saturation velocity, and large current density=> high cut-off frequency
- High quality graphene => Toward Terahertz regime in the future

High-frequency, scaled graphene transistors on diamond-like carbon

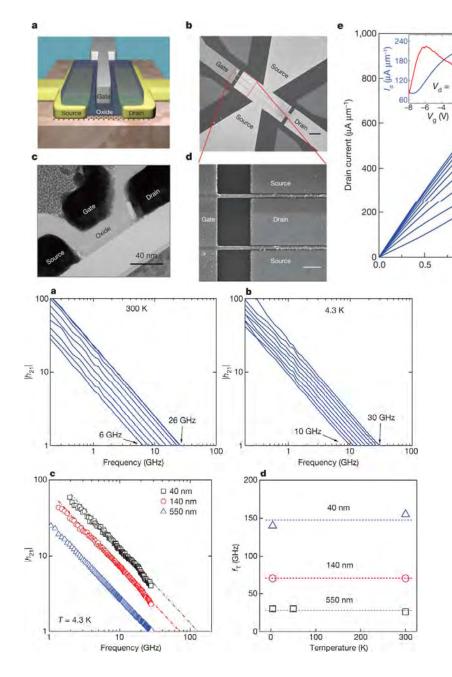
= -8 V to 0 V

= 550 nm

1.0

1.5 0.0

Drain voltage (V)



Cut-off frequencies as high as 155 GHz have been obtained for the 40-nm transistors, and the cut-off frequency was found to scale as 1/(gate length).

 $L_a = 40 \text{ nm}$

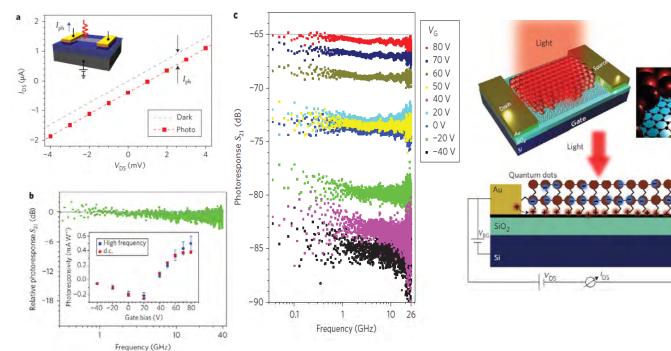
1.0

0.5

Wu, Y., et. al. *Nature*, 2011, 472,74–78

Ultra fast and Ultra high gain Photodetector

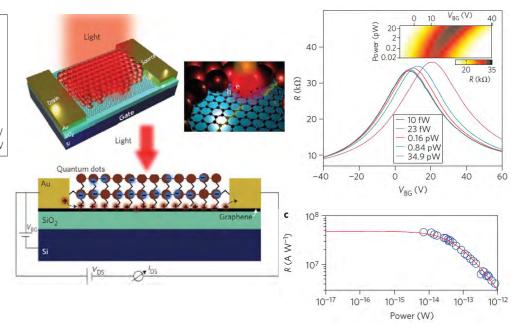
Ultra fast photodectector



Nature Nanotech. 4, 839-843 (2009)

- Light is absorbed by graphene
- P-n junction between channel and graphene covered with metal
- Gate dependent photoresponse
- Could be operated at frequency as high as 40GHz

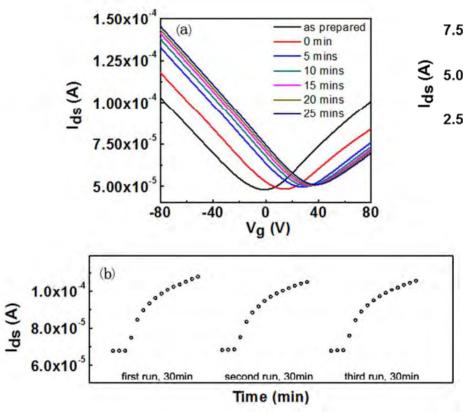
Ultra high gain photodectector



Nature Nanotech. 7, 363-368 (2012)

- Light is absorbed by photo-active material on graphene
- Charge transfer from photo-active material to graphene
- Gain could be very large due to inherent high mobility of graphene

Detection of sulfur dioxide (SO₂) gas with graphene field effect transistor



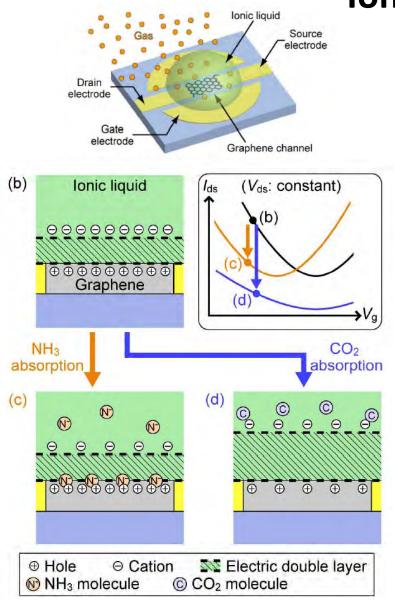
SO₂ out SO2 out 7.50x10 set gate bias 5.00x10 SO2 in SO₂ in 2.50x10⁻¹ SO2 in 120 180 240 300 360 60 Time (min)

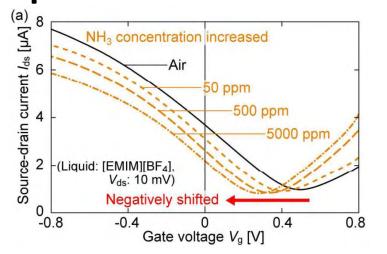
SO₂ strongly p-dopes the graphene

- the Dirac point shifted 0.678V/ppm to the positive side
- 2. the resistance decreased about 60% at a SO_2 concentration of 50 ppm.

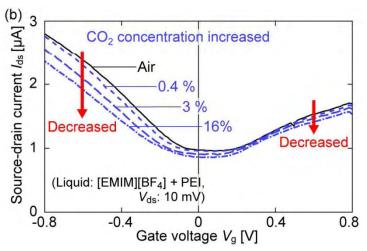
Reproducibility of the graphene FET as a SO₂ gas detector

A Graphene FET Gas Sensor (CO₂, NH₃) Gated by Ionic Liquid



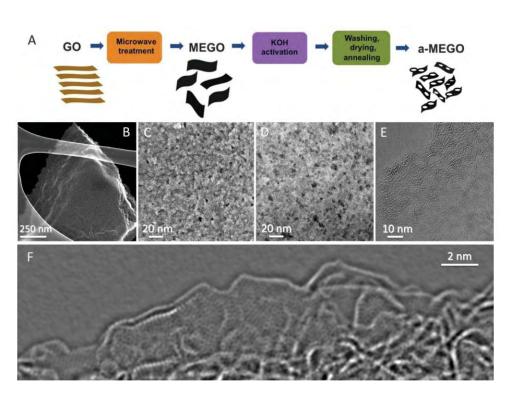


NH₃ molecules transferred negative charge to graphene channel

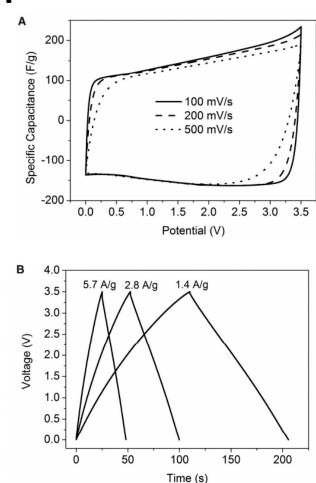


The decrease in $I_{\rm ds}$ over the entire voltage caused by ${\rm CO_2}$ denotes that capacitance of the EDL was reduced.

Carbon-Based Supercapacitors Produced by Activation of Graphene

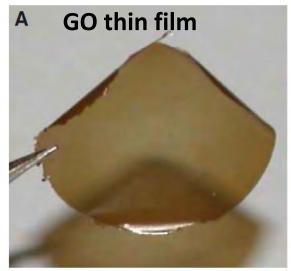


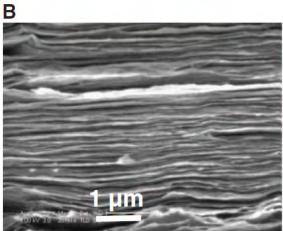
The advantages of MEGO:
High electrical conductivity
Low oxygen and hydrogen content.
sp²-bonded carbon with continuous 3D network

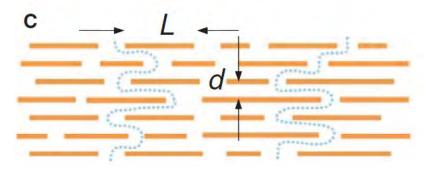


For a packaged cell, the power density of ~75 kW/kg is one order higher than the values from commercial carbon supercapacitors.

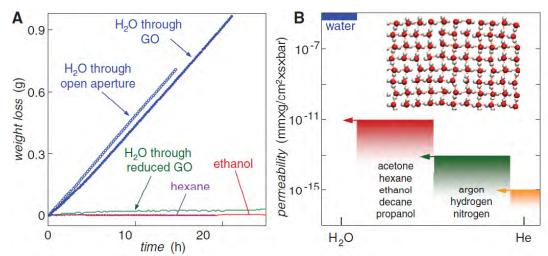
Unimpeded Permeation of Water Through Helium-Leak— Tight Graphene-Based Membranes





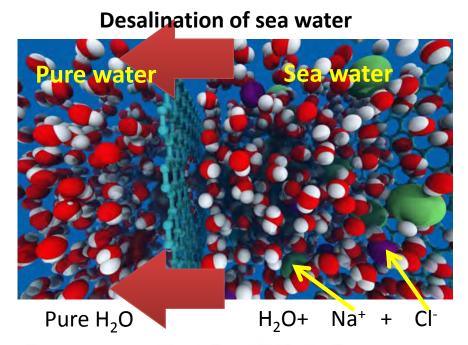


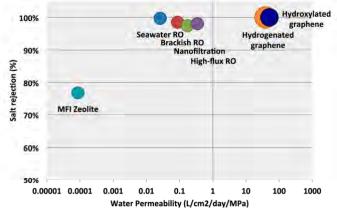
Completely impermeable: liquids, vapors, and gases Unimpeded permeation: water H₂O



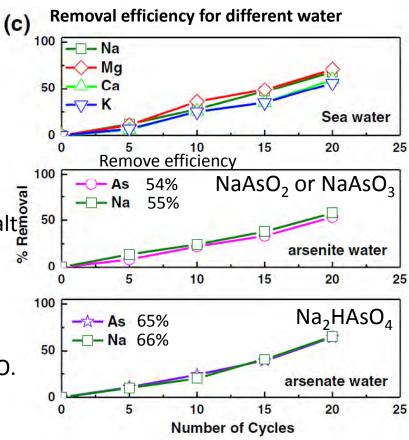
H₂O permeates through the GO at least 10¹⁰ times faster than He gas

Graphene sheets for desalination of sea water and arsenic removal



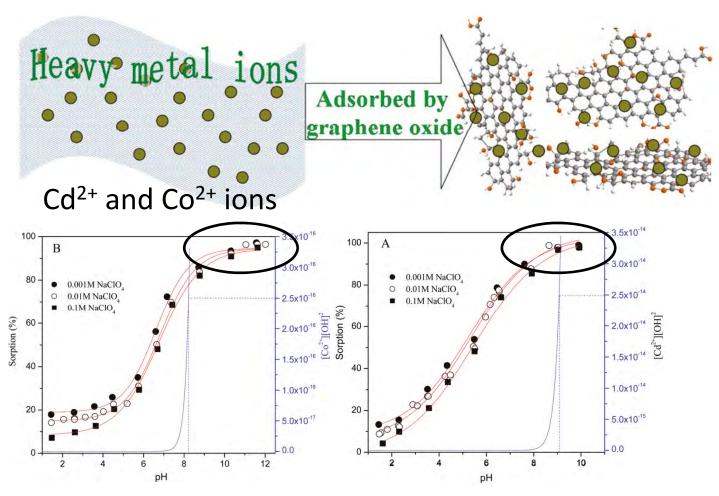


The graphene
nanopores reject salts
ions with a water
permeability 2–3
orders of
magnitude higher
than commercial RO.



Cohen-Tanugi D. et. al., Nano Lett. 2012, 12, 3602–3608 Ashish Kumar Mishra, et. al., Desalination 282 (2011) 39–45

Few-Layered Graphene Oxide Nanosheets As Superior Sorbents for Heavy Metal Ion Pollution Management



Most Cd^{2+} and Co^{2+} is adsorbed on GO nanosheets at pH > 9.