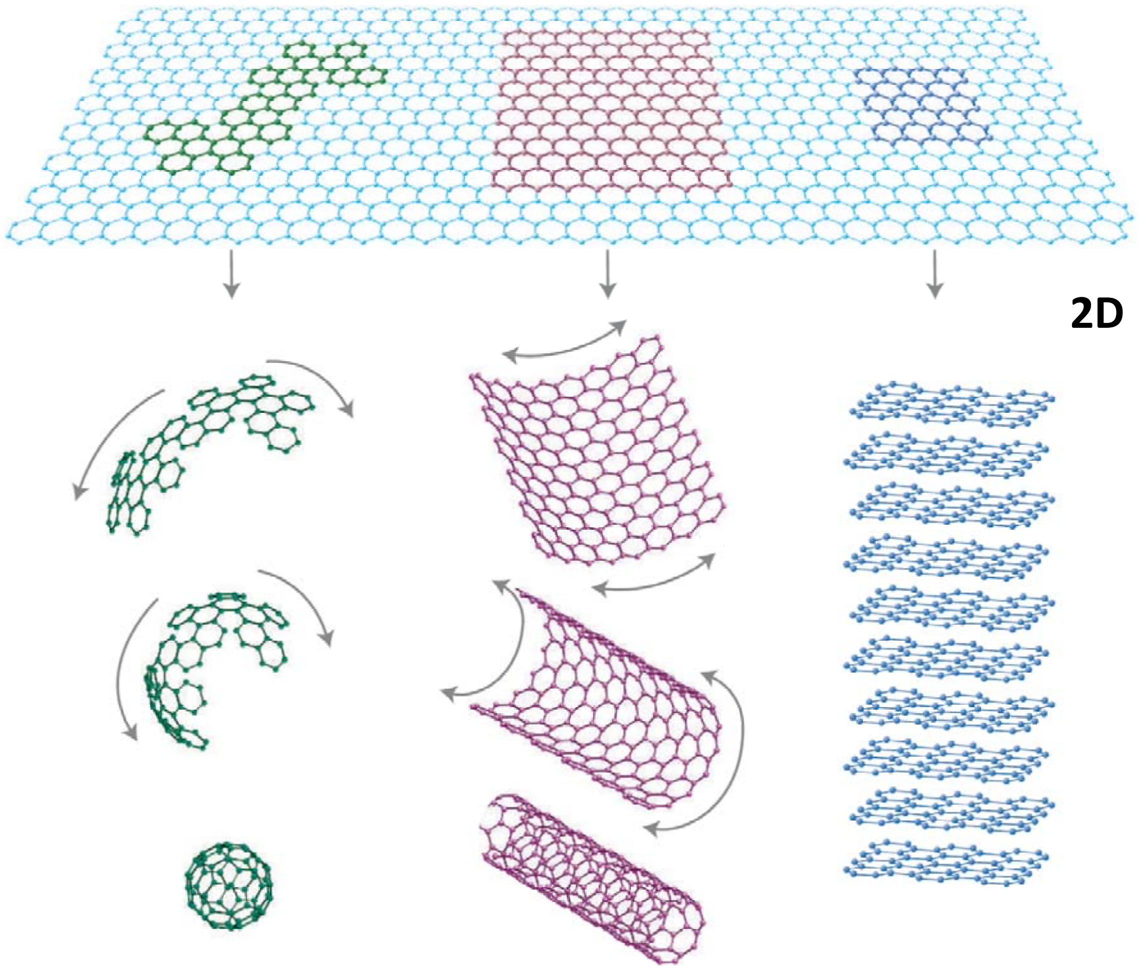
Part II. Introduction of Graphene

Graphene (Mother of all-graphitic form)



2D honeycomb lattice
Graphene

0D
bulky ball

1D
Nanotube

3D
Graphite

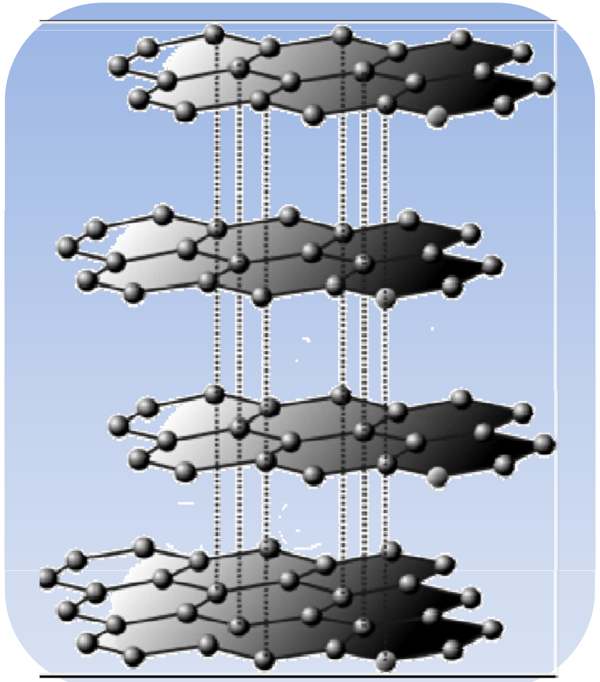
Geims et al, Nature Materials,Vol.6 183, 2007

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.)

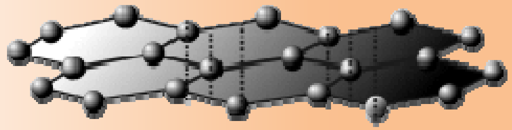
- 2005: Anomalous quantum Hall effect was observed
- 2010: ***Nobel prize in Physics*** for Andre Geim and Konstantin Novoselov
- Now: Stimulate wide researches and be applied to various fields

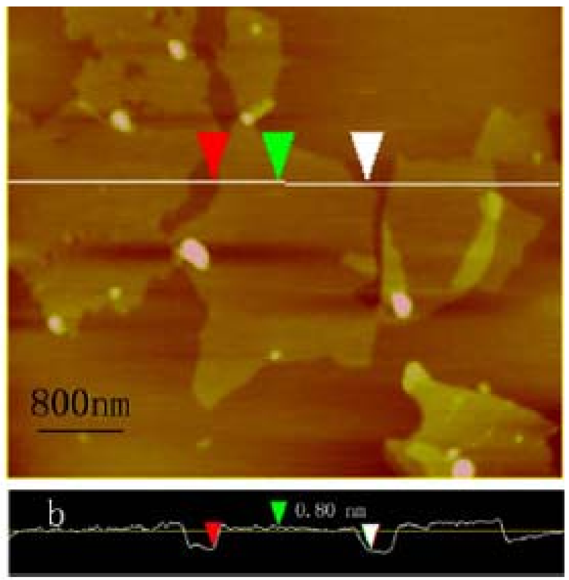
From graphite to graphene



Graphite
Multilayer carbon atom

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





2010 The Nobel Prize in Physics

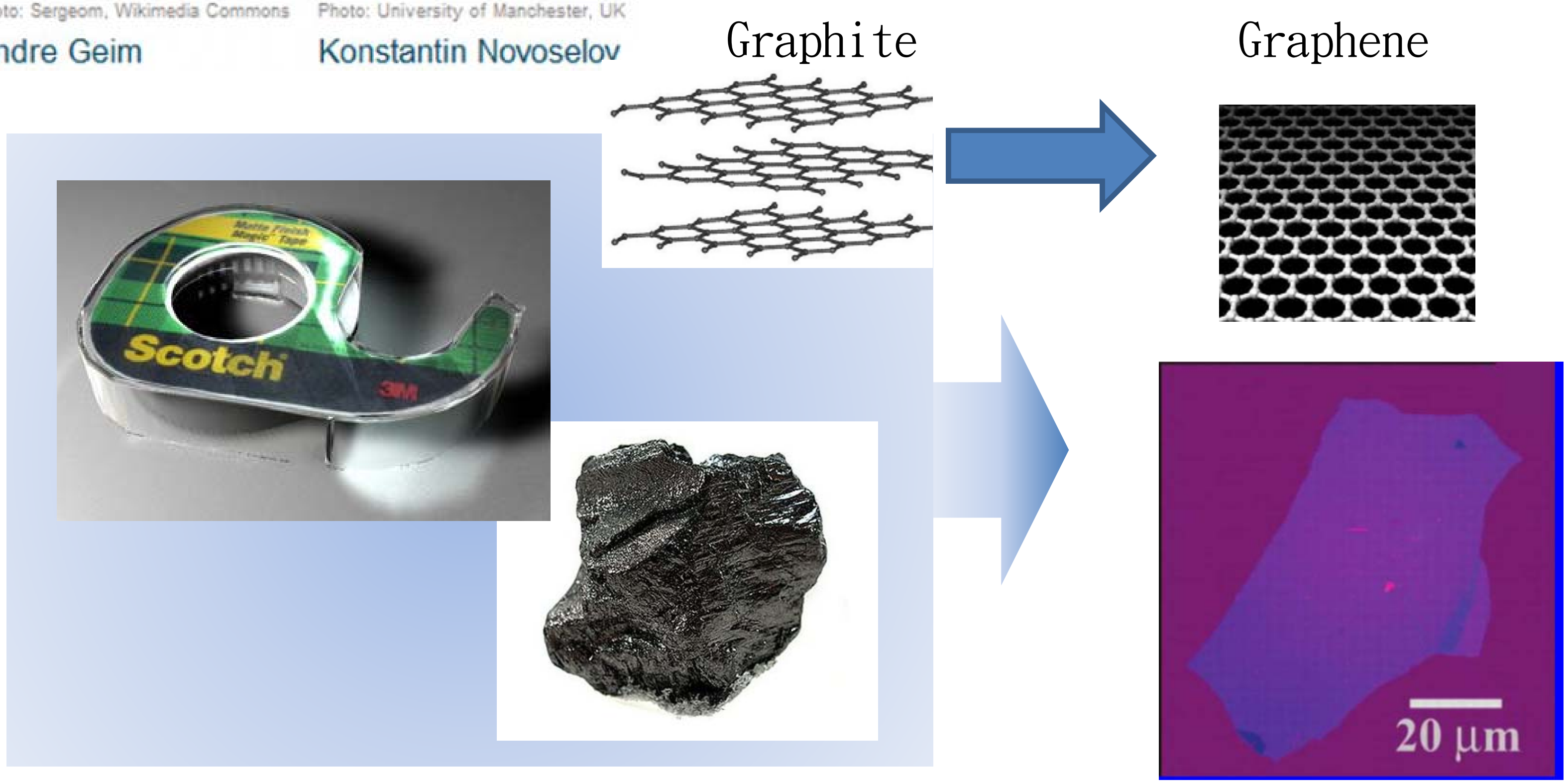
Photo: Sergeom, Wikimedia Commons

Andre Geim

Photo: University of Manchester, UK

Konstantin Novoselov

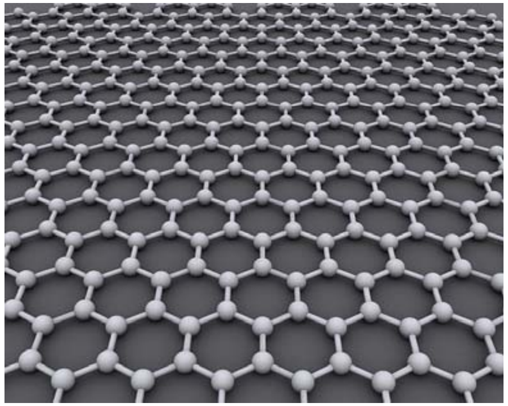
Prof. Andre Geim and Konstantin Novoselov at the U. Manchester for groundbreaking experiments regarding the 2-D material graphene



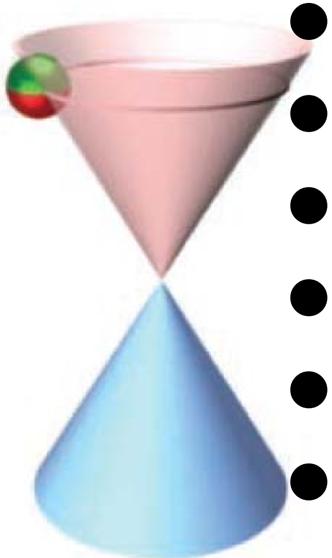
The 6th International Conference on Recent Progress in Graphene Research (RPGR 2014), Taipei, 9/21-9/25/2014

Nobel Laureate , Sir Prof. Andre Geim for a plenary speech

Around 500 participants from 20 countries



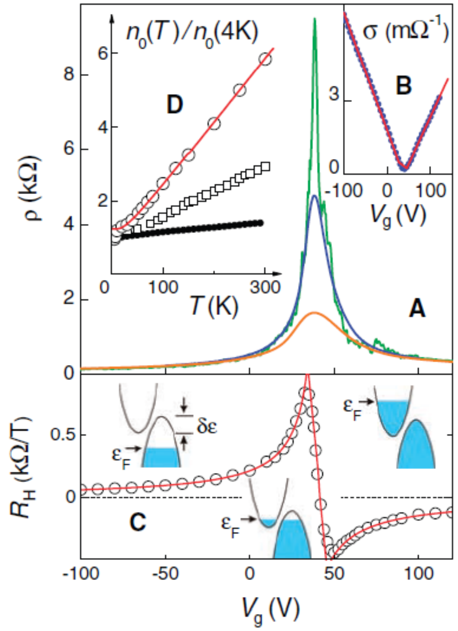
Graphene



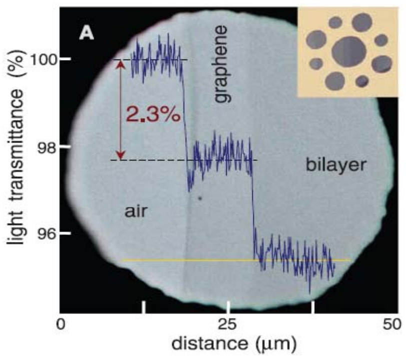
- Atomic-thick layer of carbon atom
- Zero bandgap
- Massless Dirac fermions
- High transparency and Flexible
- Low Resistivity about 10^{-6} Ω·cm, (< siliver)
- Ultrahigh high mobility ($1000\sim300000 cm^2V^{-1}S^{-1}$)
- etc…

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

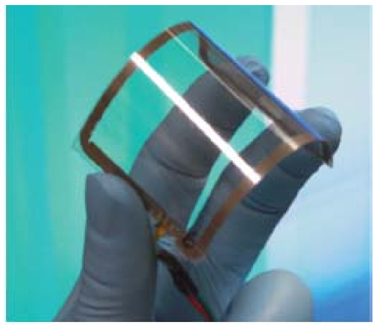
A. K. Geim, Science (2009)



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



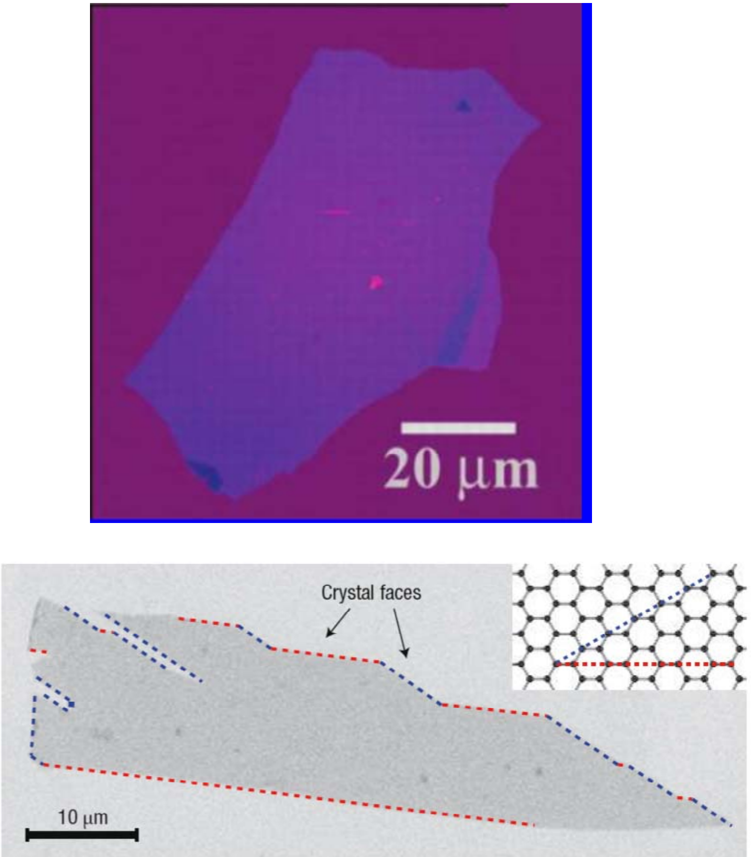
Nair et al., Science, (2008)



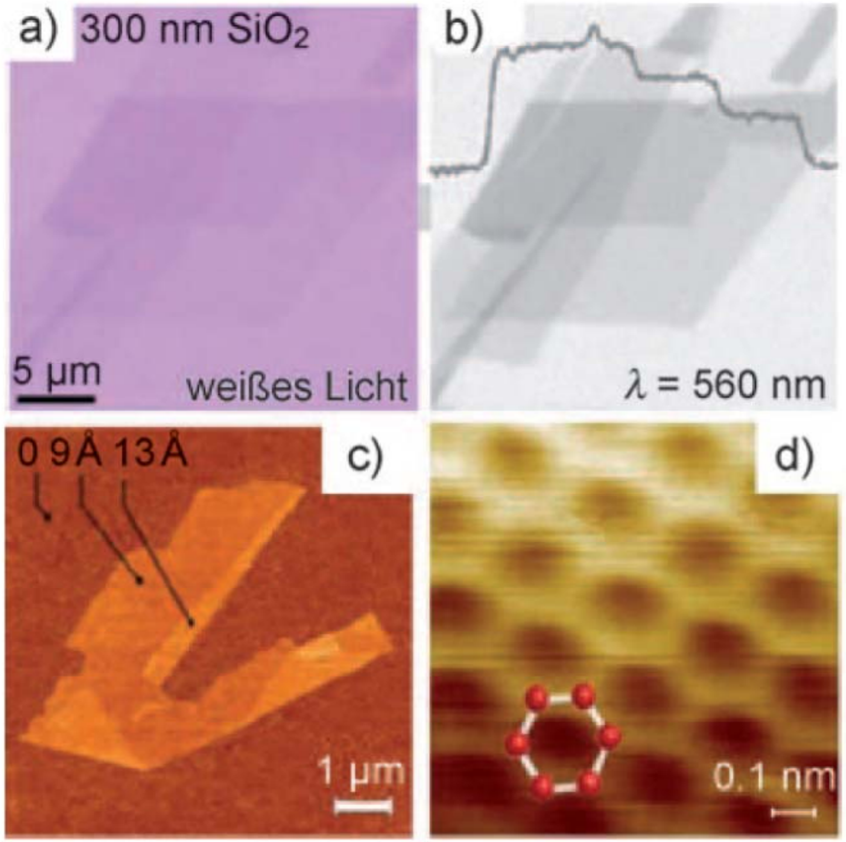
Bae. S *et al.* Nat. Nanotechnol. (2011)

Atomic structure of graphene

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



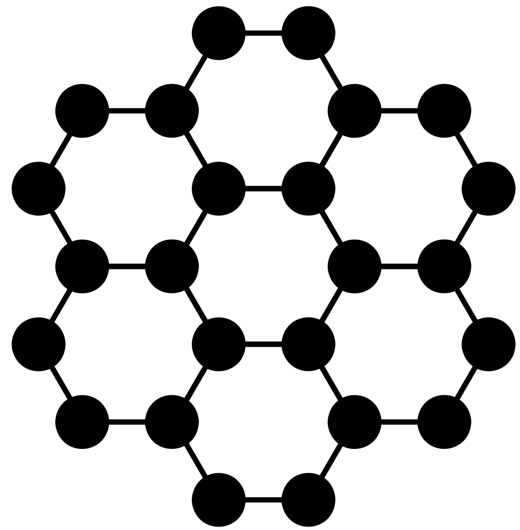
Kraner et al. Chem. Rev. 2010,110,132

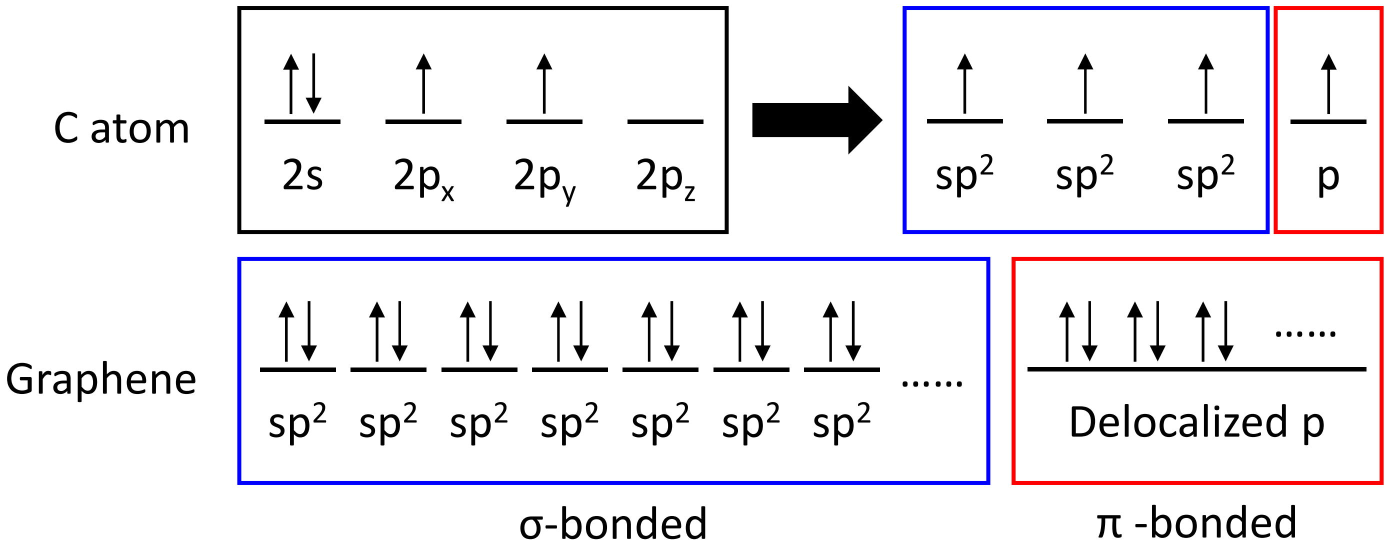


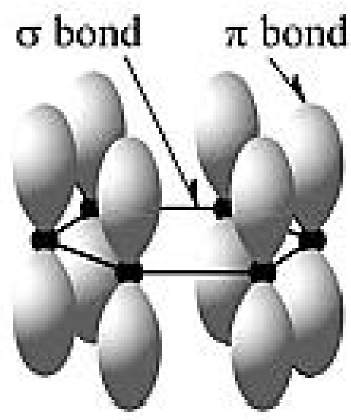
Rao et al, Angew. Chem., 2009,48,7752

Electronic Structure of Graphene

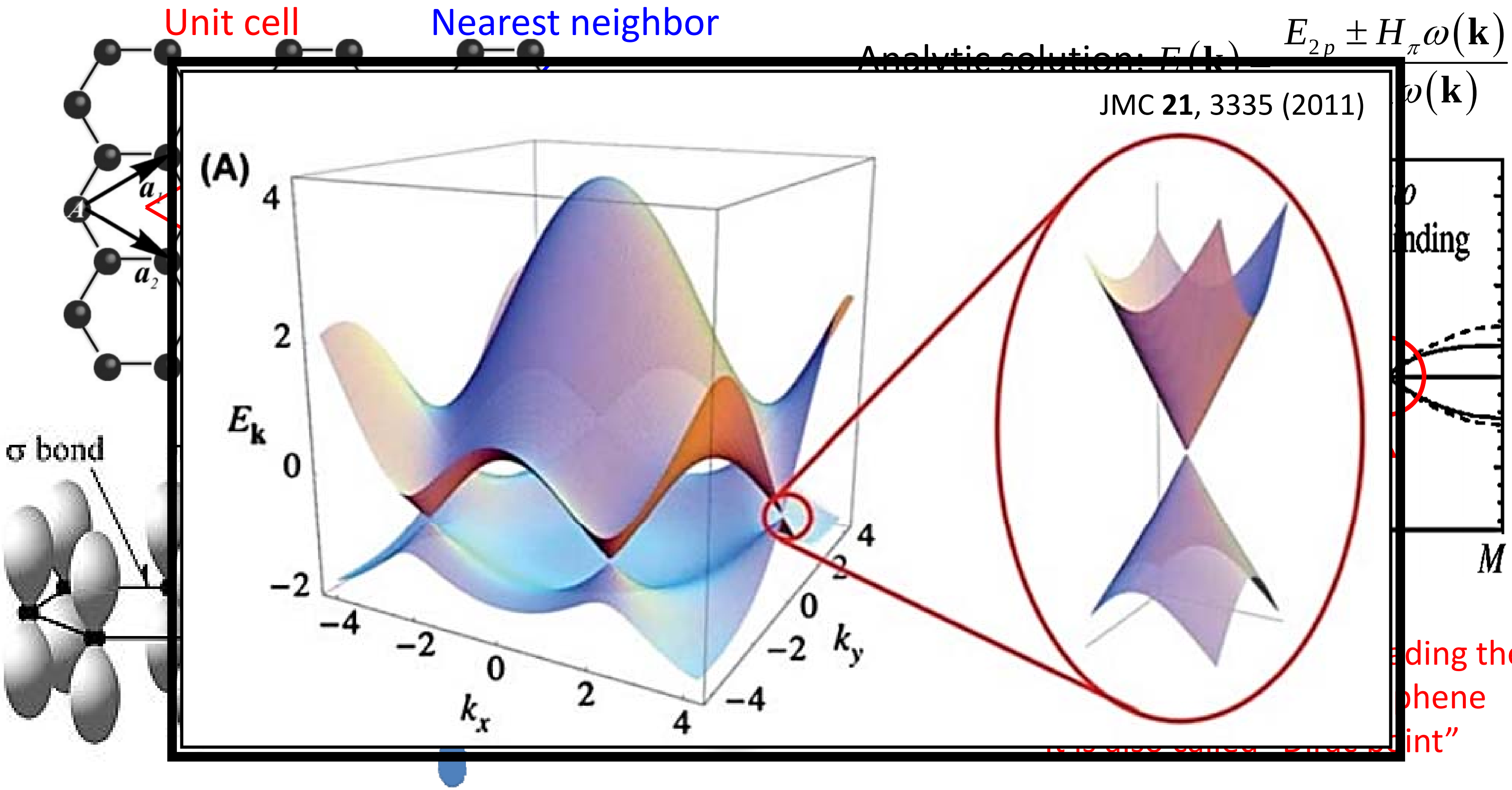
- All C atoms are sp^2-bonded to adjoining C atoms
  - sp^2 electrons form σ bonds
    - Form the honeycomb net of C atoms
  - Delocalized p electrons form π bonds







Tight-binding

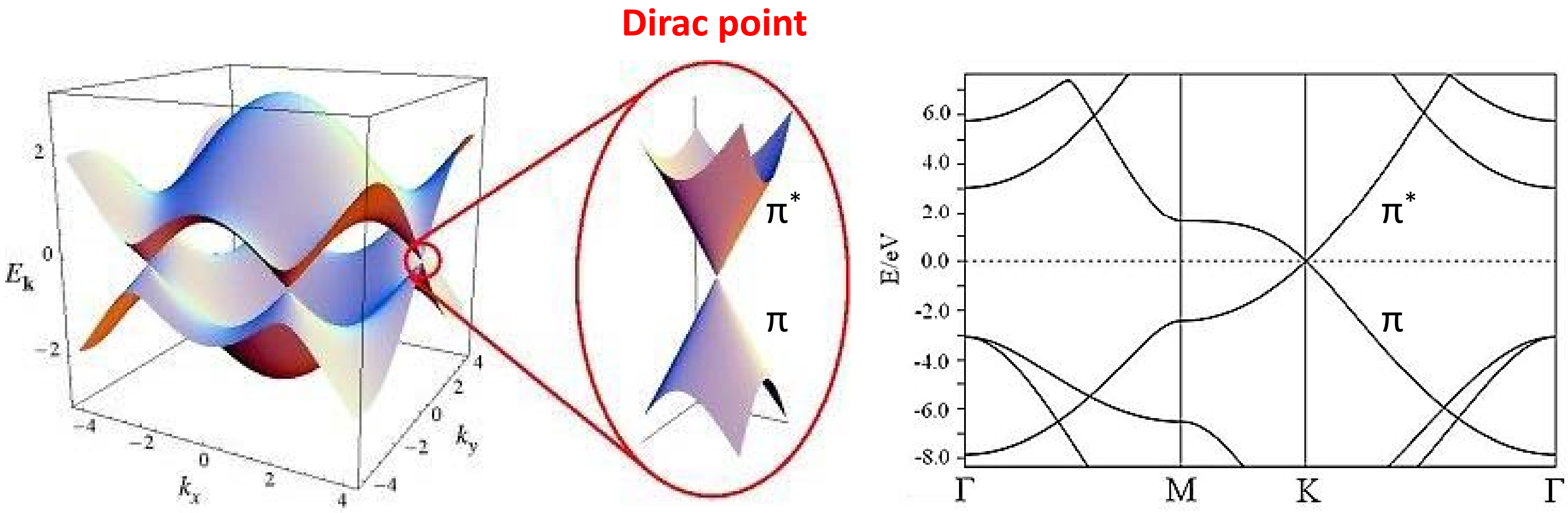


- Bonds with adjacent atoms are most important, therefore the "nearest-neighbor tight-binding description" is usually used

Phys. Rev. B **66**, 035412 (2002)

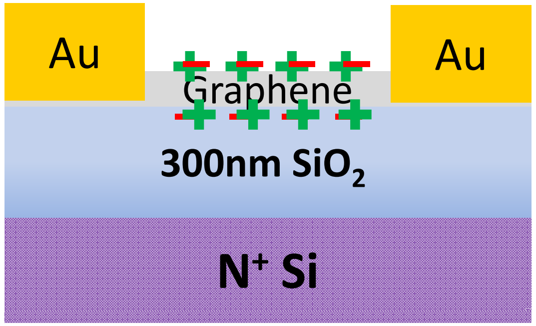
1-2. Fundamental Properties of Graphene

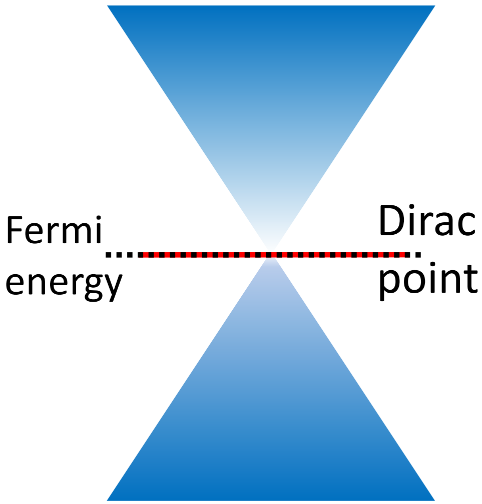
Band Structure of Graphene



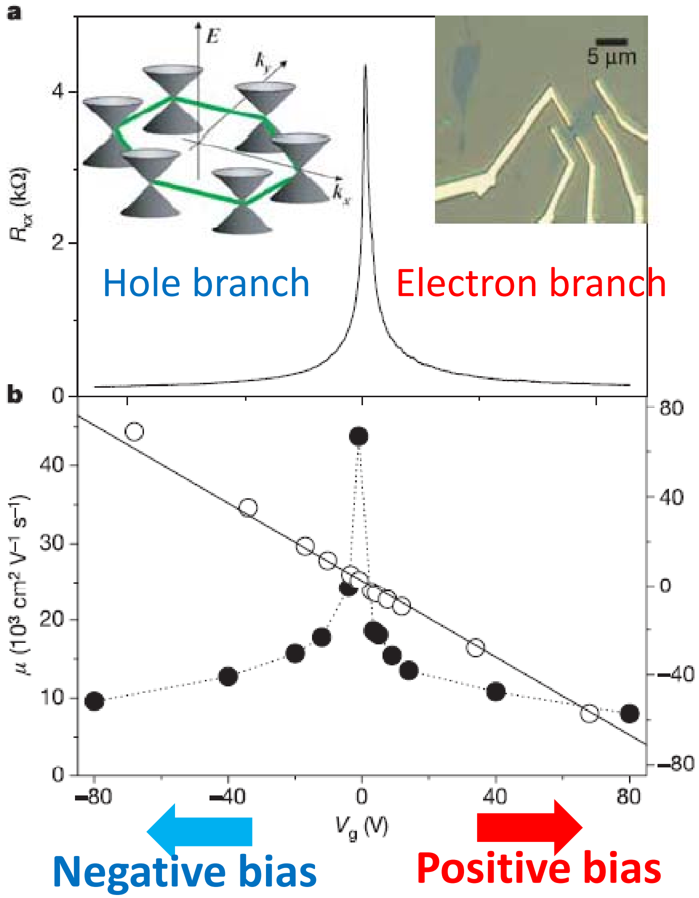
- The valence band and the conduction band meet at Dirac point
  - Metallic behavior
  - “Semi-metal” or “zero-bandgap semiconductor”
- Linear E-k dispersion near Dirac point
  - “Massless” electrons and holes

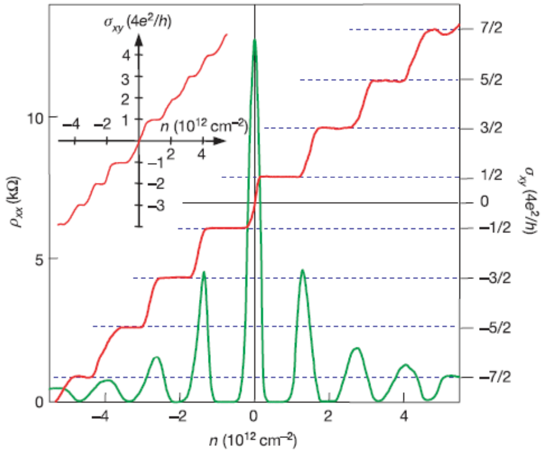
Graphene
Ambipolar transport





Yuanbo Zhang, et al., Nature(2005)





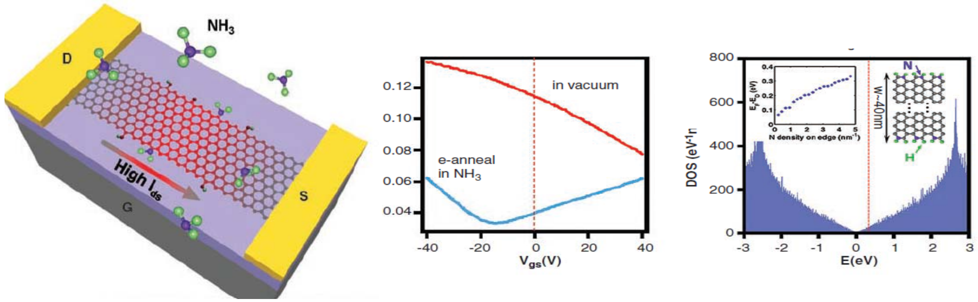
K. S. Novoselov, et al., Nature (2005)

Disadvantage of graphene

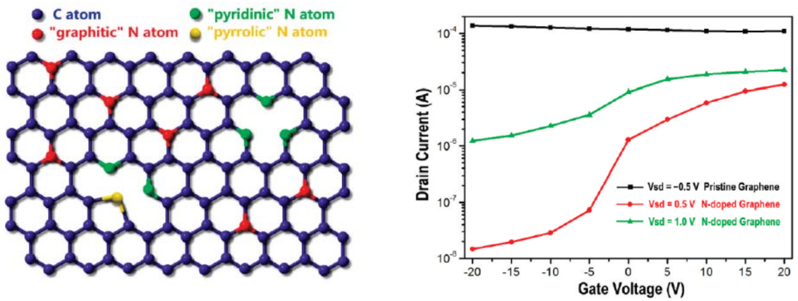
1. **Low on/ off ratio**
2. **Usually P-type in air**
3. **Poor air stability**

Doped graphene

1. Covalent functionalized or substitutional doping

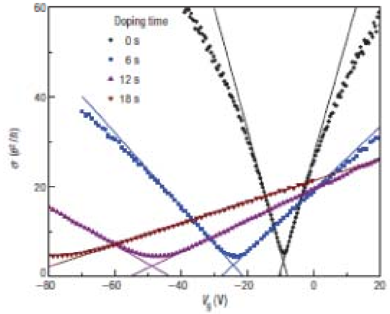


Xinran Wang, *etal.* Science (2007)

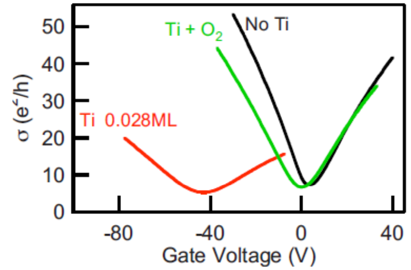


Dacheng Wei, *etal.* Nano lett. (2009)

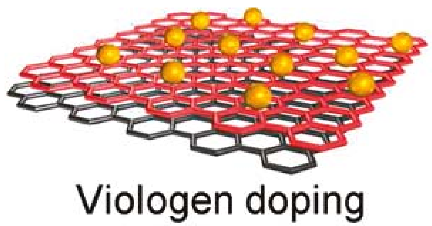
2. Surface charge transferred doping



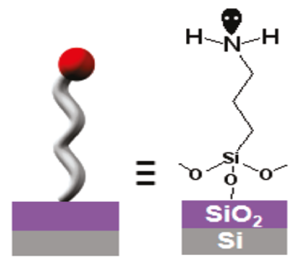
J.–H. Chen. *et al.* Nature (2008)



McCreary, K. *etal. Appl. Phys. Lett.* **2011**



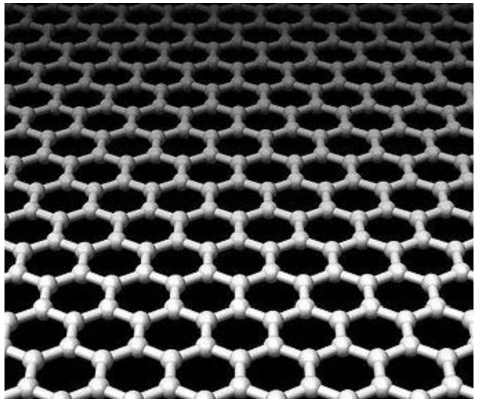
Yu, W. *etal. Nano Lett.* **2011**



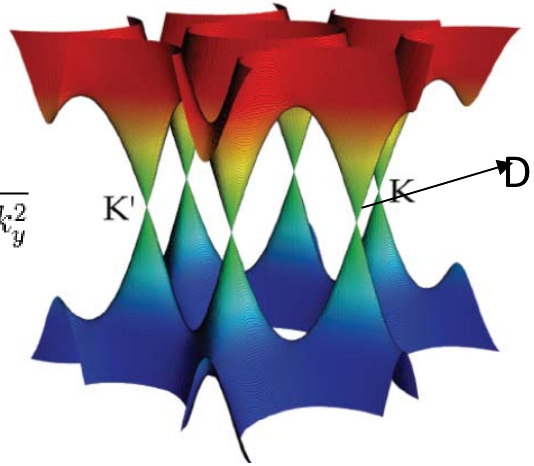
Wang, Y.; *etal. J. Phys. Chem. C* (**2008**)

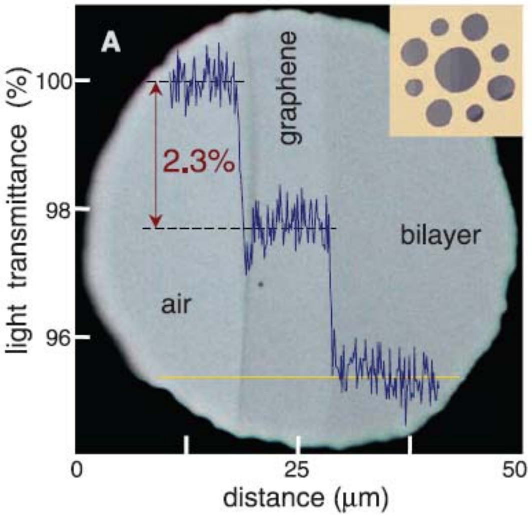
- Most of doping methods could considerably damage carrier mobilities of graphene.
- The doping level could not easily be easily controlled.
- The doping devices are very vulnerable to environment, especially for n-type doping.

High transparency of Graphene



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





Nair et al., Science, (2008)

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, (< silver)**
- **etc…**

Optics

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

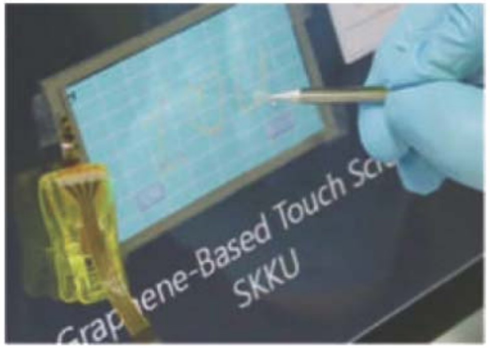
Great potential for electronic and optoelectronic applications!

15

Optoelectronics application of Graphene

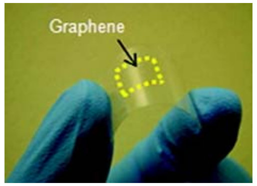
- **Transparent conducting electrode**

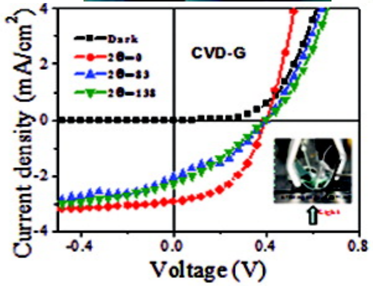
TOUCH PANEL

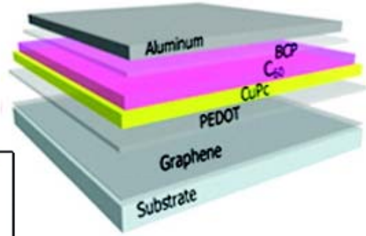


Bae, S. *et al.*
Nature Nanotech. ***4, 574–578 (2010).***

SOLAR CELL

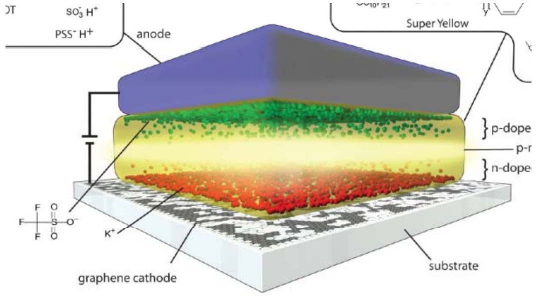


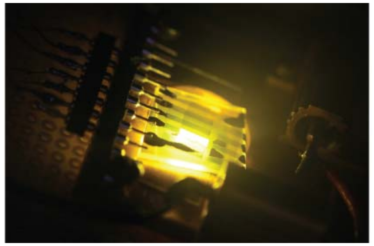




De Arco, L. G. *et al*
ACS Nano ***4,*** **2865–2873 (2010)**

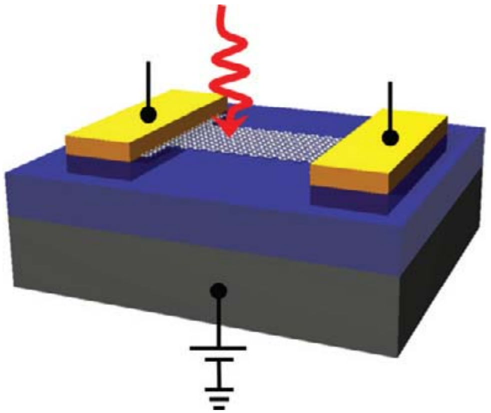
Light emitting diode

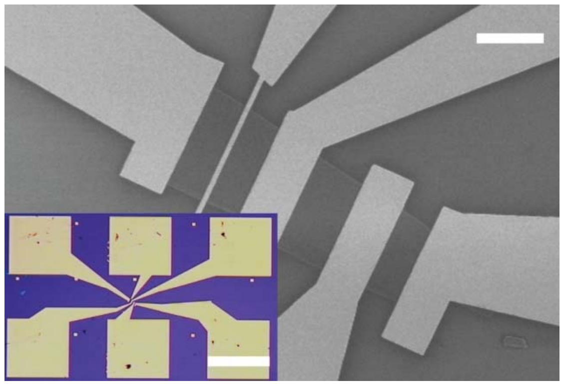


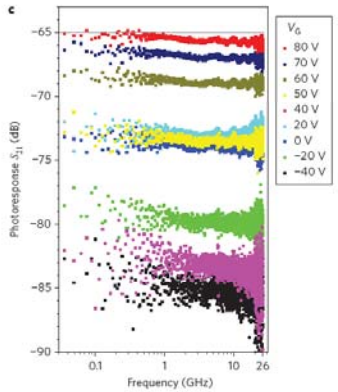


Matyba, P. *et al.*
ACS Nano ***4, 637–642 (2010).***

- **Ultra fast Photodetector**





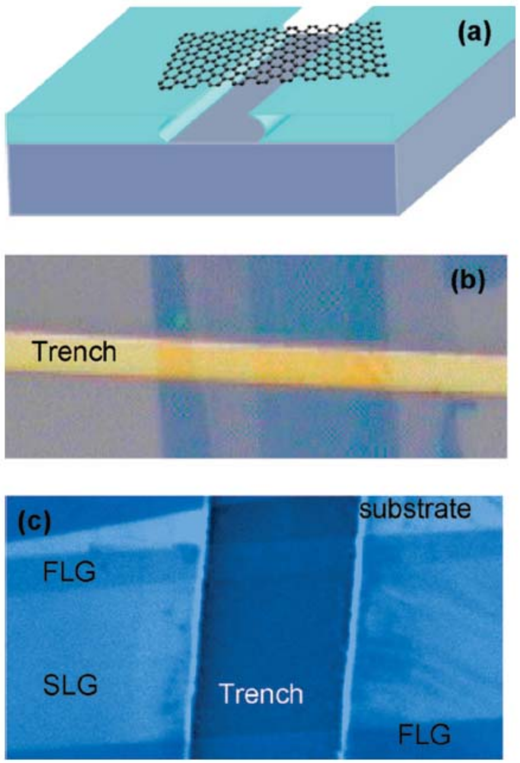


Xia, F. *et al.* *Nature Nanotech.* ***4, 839–843 (2009).***

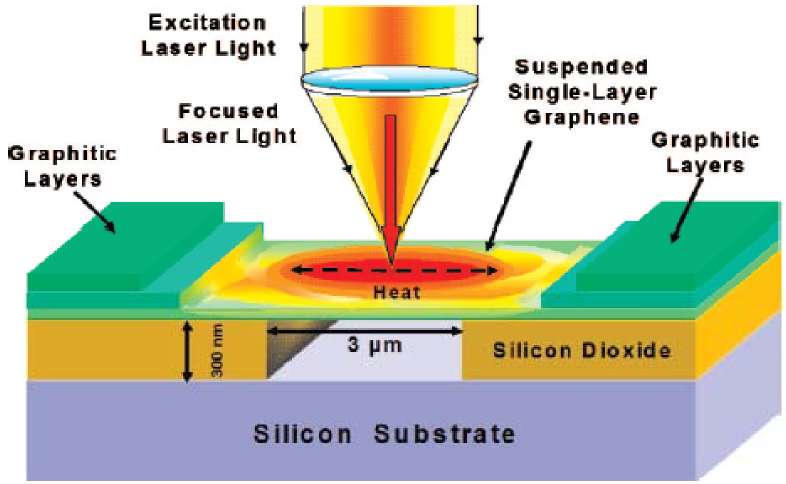
Thermal conductivity of graphene

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	~3500	electrical	individual; suspended	Pop et al.[16]
SW-CNT	1750–5800	thermocouples	bundles	Hone et al.[17]

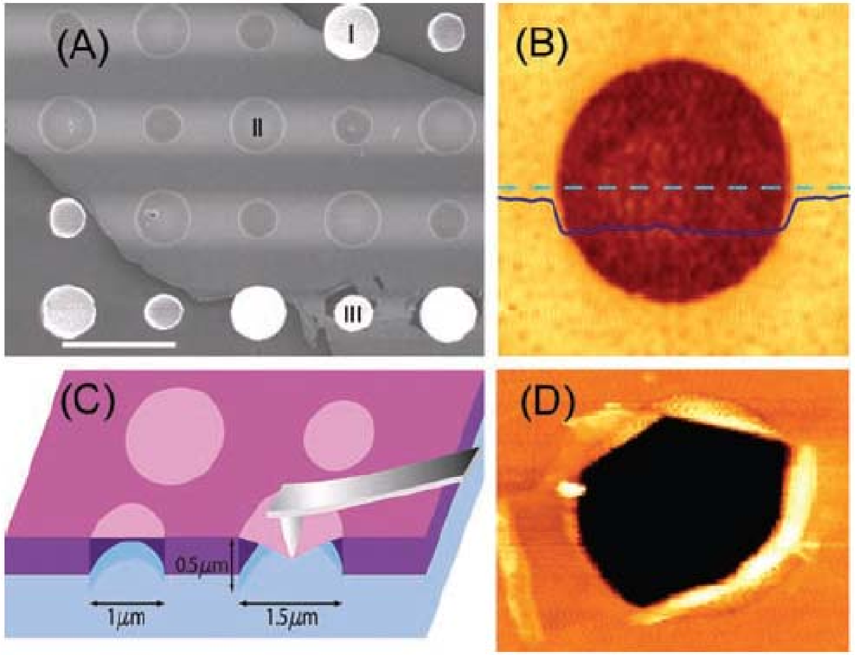


The extremely high value of the thermal conductivity suggests that graphene can outperform carbon nanotubes in heat conduction.



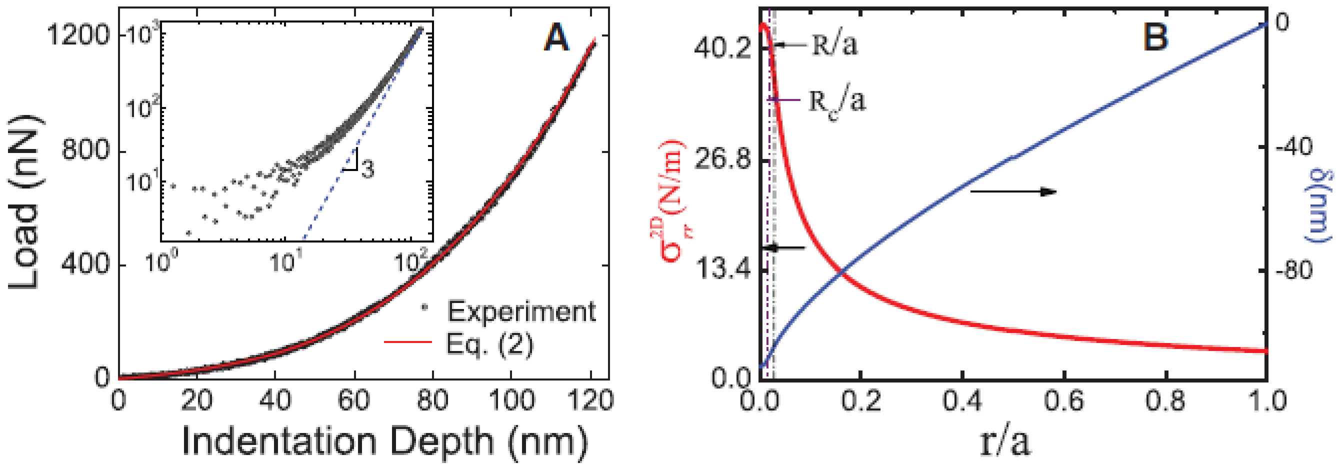
Nano Letters, 2008,Vol.8, 902

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.



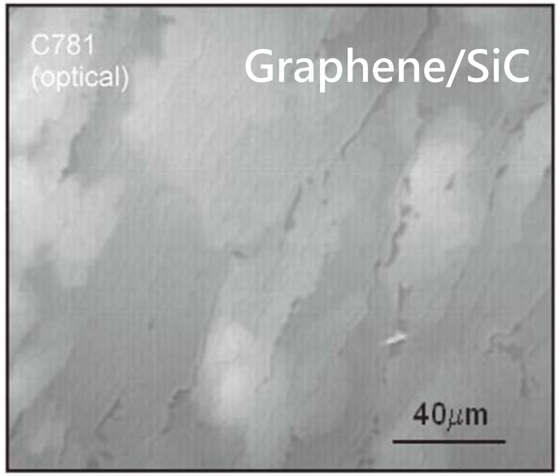
Hones et al, Science,Vol. 321, p385, 2008

Synthesis of Graphene

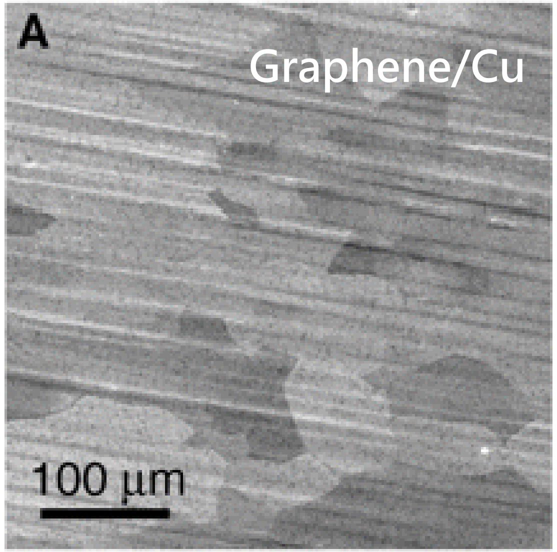
- **Mechanical exfoliation**
- **Epitaxial growth on silicon carbide**
- **Epitaxial growth on metal substrates**
- **Reduction of graphene oxide**

=> solution processible, mass producible, simple and cheap

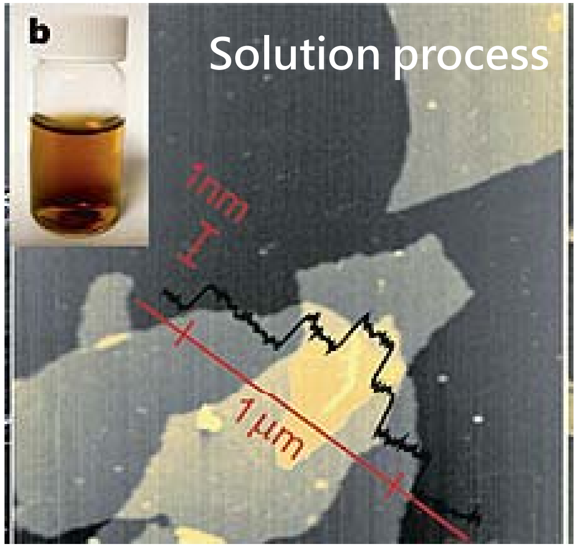
Novoselov et al., *Science* (2004)



de Heer et al, *Science* (2006)



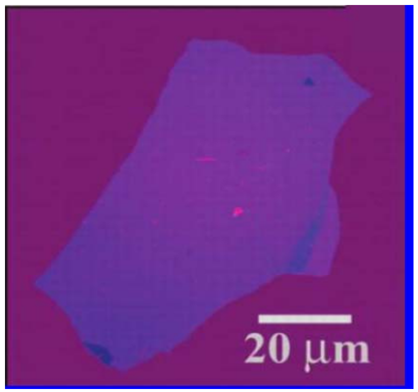
Ruoff et al., *Science*, vol. 324, pp1312-1314, **2009**



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

Exfoliation process

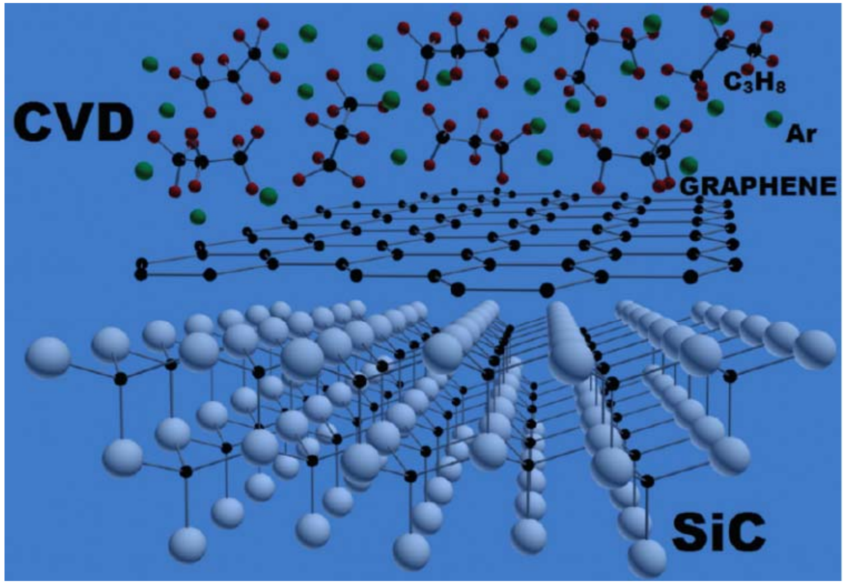
– In 2004, Andre Geim and Konstantin Novoselov suggest this method[4]
– Use tapes to split one layer of C atoms from graphite and form graphene flake
– Free-standing graphene
– Demonstrate the first graphene transistor
– 2010 Nobel Prize in Physics



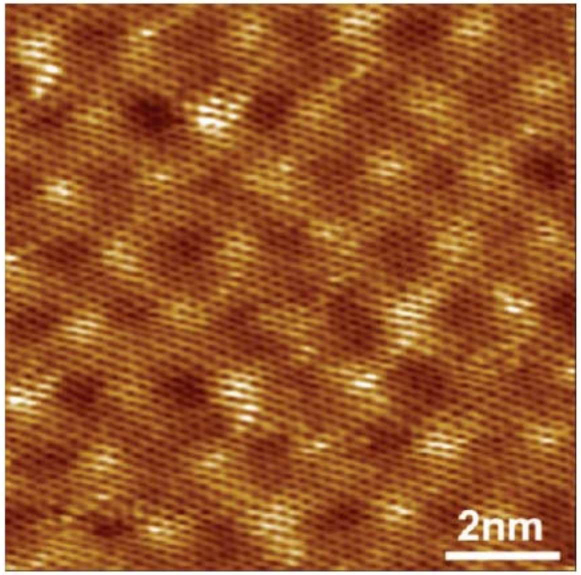
Novoselov, K. S.; Geim, A. K. et al, *Science* **306** (5696), 666 (2004)

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

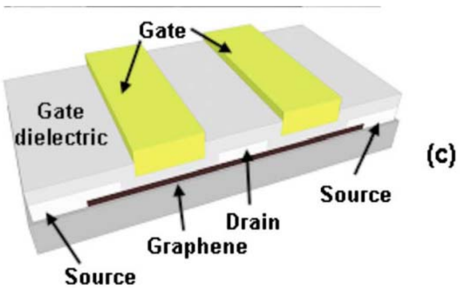
Epitaxial Graphene on SiC substrate by Chemical Vapor Deposition

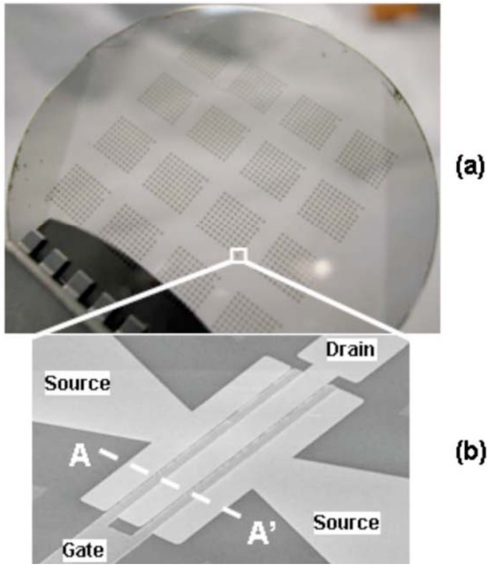


STM image of a CVD-EG layer grown on a 4HSiC(0001) substrate



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



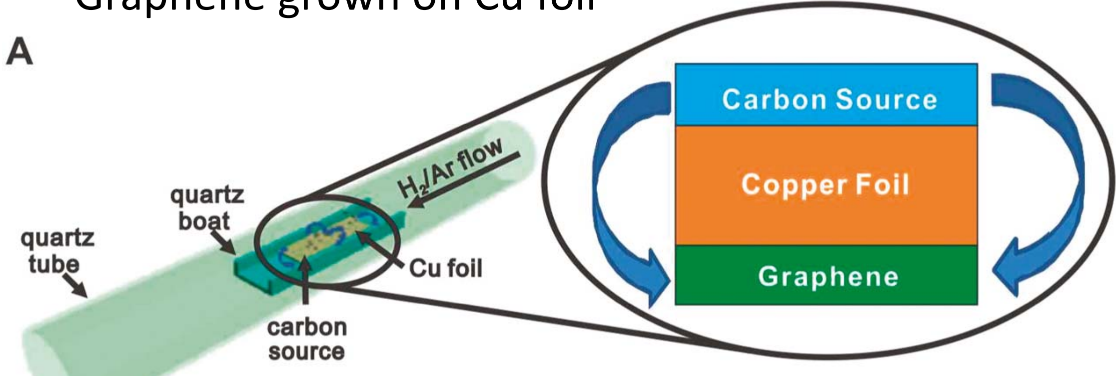


IBM wafer-scale epitaxial graphene

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

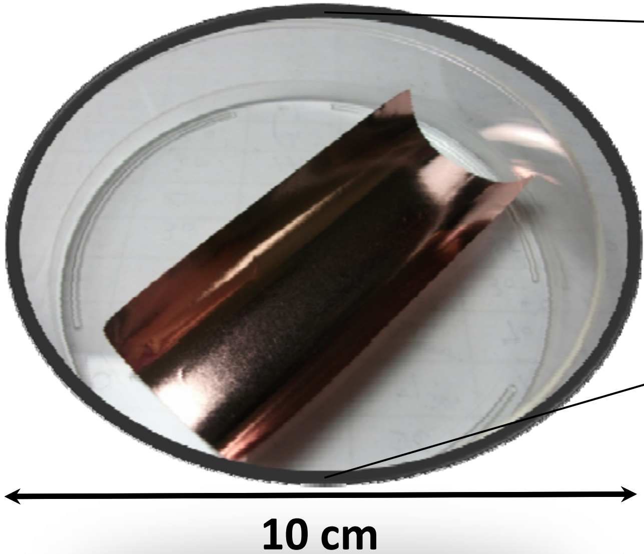
Large area fabrication of graphene on Cu by using CVD processes

Graphene grown on Cu foil



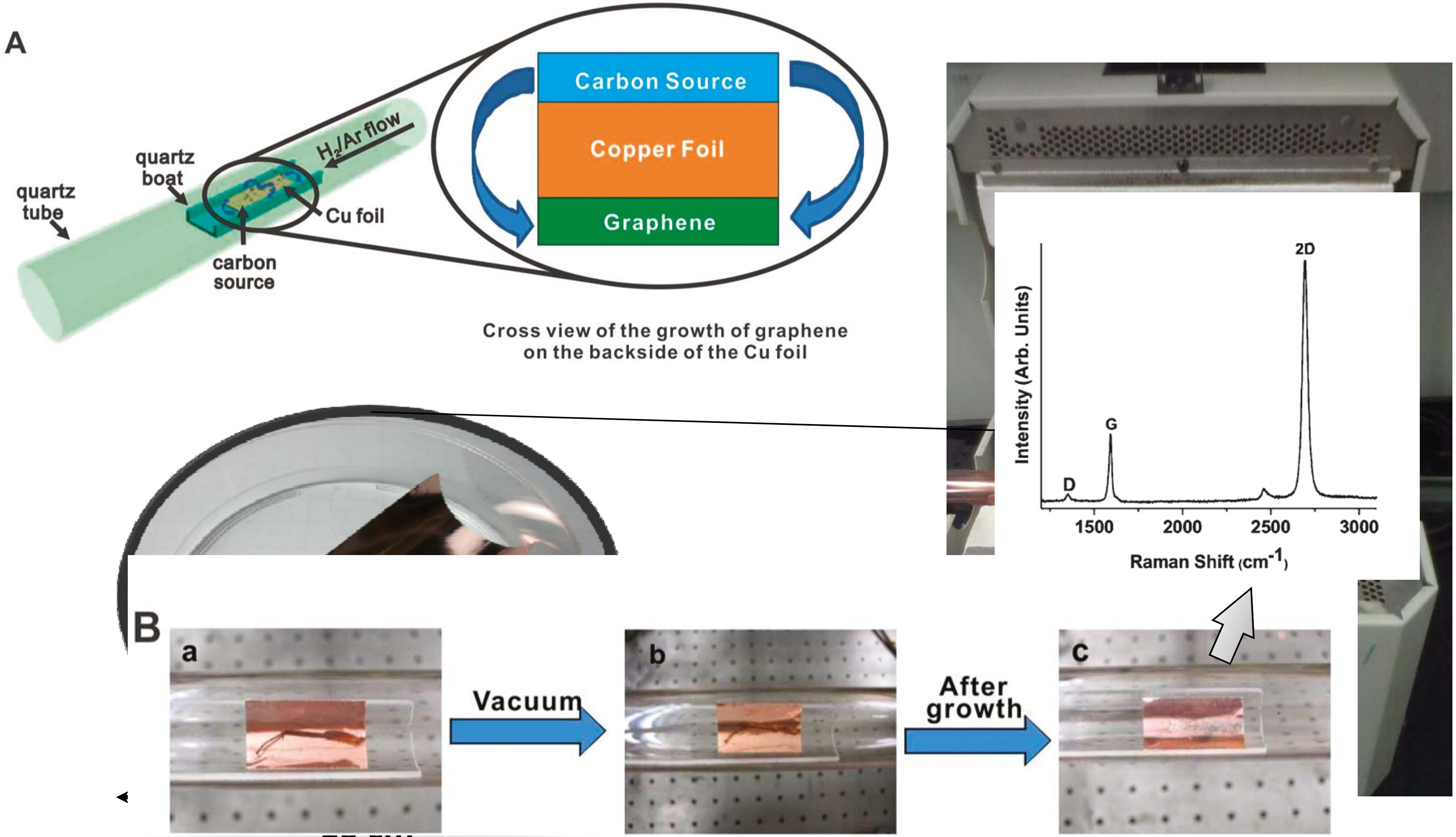
Cross view of the growth of graphene
on the backside of the Cu foil

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



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

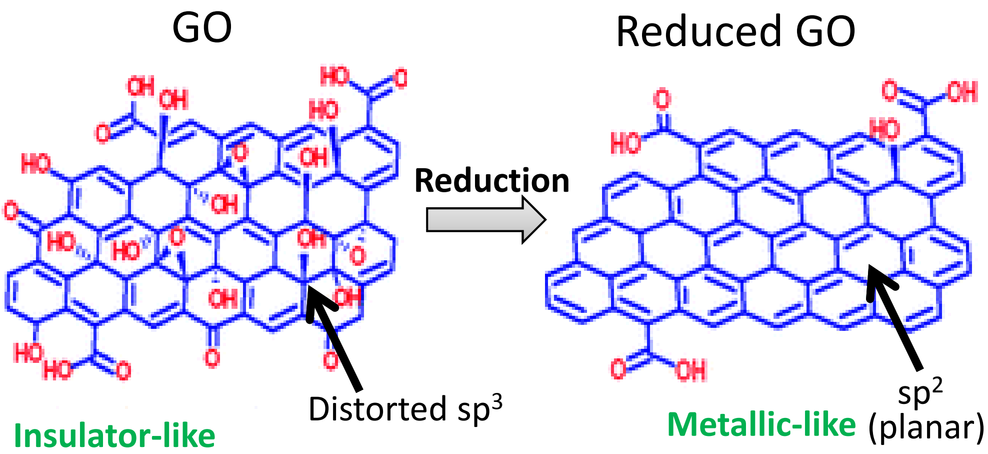
Fabrication process of CVD graphene

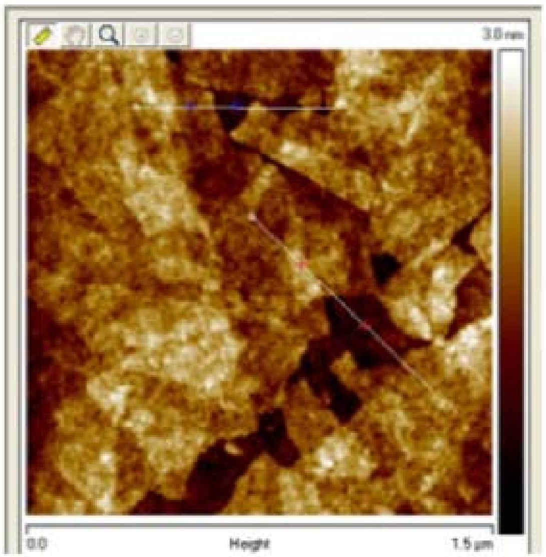


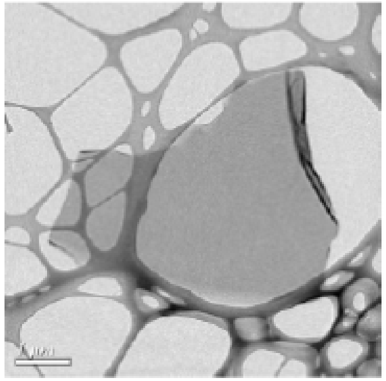
Cockroach leg

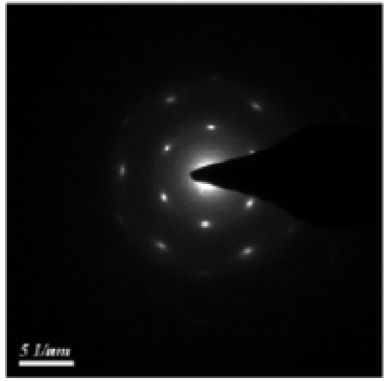
Ruan, G. et. al., *ACS Nano* **2011**, *5*, 7601-7607.

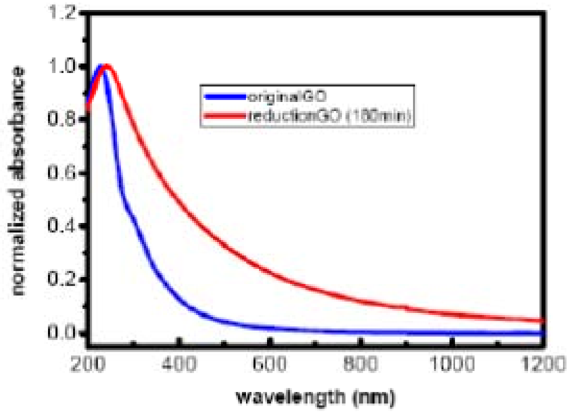
Chemical exfoliation of graphene from reduced graphene oxide







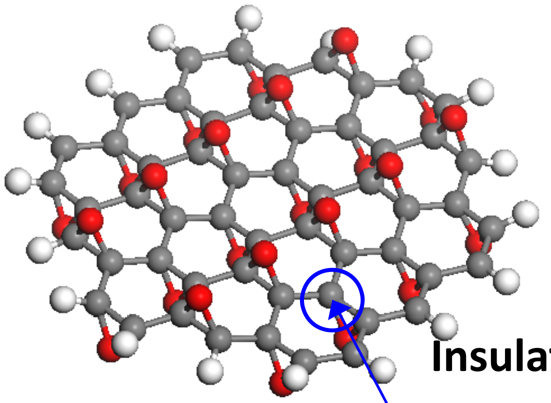




Eda *et al*. *Nature Nanotech.* 3 270-274 (2008)

Atomic and electronic structure of GO/Graphene

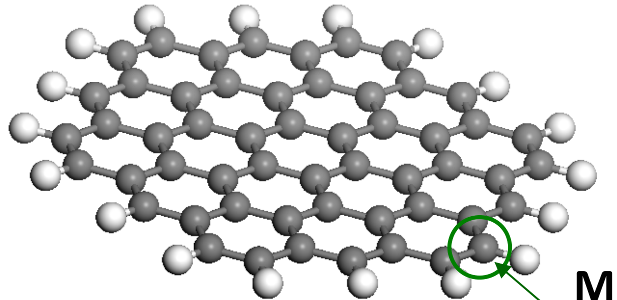
GO nanosheet



Ideal structure

Reduction

Graphene



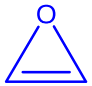
Insulator-like

Distorted sp^3

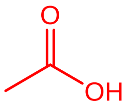
Metallic-like

sp^2 (planar)

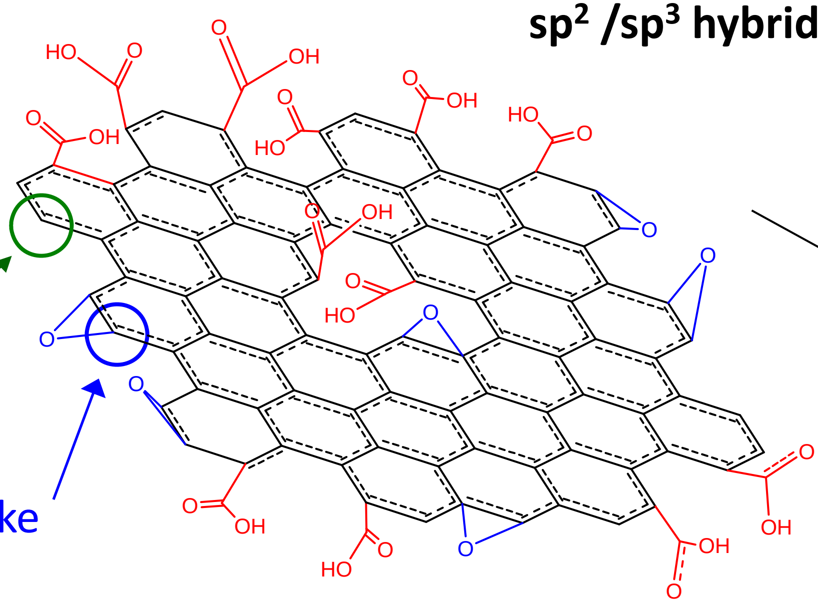
sp^2 /sp^3 hybrid (Real structure)



Epoxide group

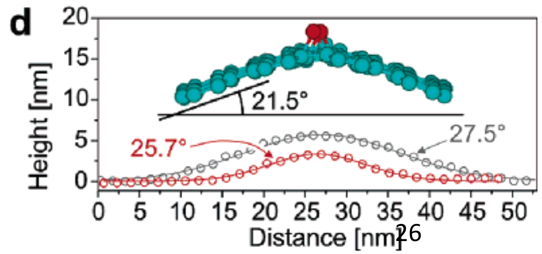


Carboxyl group



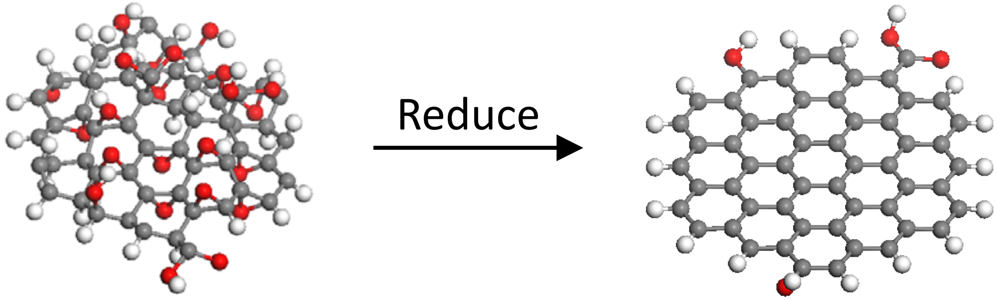
Sp^2-like

sp^3-like

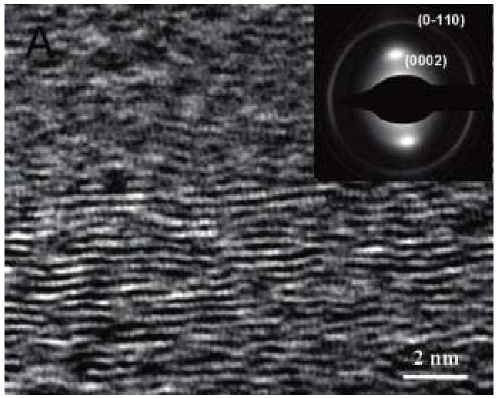


Akasay et al, J of Phys. Chem. B Lett., 110, 8535, 2006

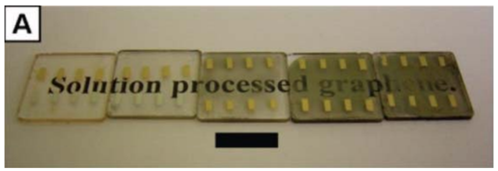
Preparation of reduced GO



UHV thermal anneal

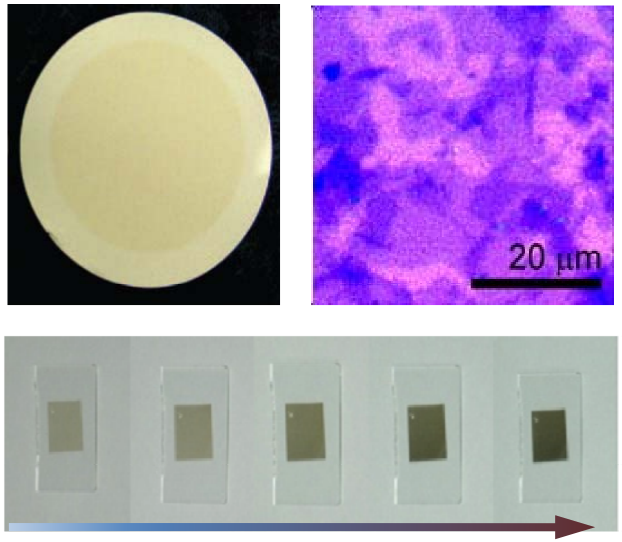


X. Wang *et al. Nano Lett.* 8 323-327 (2008)



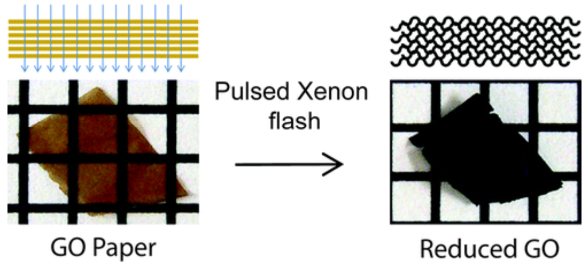
H. A. Becerril *et al. ACS Nano* 2 463-370 (2008)

N_2H_4 vapor



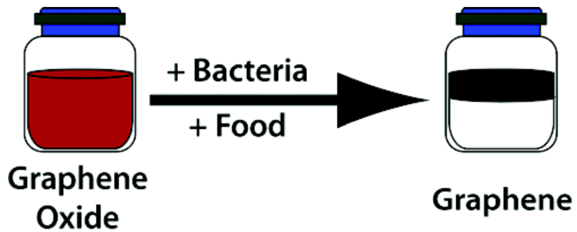
Eda *et al. Nature Nanotech.* 3 270-274 (2008)

Flash light reduction



L. J. Cote *et al. JACS* 131 11027-11032 (2009)

Biological reduction



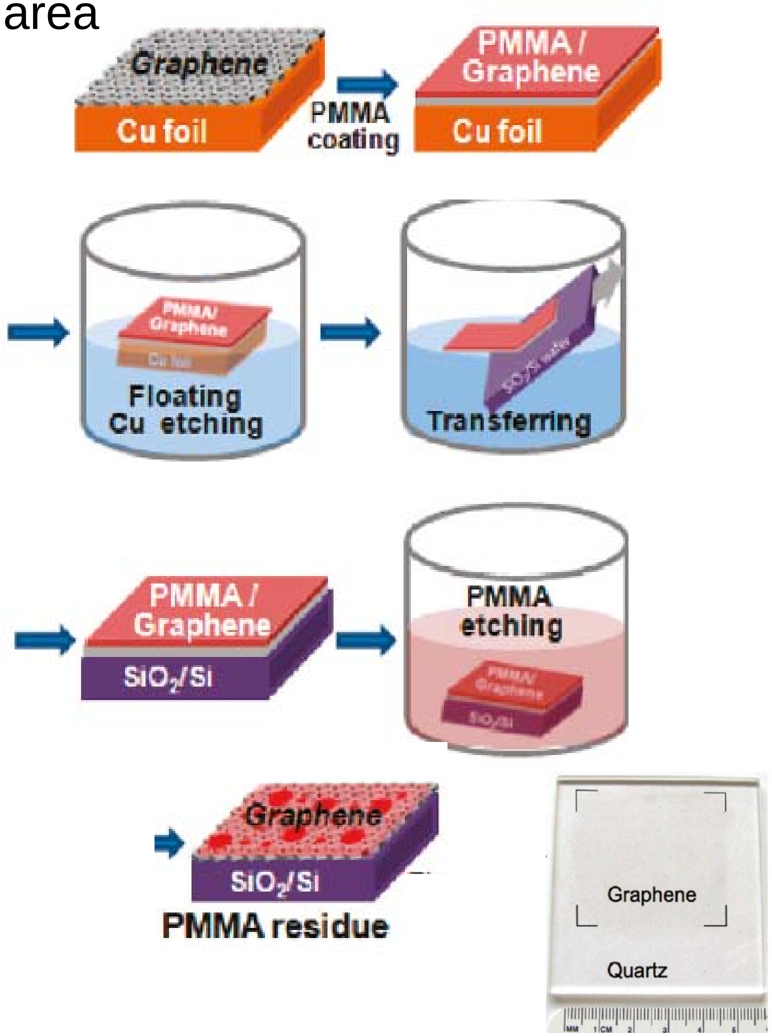
E. C. Salas *et al. ACS Nano* 4 4852-4856 (2010)

Transfer of graphene

Two Traditional Transfer Methods for CVD Graphene in the World

PMMA Transfer Method

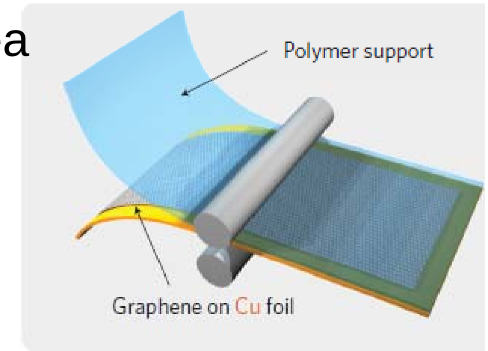
Small area

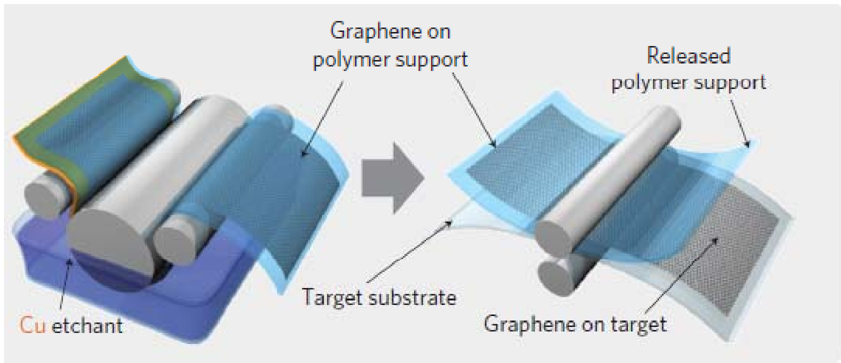


Lee, W. H., et. al, *J. Am. Chem. Soc.* , **2010**, 133 , *4447*

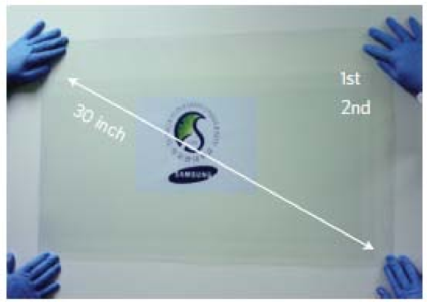
Roll to Roll Transfer Method

Large area



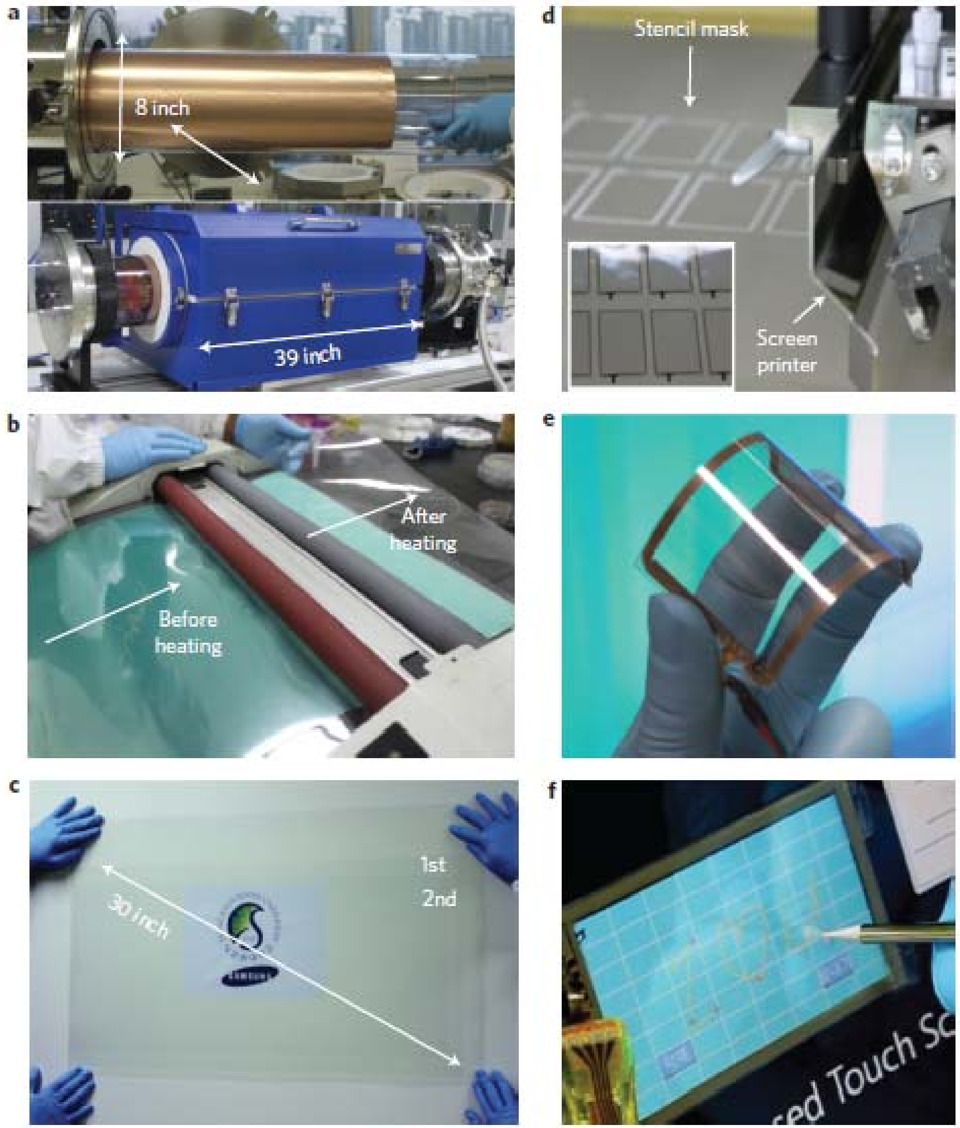


c



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

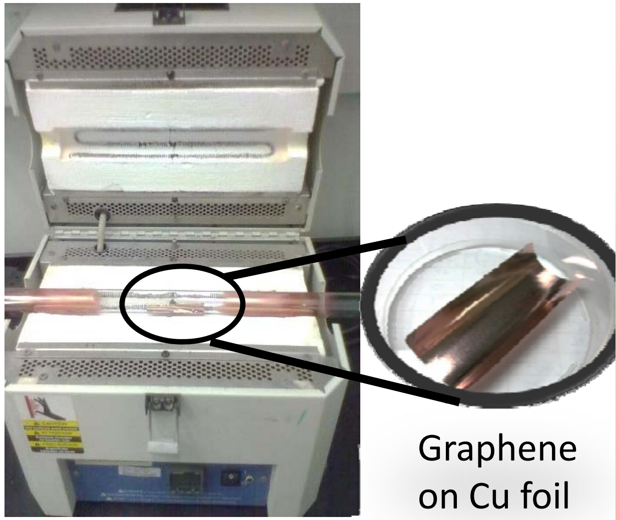
Roll-to-roll production of 30-inch graphene films for transparent electrodes



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

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

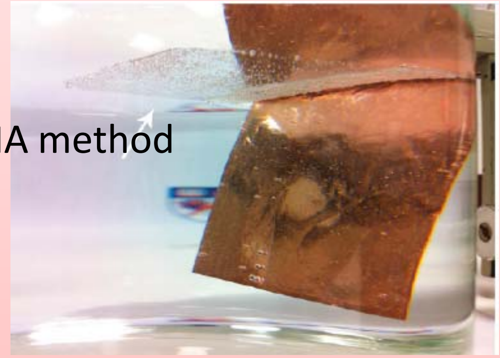
Graphene Growth



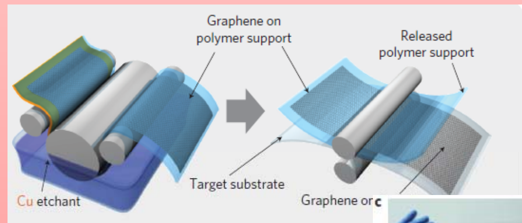
Graphene on Cu foil

Graphene Transfer

PMMA method



Organic support protection

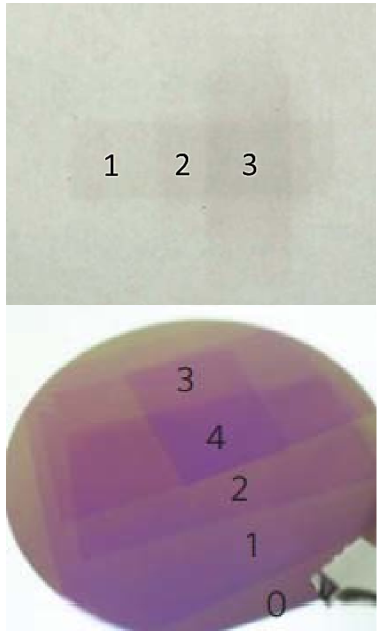


R2R method

A critical step

Cu foil Etching

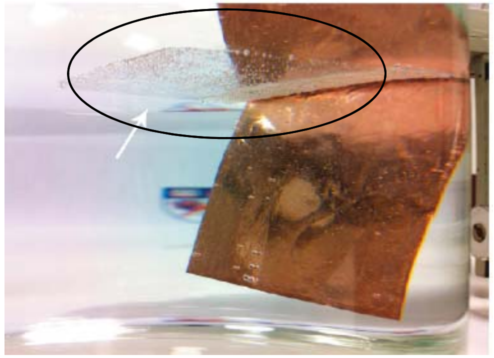
Graphene Film



Yu Wang *et al*, *ACS Nano*, **2011**, 5 , 9927–9937
Bae, S., et. al., *Nat. Nanotech.*, **2010**, *5*, 574

Problems of PMMA and R2R Transfer Methods

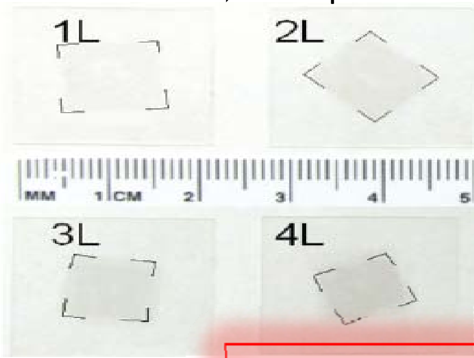
PMMA method

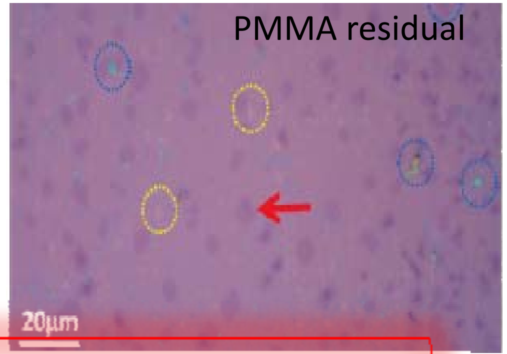


PMMA protection

Difficulty in handling

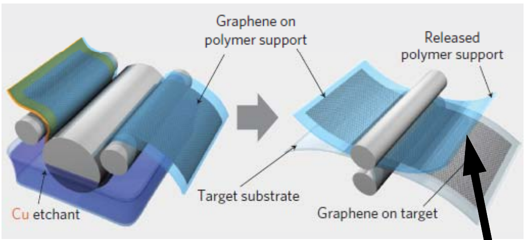
→stack problem





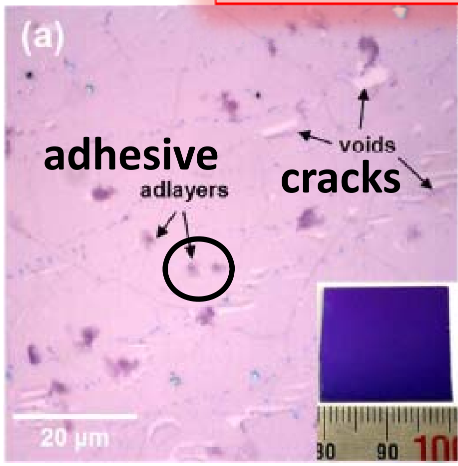
Organic Residue

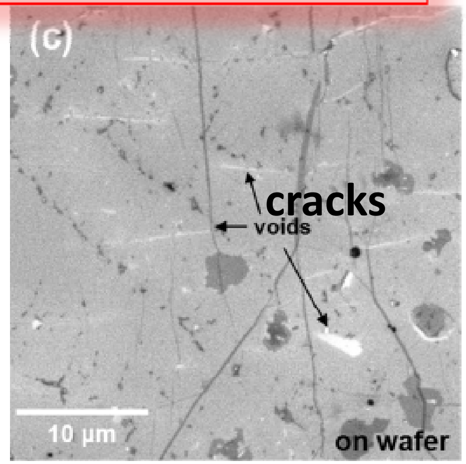
R2R method



Thermal released tape

1. undesired mechanical defects
2. organic adhesive from tape





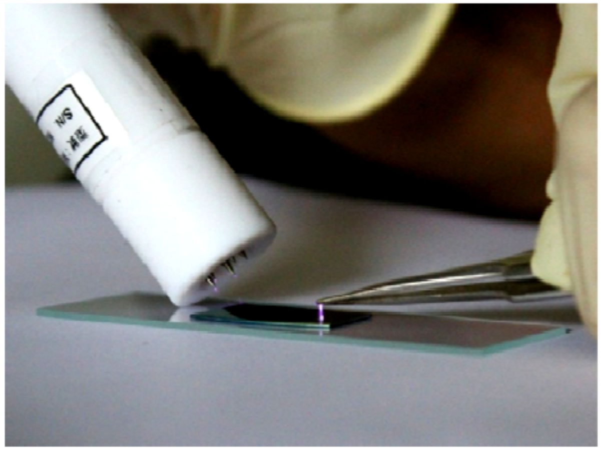
Junmo Kang ***et al***, *ACS Nano*, **2012,** 6, 5360.

Xuesong Li ***et al***, *Nano Lett.*, **2009** , 9 , *4359–4363*

Can we transfer graphene with no organic residue ???

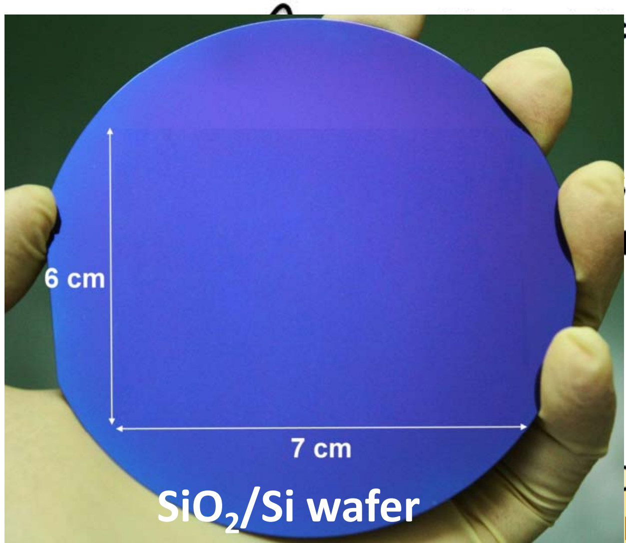
Using electrostatic attraction

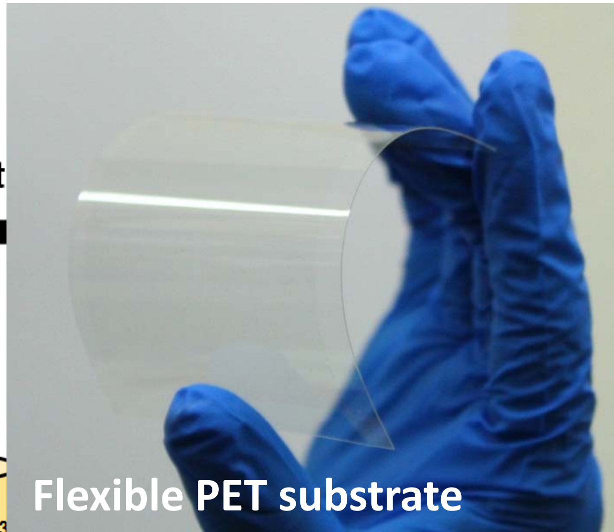
Electrostatic generator



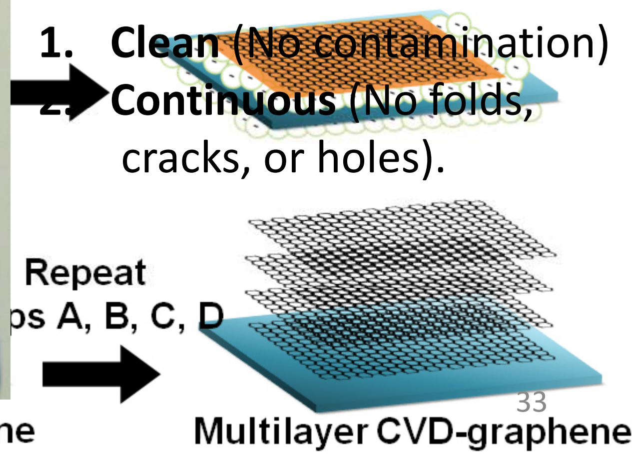
Adv. Mater. 25, 4521, (2013)
Adv. Mater. 25, 4521, (2013)

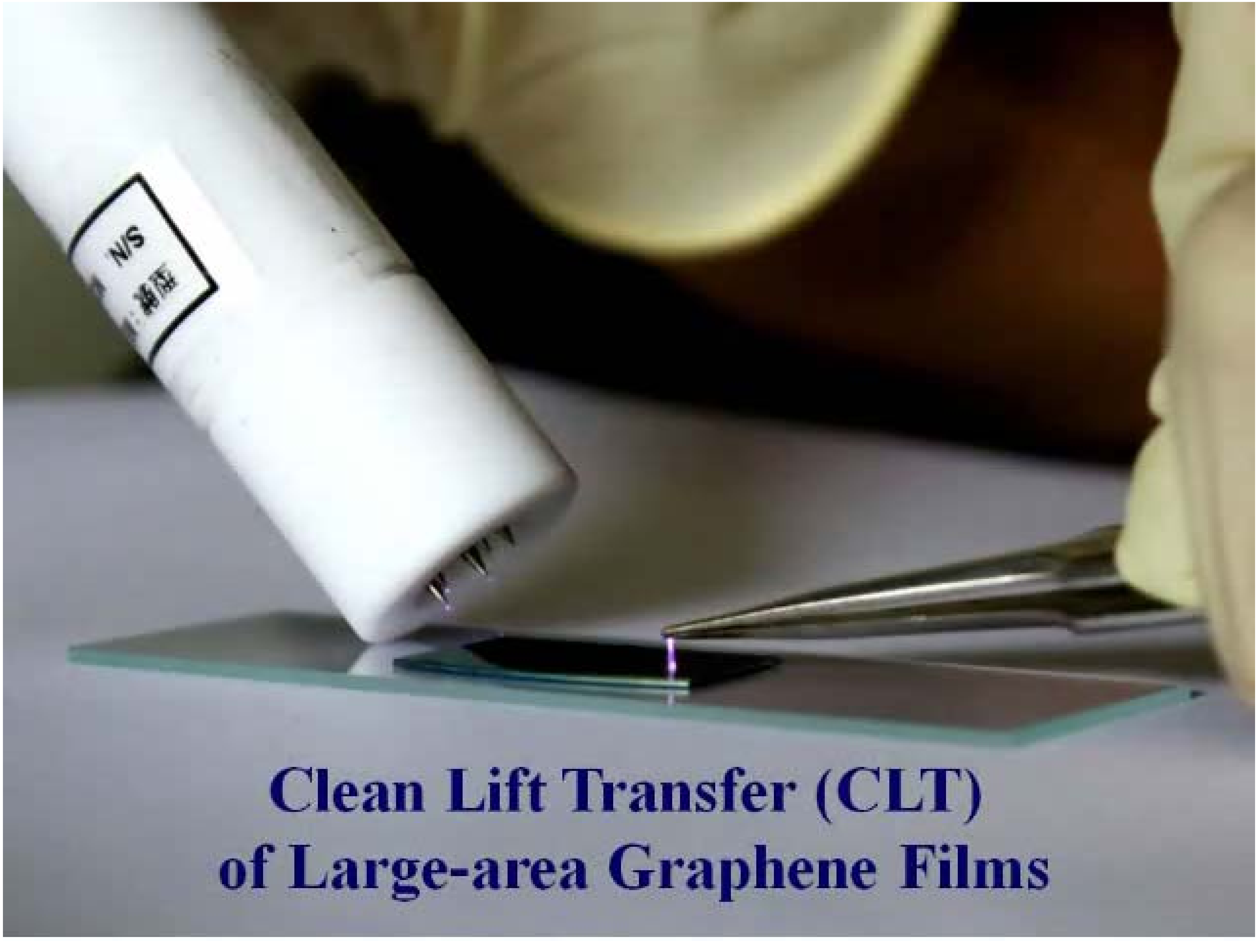
Clean-Lifting Transfer (CLT) Technique





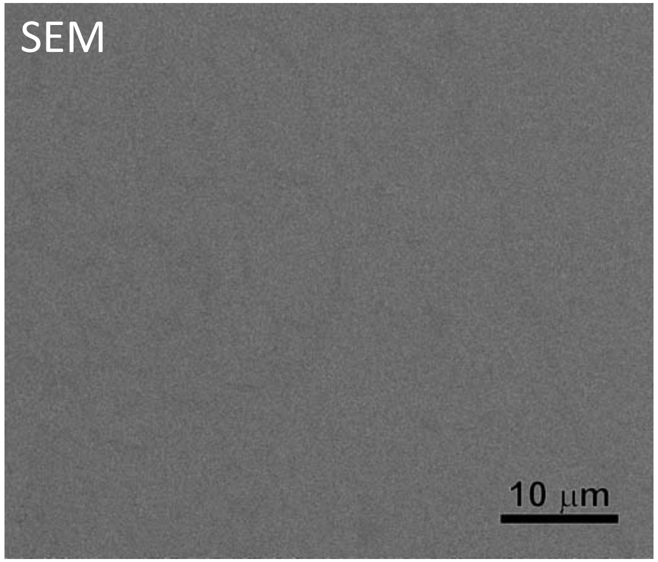
1. **Clean** (No contamination)
2. **Continuous** (No folds, cracks, or holes).

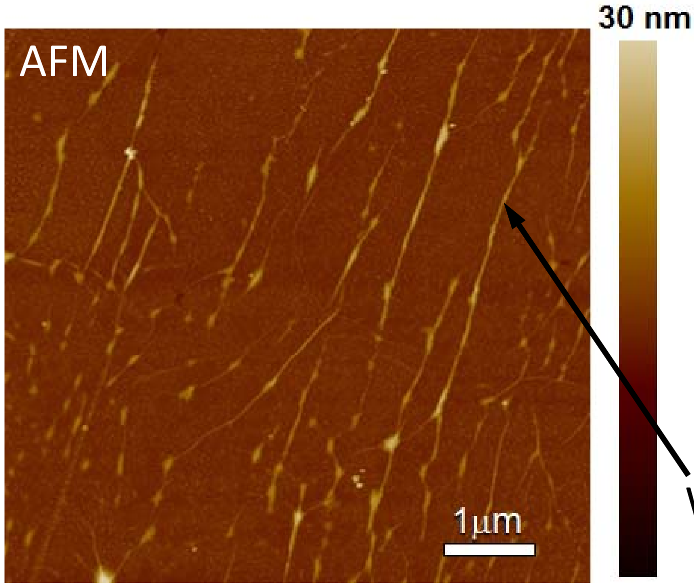




Clean Lift Transfer (CLT)
of Large-area Graphene Films

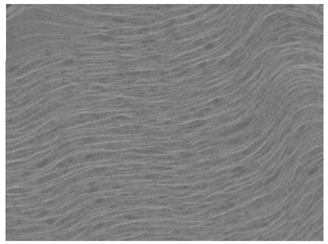
High quality CVD graphene of transferred by the CLT technique

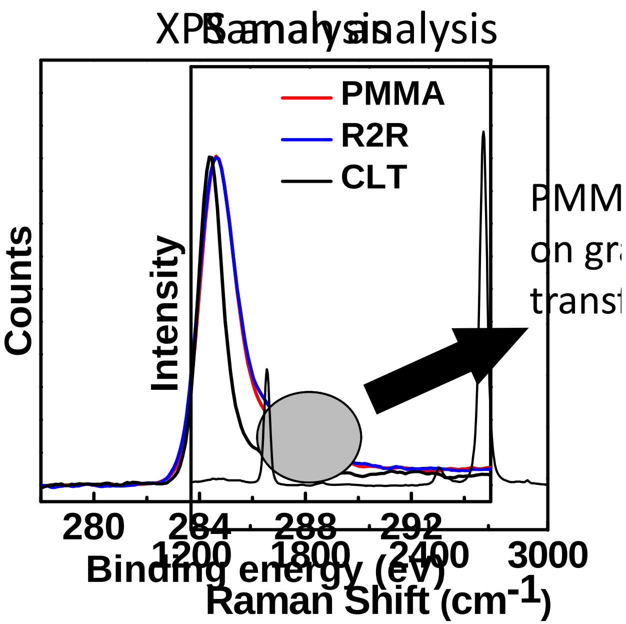




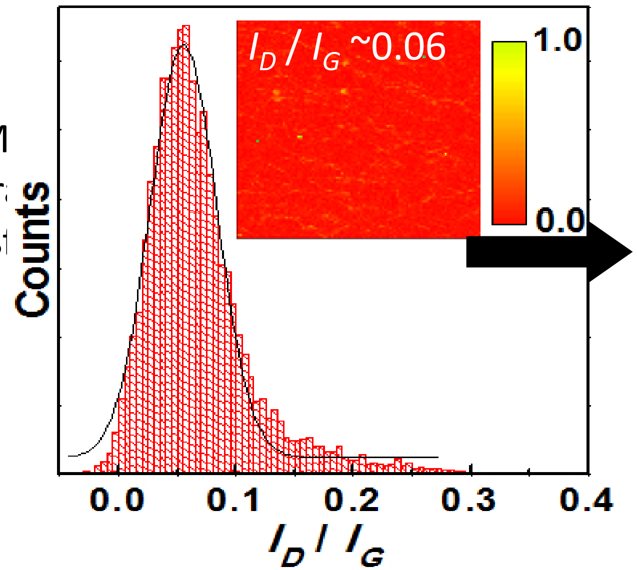
1. Clean
2. Uniform morphology
3. No significant macroscopic defects,

Wrinkles from the Cu foil



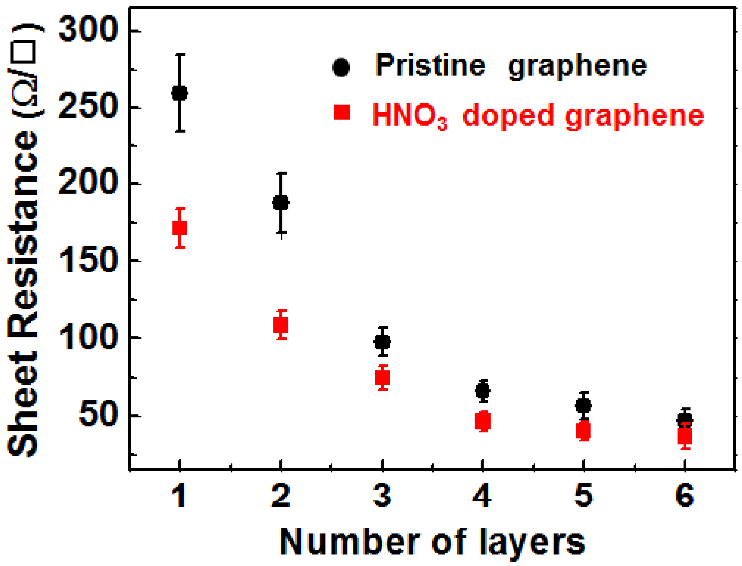


Raman mapping



1. High quality
2. Good uniformity

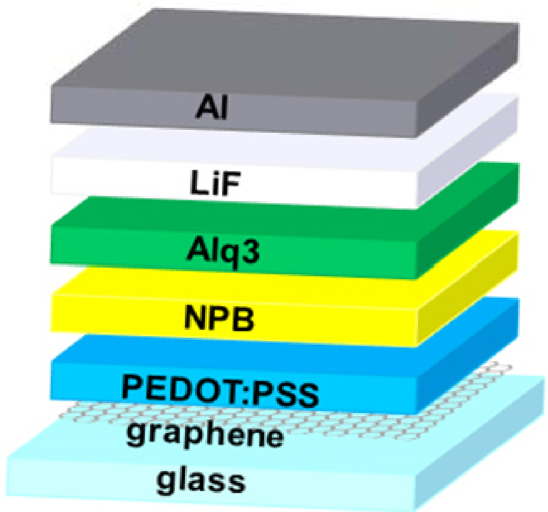
Multilayered graphene films by the CLT technique as transparent electrodes for OLED application

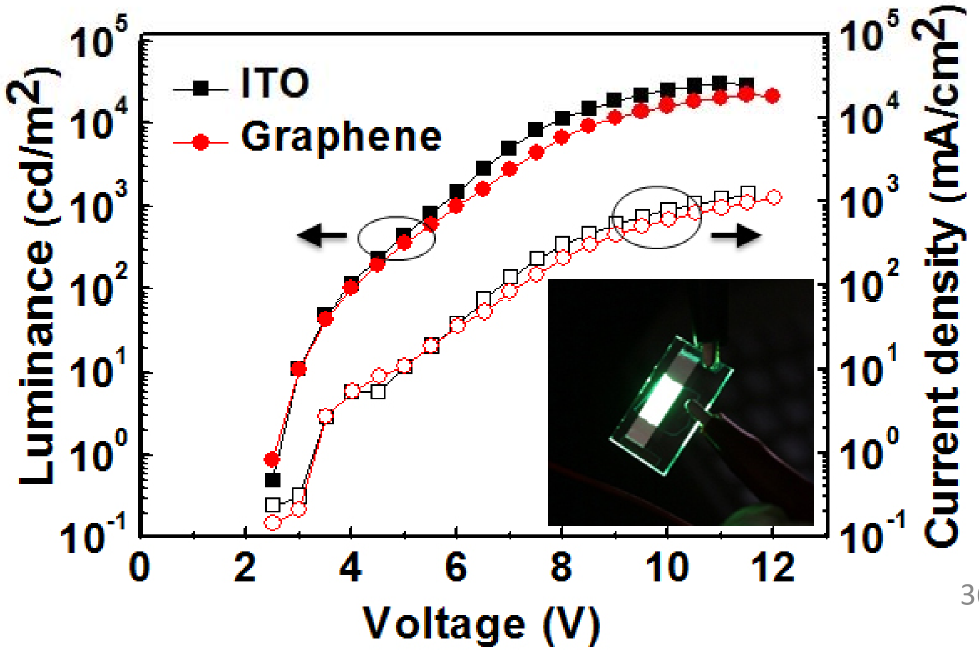


HNO_3-doped 4-layered graphene
~a transparency of ~90%
~an average sheet resistance of 50 Ω/□

Advanced Materials, 2013 (in press)

The efficiency of Gr-OLED device
~85 % of that of ITO-OLED





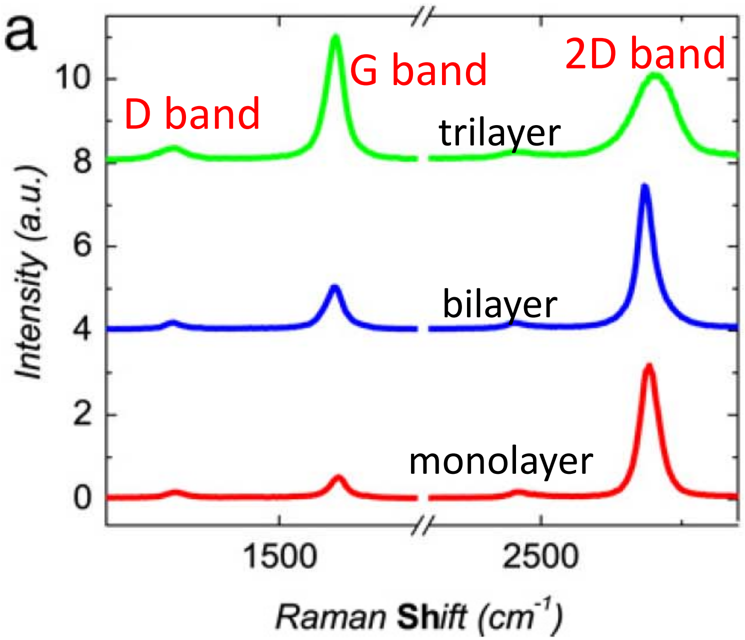
CLT of graphene by a screen protector

Characterizations of garphene

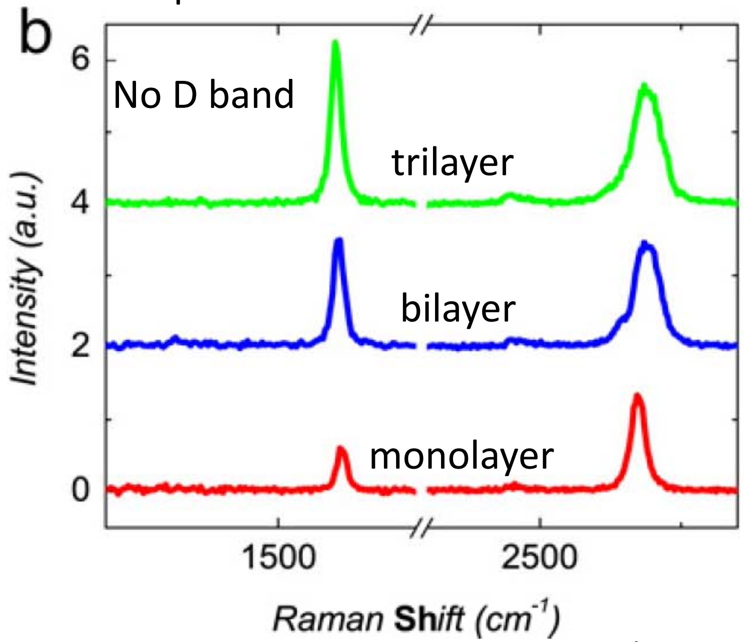
Raman Spectra of graphene

Identification of the layer number of graphene

CVD graphene grown on Ni



Graphene fron mechanical exfoliation of HOPG

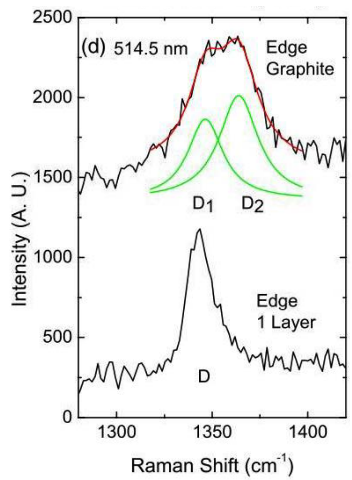


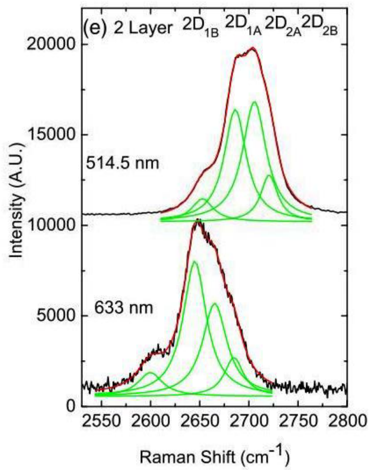
I_G / I_{2D} ~1.25

I_G / I_{2D} ~1.05

I_G / I_{2D} ~0.4

A. Reina et. al., Nano Lett. 9 (2009) 3035.

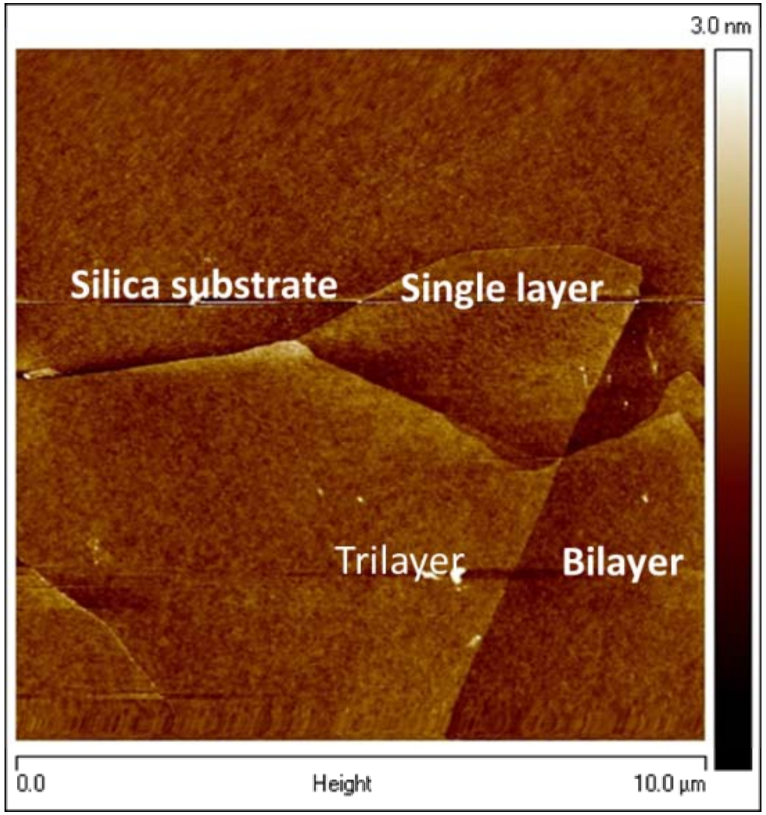




A. C. Ferrari et al., *PRL* **97**, 187401 (2006)

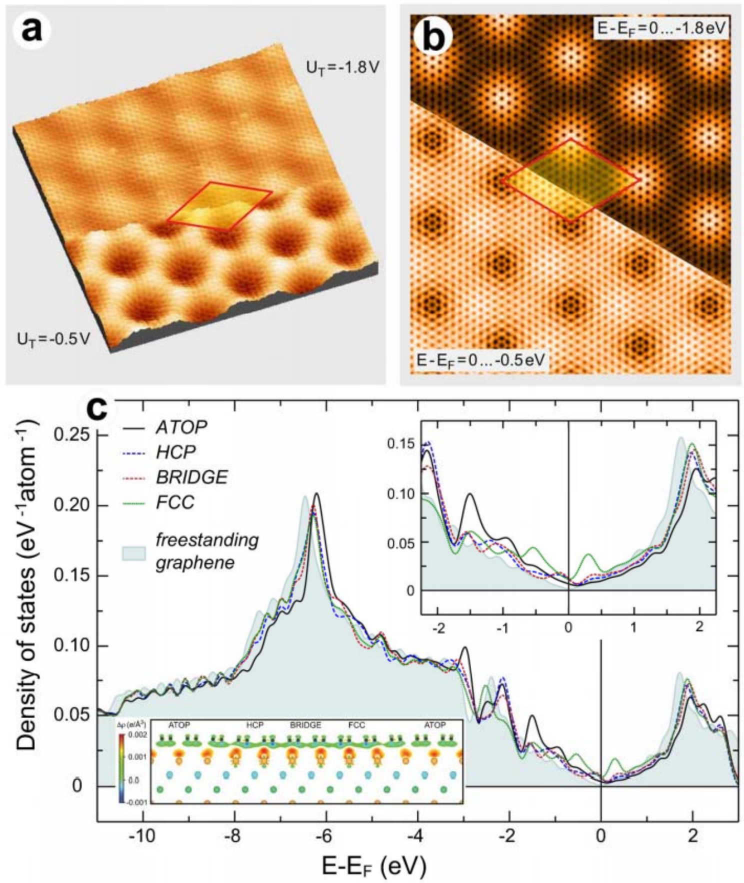
AFM and STM image of graphene

AFM images of graphene on SiO_2



STM images of graphene/Ir(111)

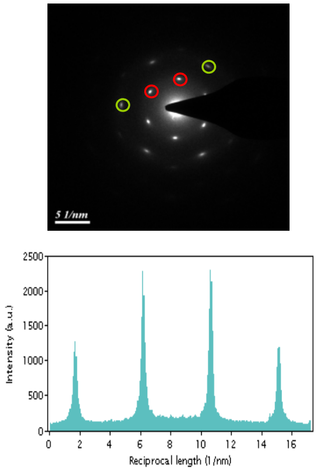
Experimental calculated



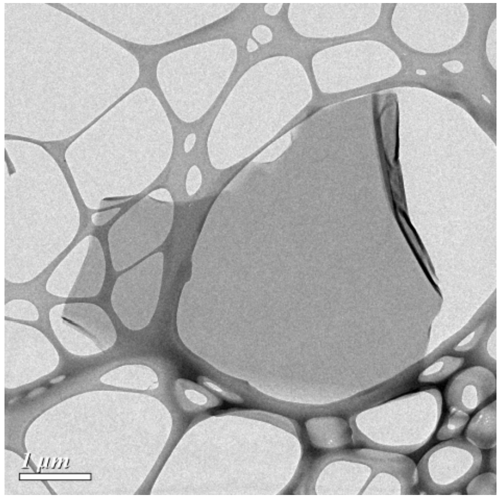
Voloshina, E. N. Science Report, 2013, 3, 1

Photothermal reduction method for GO and r-GO

(a)

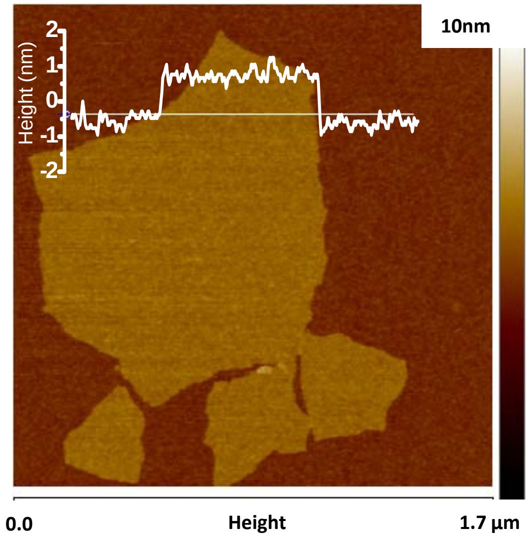


TEM of GO



(b)

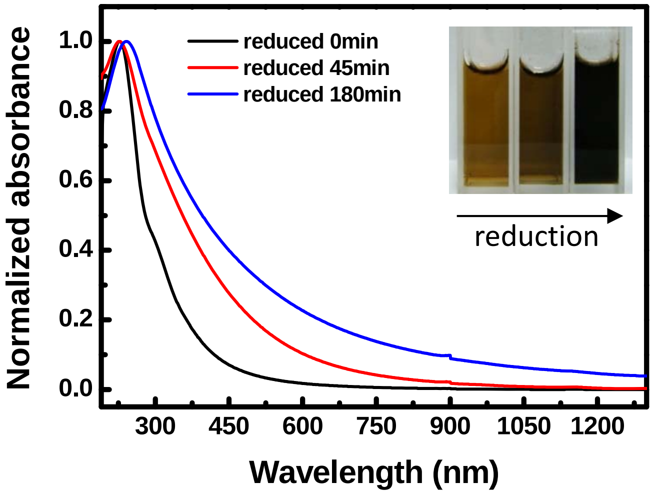
AFM of GO

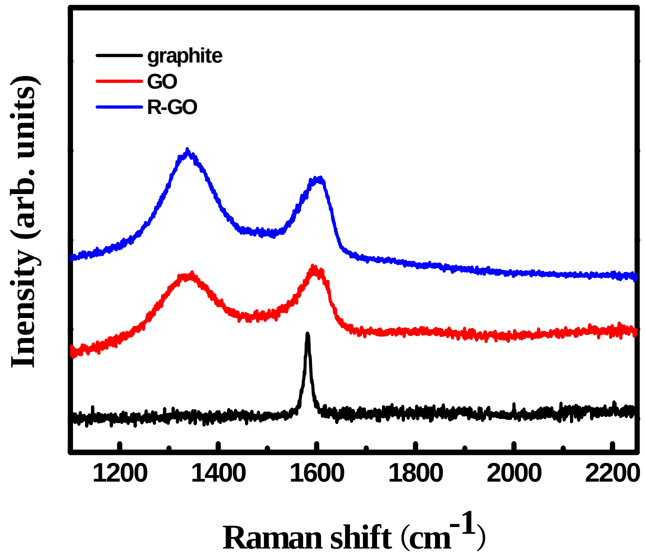


(c)

(d)

Xe Lamp



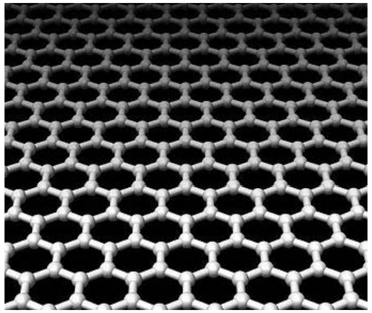


Mild reduction processes

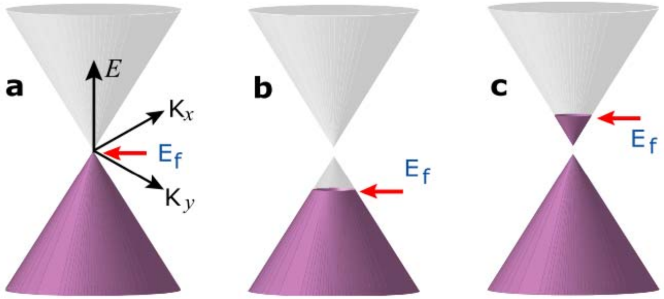
Electrical properties of graphene

Tunable electrical and optical platform of graphene

Atomically thin structure

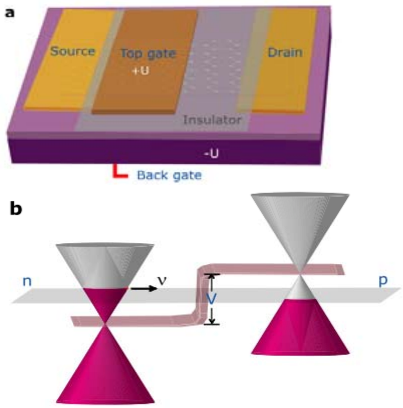


Tunable electronic structure



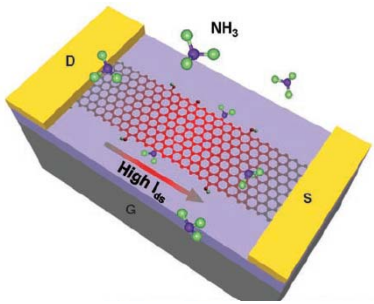
Easily modulated by electrical, or chemical , optical and mechanical methods

Electrical gating



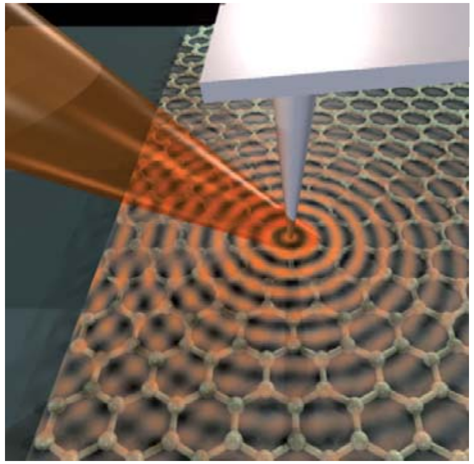
B. Guo et al., *Insciences J.* **1** (2), 80 (2011)

Chemical Doping



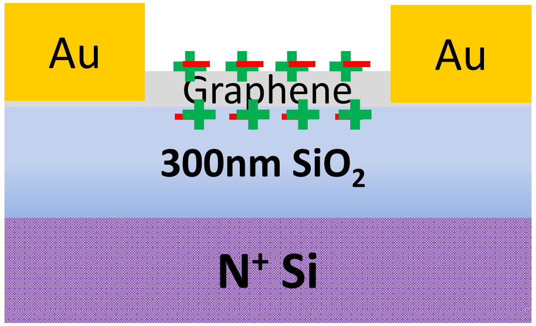
Xinran Wang, *et al.* Science (2007)

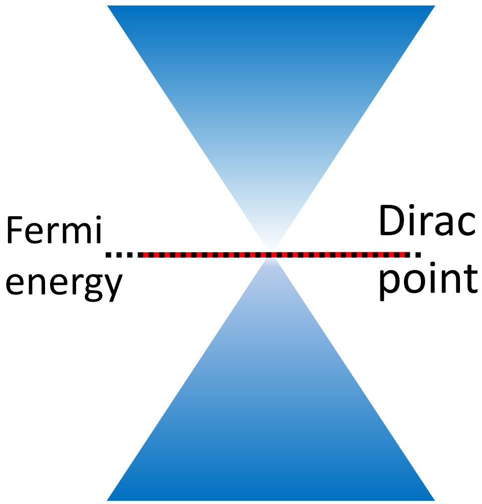
IR Nano imaging



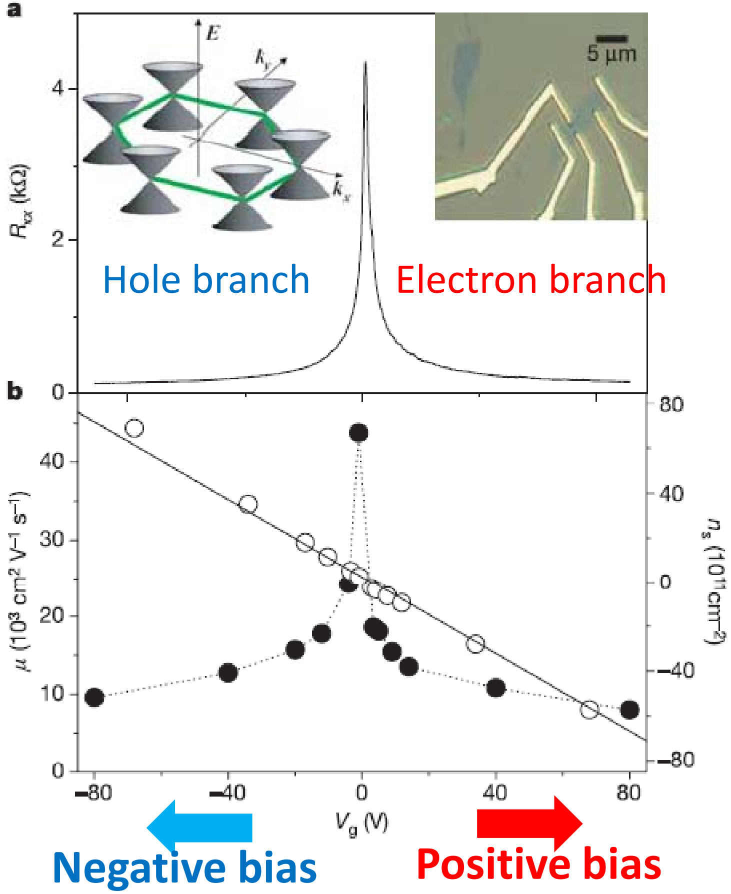
Fei. Etal, Nature, 82, V 487, 2012

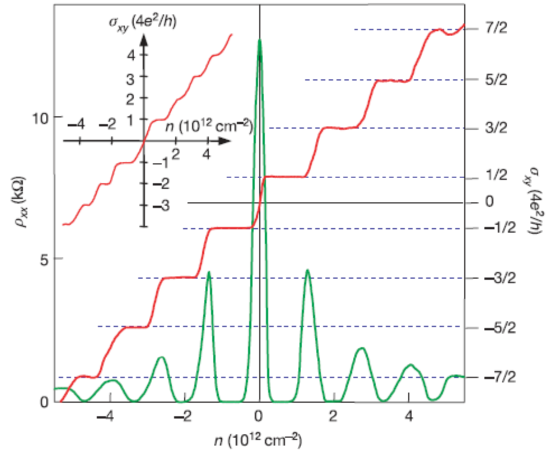
Graphene
Ambipolar transport property





Yuanbo Zhang, et al., Nature(2005)



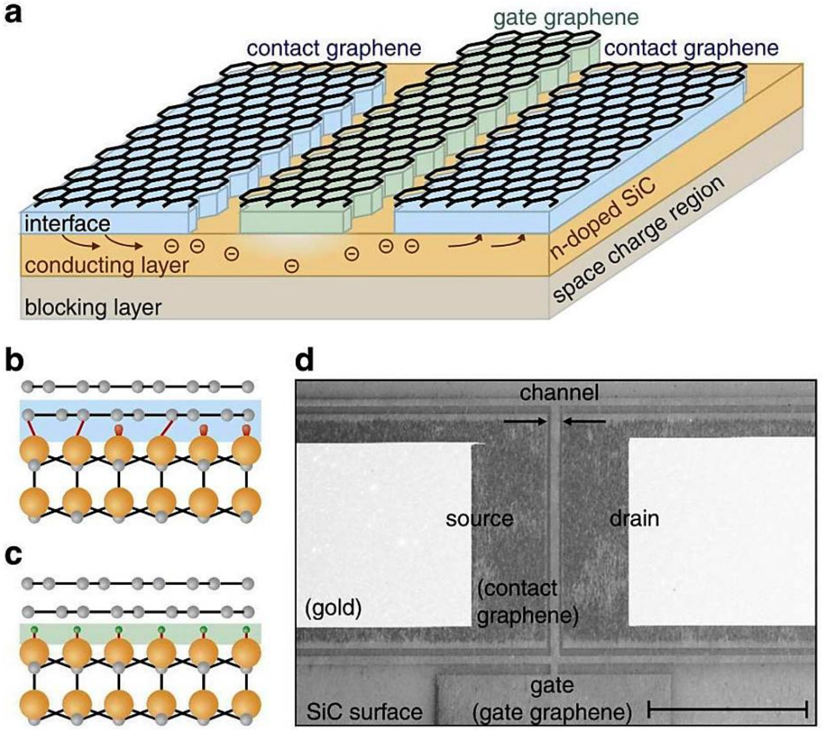


K. S. Novoselov, et al., Nature (2005)

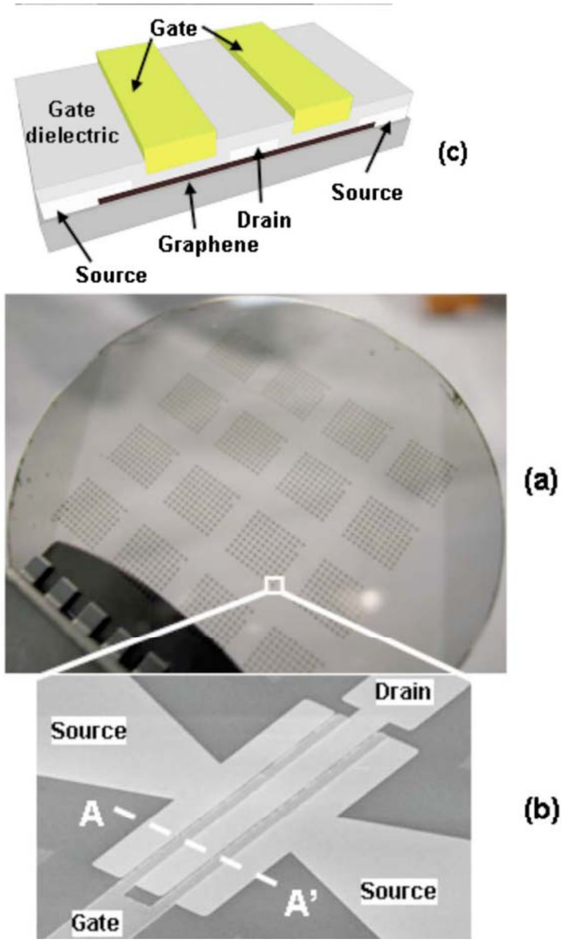
Disadvantage of graphene

1. 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)

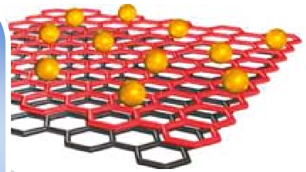


IBM wafer-scale epitaxial graphene

Effects on Transport Properties

Charge impurities

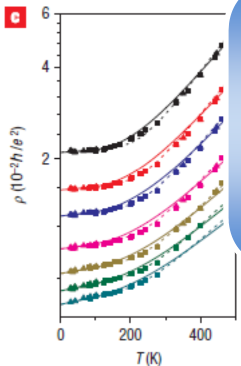
(Doping, Absorbate)



Yu, W. *etal. Nano Lett.* (2011)

Phonon Scattering

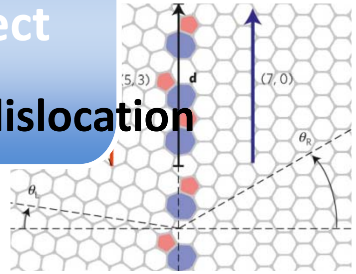
(Temperature)



J.–H. Chen,*et al,* Nat. Nanotechnol.(2008)

Intrinsic Defect

Grain boundary, dislocation

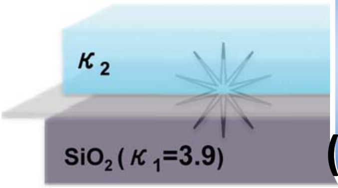


Oleg V. Yazyev, Steven G. Louie. Nat. Mater. (2010)

Could be modified

Environmental Condition

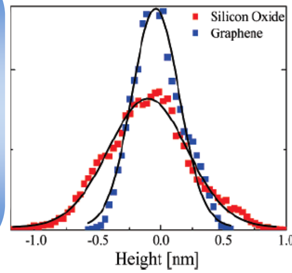
(Atmosphere, Dielectric)



F. Chen.*et al.* Nano Lett. (2009)

Surface Roughness

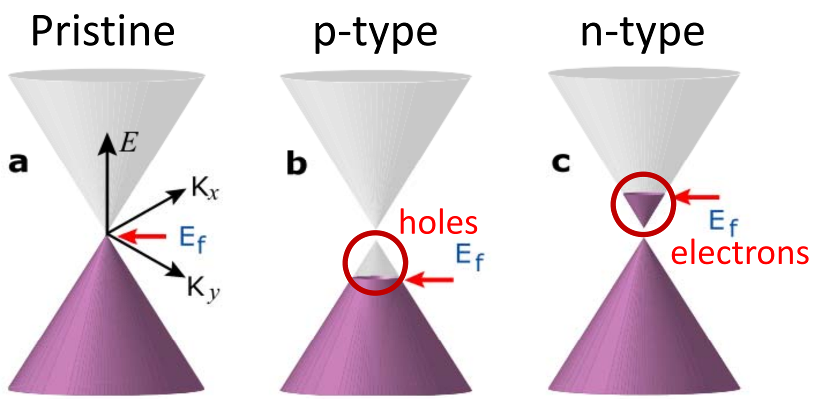
(Substrate)

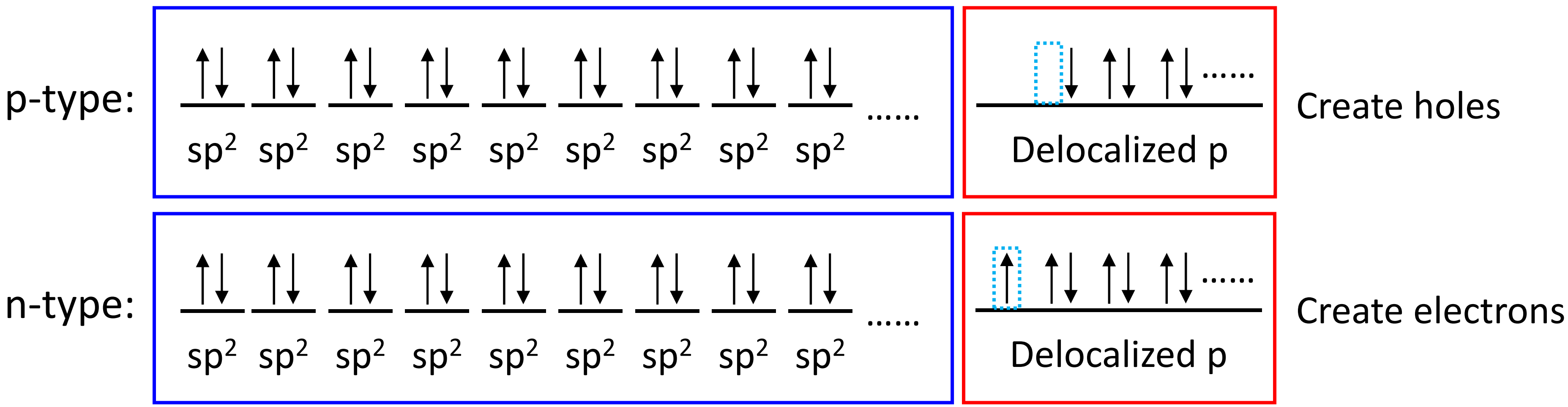


Ishigami, M. *et al.* Nano Lett. (2007)

Doped Graphene by heteroatoms

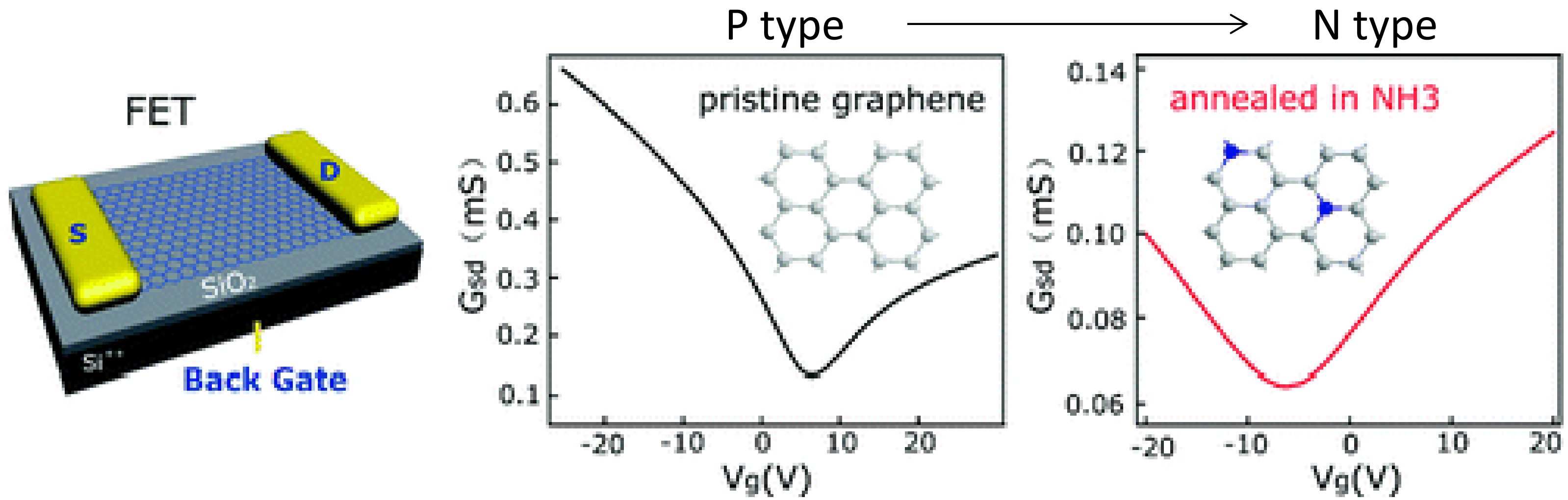
- Doping by heteroatoms
  - p-type doping
  - n-type doping





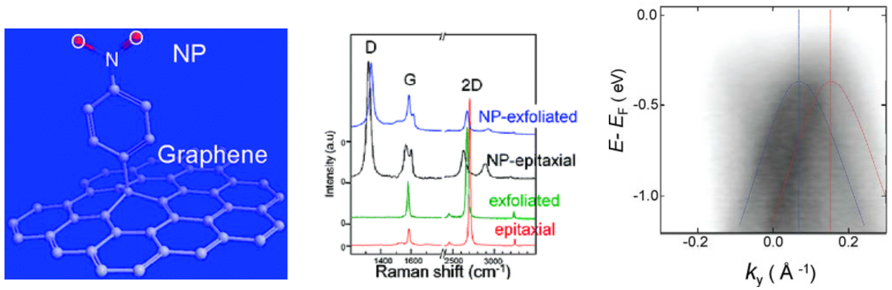
Doped Graphene by chemical modification

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

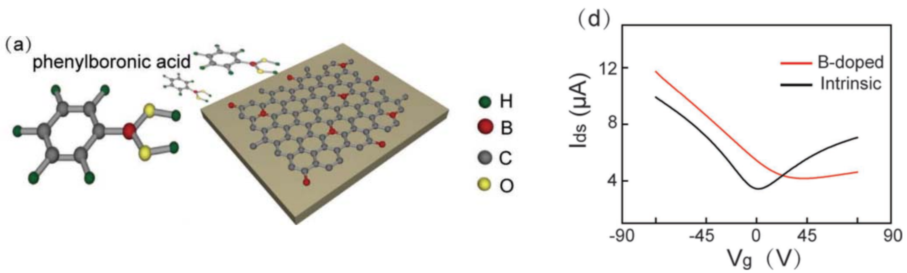


p-type doped graphene

1. Covalent functionalized or substitutional doping

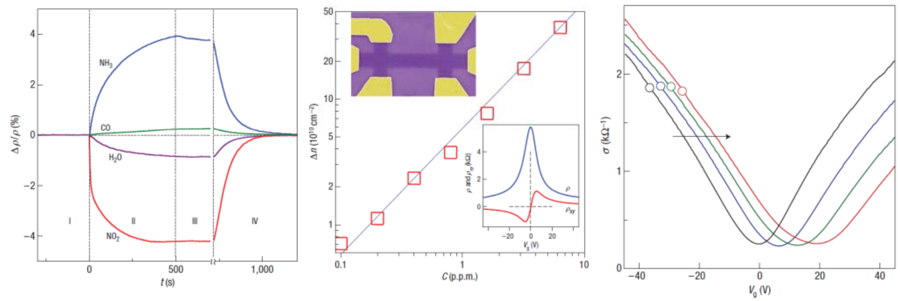


Nano Lett. *10*, 4061–4066 (2010)

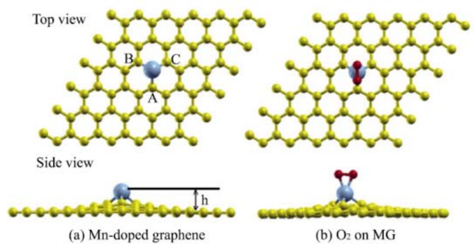


Small, *9,* No. 8, 1316–1320 (2013)

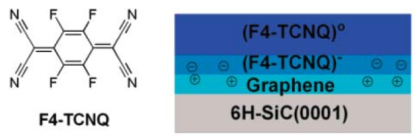
2. Surface charge transferred doping



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



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

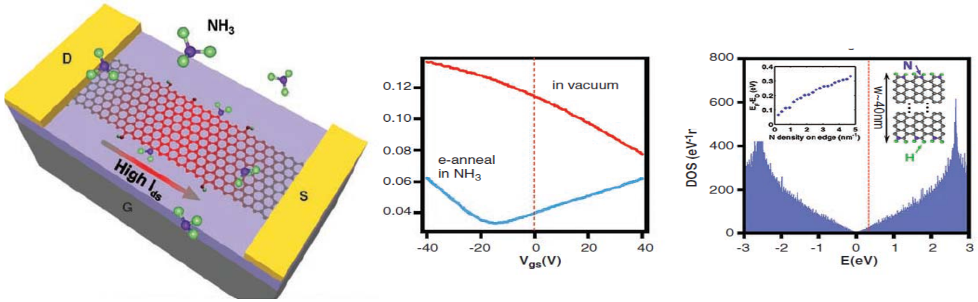


J. Am. Chem. Soc. 129, 10418-10422 (2009)

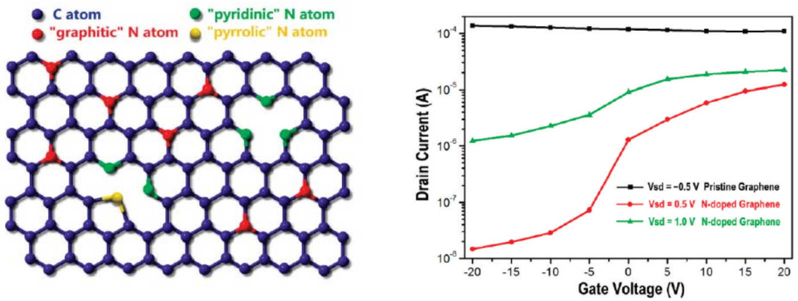
- Covalent functionalized and substitutional doping => destruction of sp2, low mobility
- Surface charge transfer => Graphene is vulnerable to atmosphere

n-type doped graphene

1. Covalent functionalized or substitutional doping

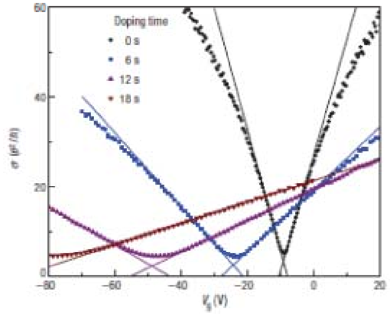


Science 324, 768 (2009)

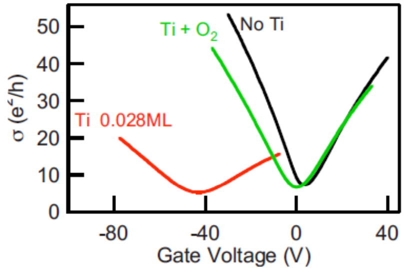


Nano Lett. 9, 1752 (2009)

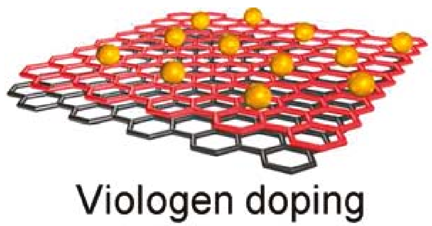
2. Surface charge transferred doping



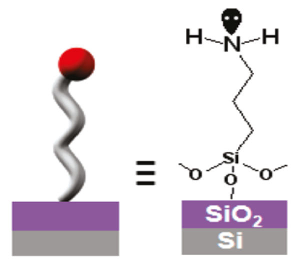
Nat. Phys. 4, 377 - 381 (2008)



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



Nano Lett. 11, 4759–4763 (2011)

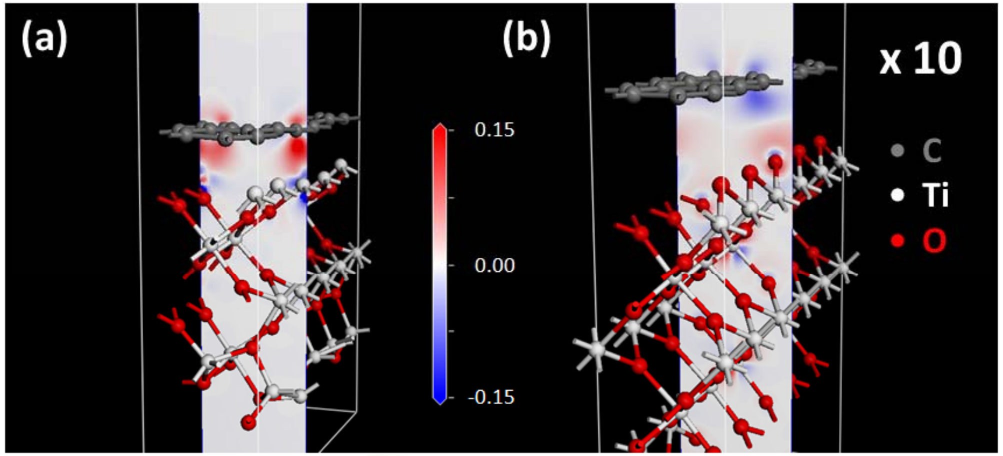


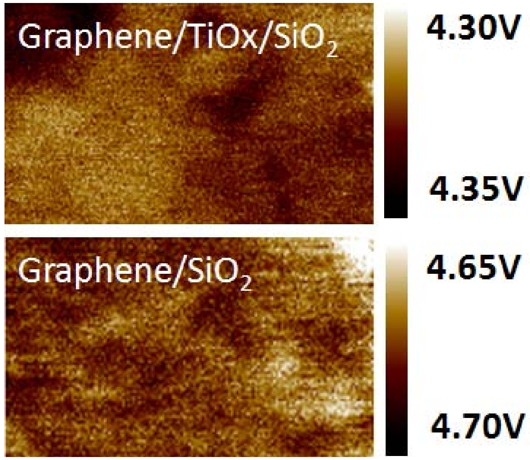
J. Phys. Chem. Lett. 2011, 2, 841–845

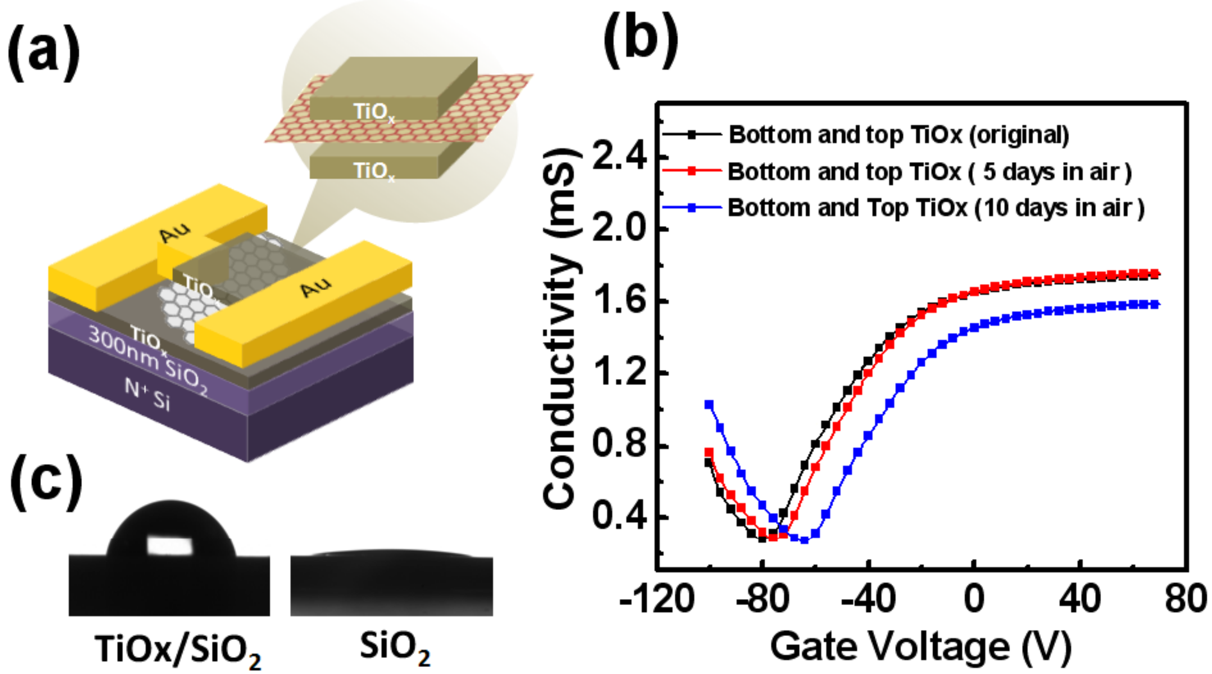
- Most of doping methods could considerably damage carrier mobilities of graphene.
- The doping level could not easily be easily controlled.
- The doping devices are very vulnerable to environment, especially for n-type doping.

Self-encapsulated doping n-type Graphene

TiOx acts as an n-type dopant and encapsulated layer



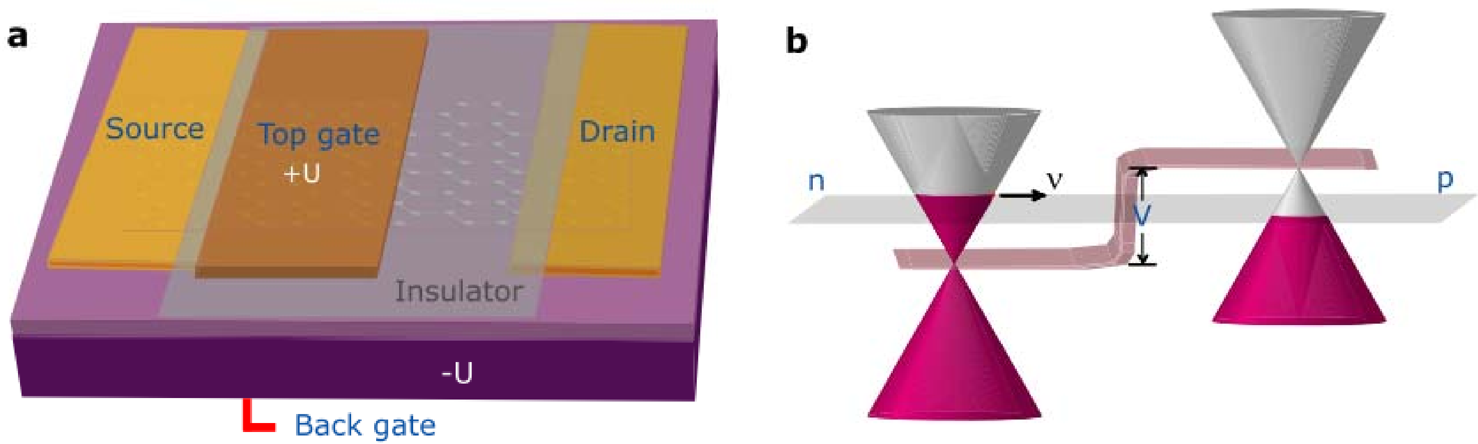




ACS Nano, No.7, 6215, 2012

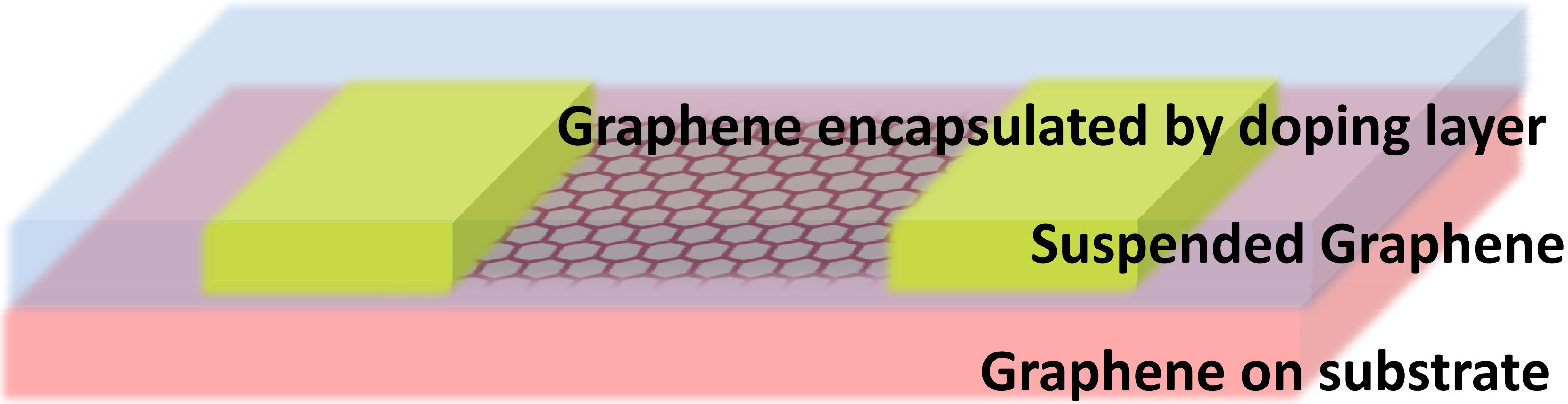
Doped Graphene by electric field

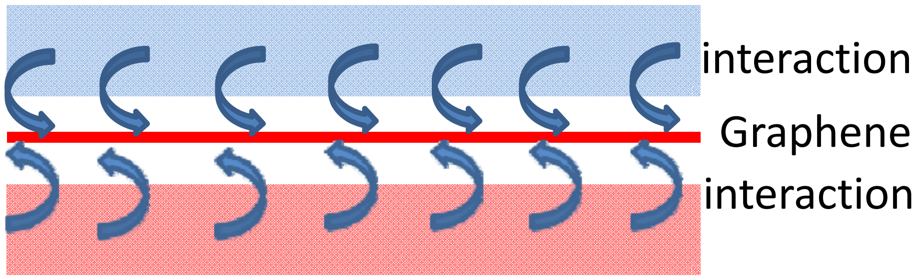
- Doping by electric field
  - Use electric field to shift the Fermi level of graphene



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

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





Bottom layer - Substrate

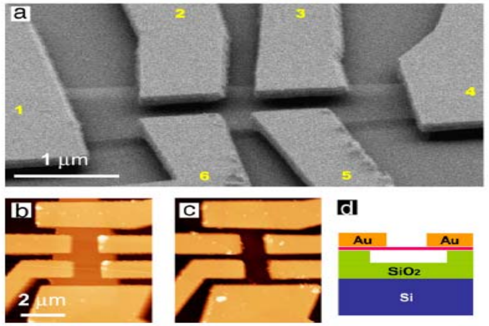
1. **Charge impurity**
2. **Surface Roughness**

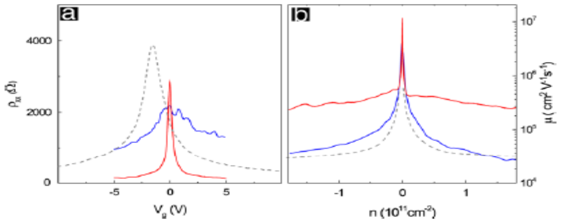
Top layer - Encapsulated layer

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

Substrate-dependent transport

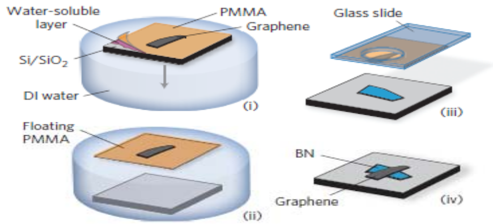
1. Suspended Graphene

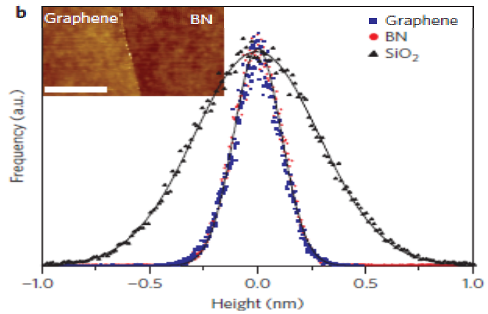




Solid State Commun. *146, 351-355* (2008)

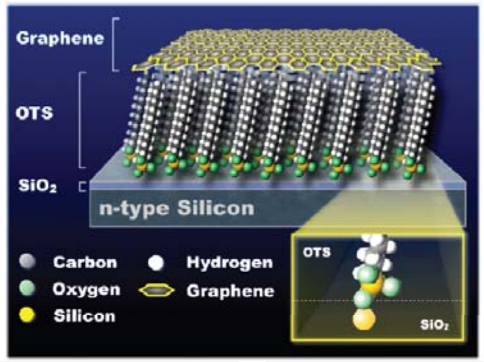
2. Graphene on Boron Nitride

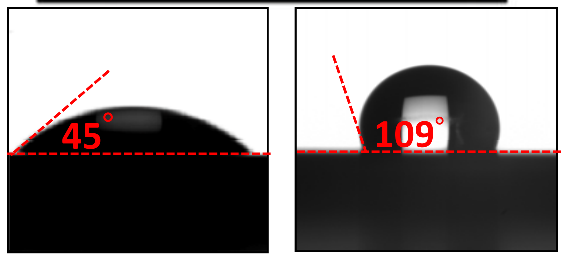




Nat. Nanotechnol. 5, 722–726 (2010)

3. Graphene on organic functionalized substrate





Nano Lett. 2012, 12, 964–969

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

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

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