STM and graphene

W. W. Larry Pai (白偉武）

Center for condensed matter sciences, National Taiwan University

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Why graphene is important:

It is a new form of material (two dimensional, single layer of atoms). More “atomic crystals” are coming.
It has the best electrical conductivity (if made perfect) of any known material.
It can be used to make very small devices (electronics, mechanical)
Its carrier has relativistic quantum mechanics properties.
Carbon is everywhere!

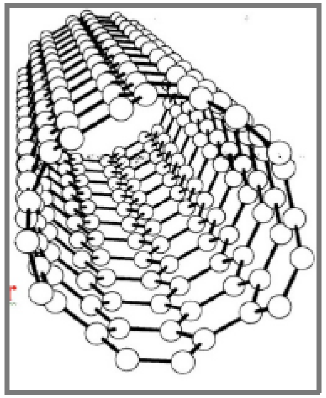
Why STM on graphene:

Provides new (spectro)microscopic insight on this interesting material.
A great tool to characterize defects.

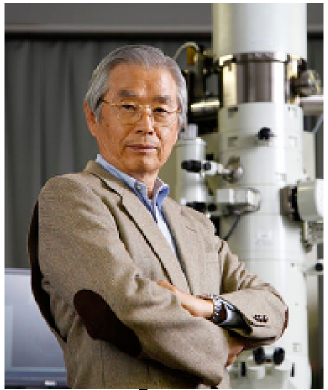
History of Carbon materials

Graphite

Carbon nanotube (fiber)



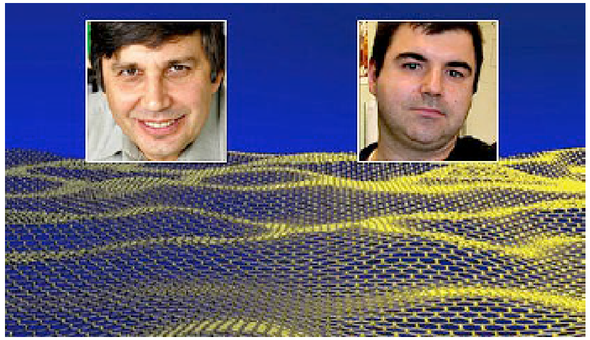
Sumio Iijima (飯島澄男)

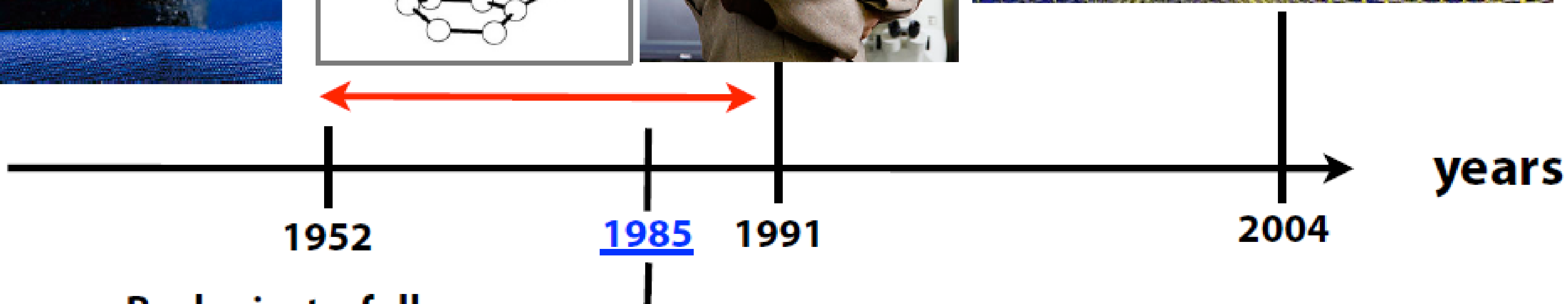


Graphene

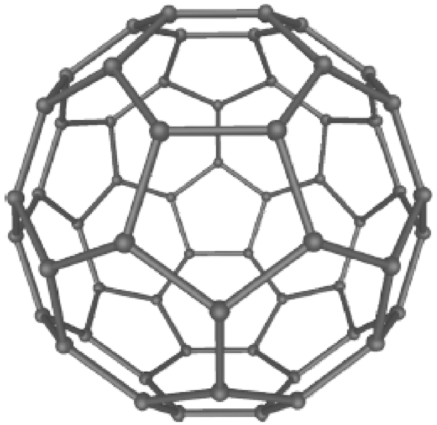
Andre Geim

Konstantin Novoselov



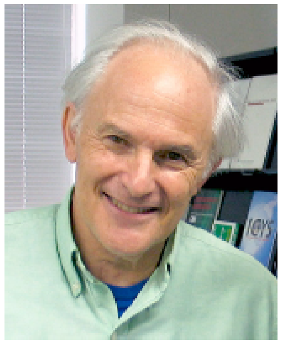


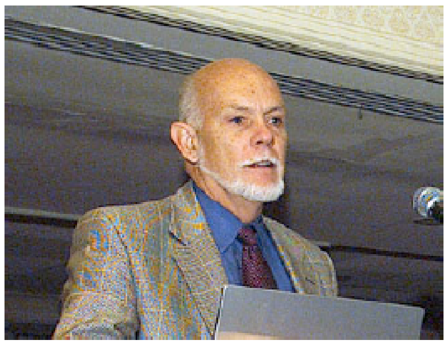
Buckminsterfullerene



Robert Curl, Harold Kroto and Richard Smalley

(1996 Nobel prize in Chemistry)





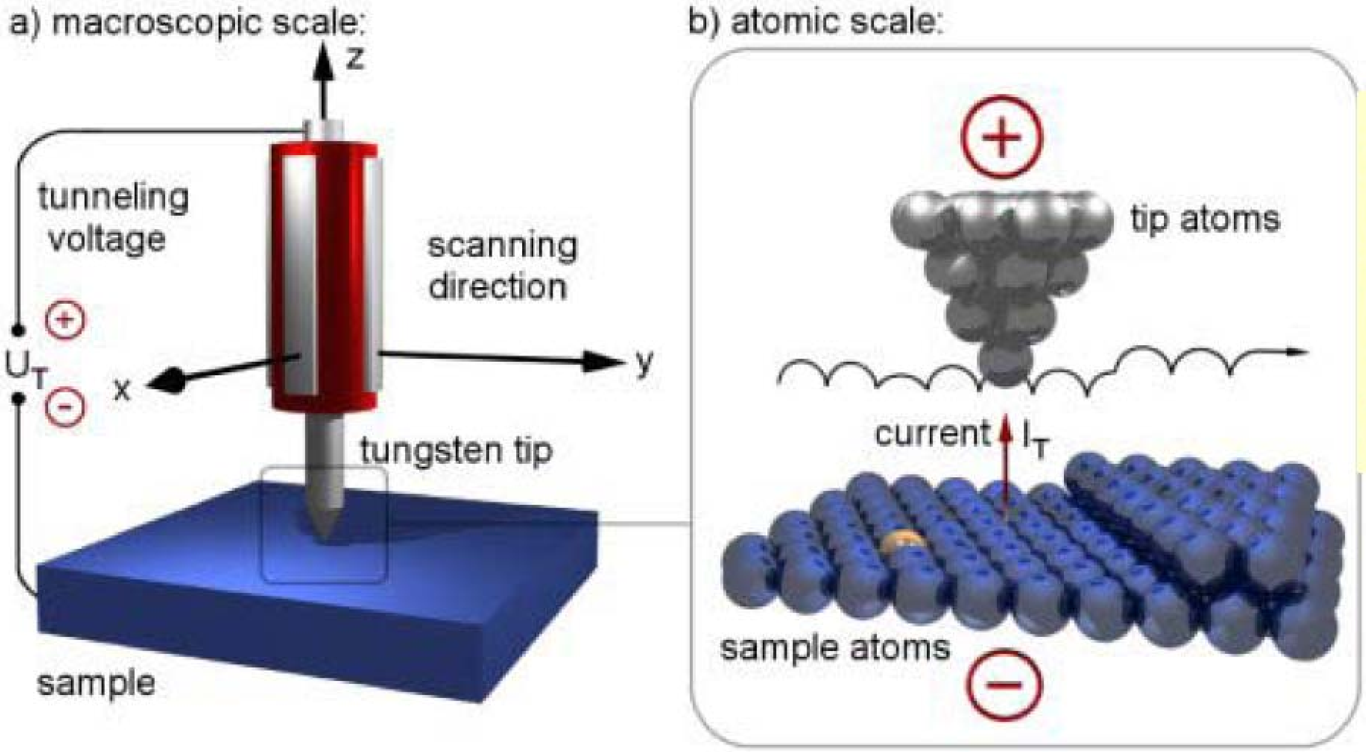
Brief History of STM

- The first member of SPM family, scanning tunneling microscopy (STM), was developed In 1982, by Gerd Binnig and Heinrich Rohrer at IBM in Zurich created the ideas of STM (Phys. Rev. Lett., 1982, vol 49, p57). Both of the two people won 1986 Nobel prize in physics for their brilliant invention.

STM is really small in size.

Nobel Laureates Heinrich Rohrer and Gerd Binnig (B. 1947)

Scanning resolution of STM

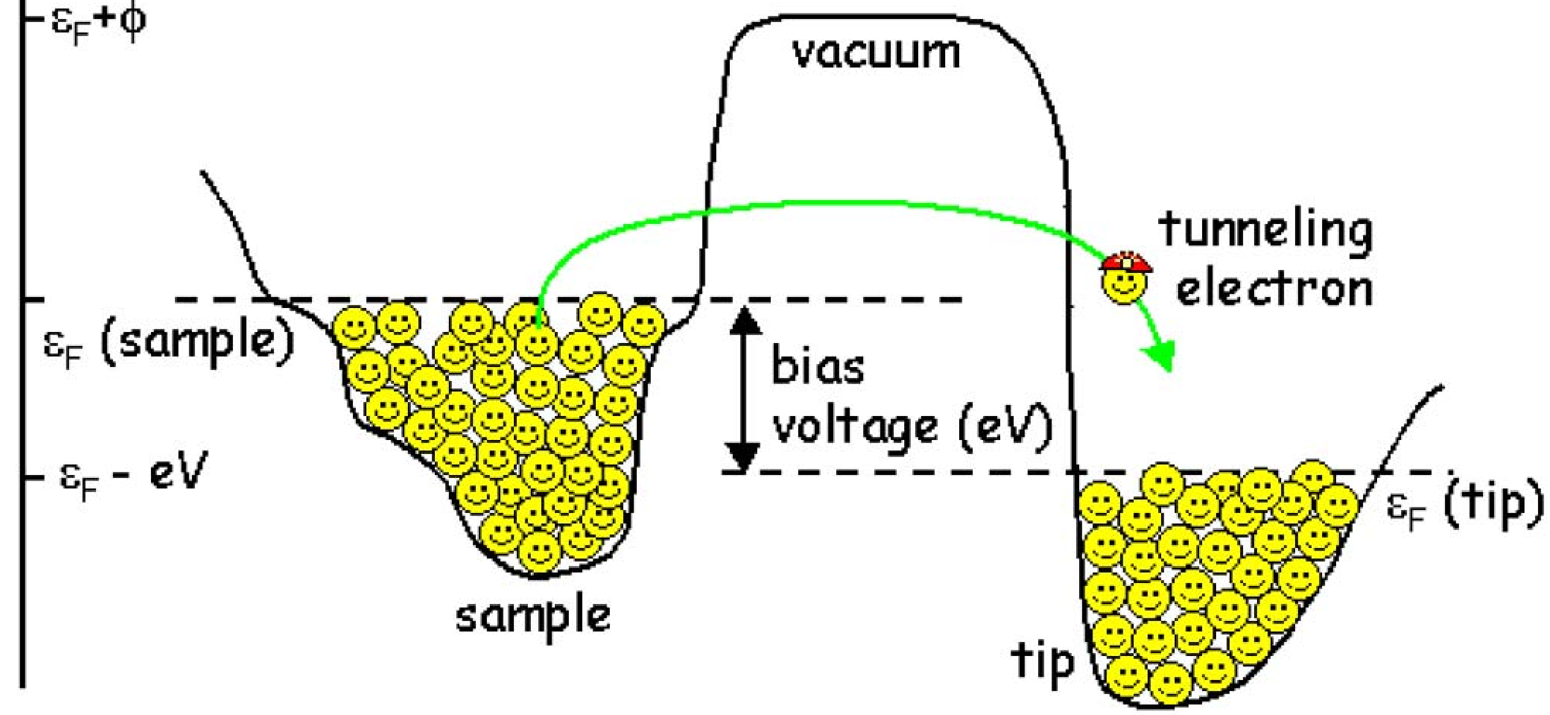


STM does NOT probe the nuclear position directly, but rather it is a probe of the **electron density,** ***i.e., the size of the whole atom.***

Principle of scanning tunneling microscopy: Applying a negative sample voltage yields electron tunneling from occupied states at the surface into unoccupied states of the tip. Keeping the tunneling current constant while scanning the tip over the surface, the tip height follows a contour of constant ***local density of states.***

Tunneling current at bias

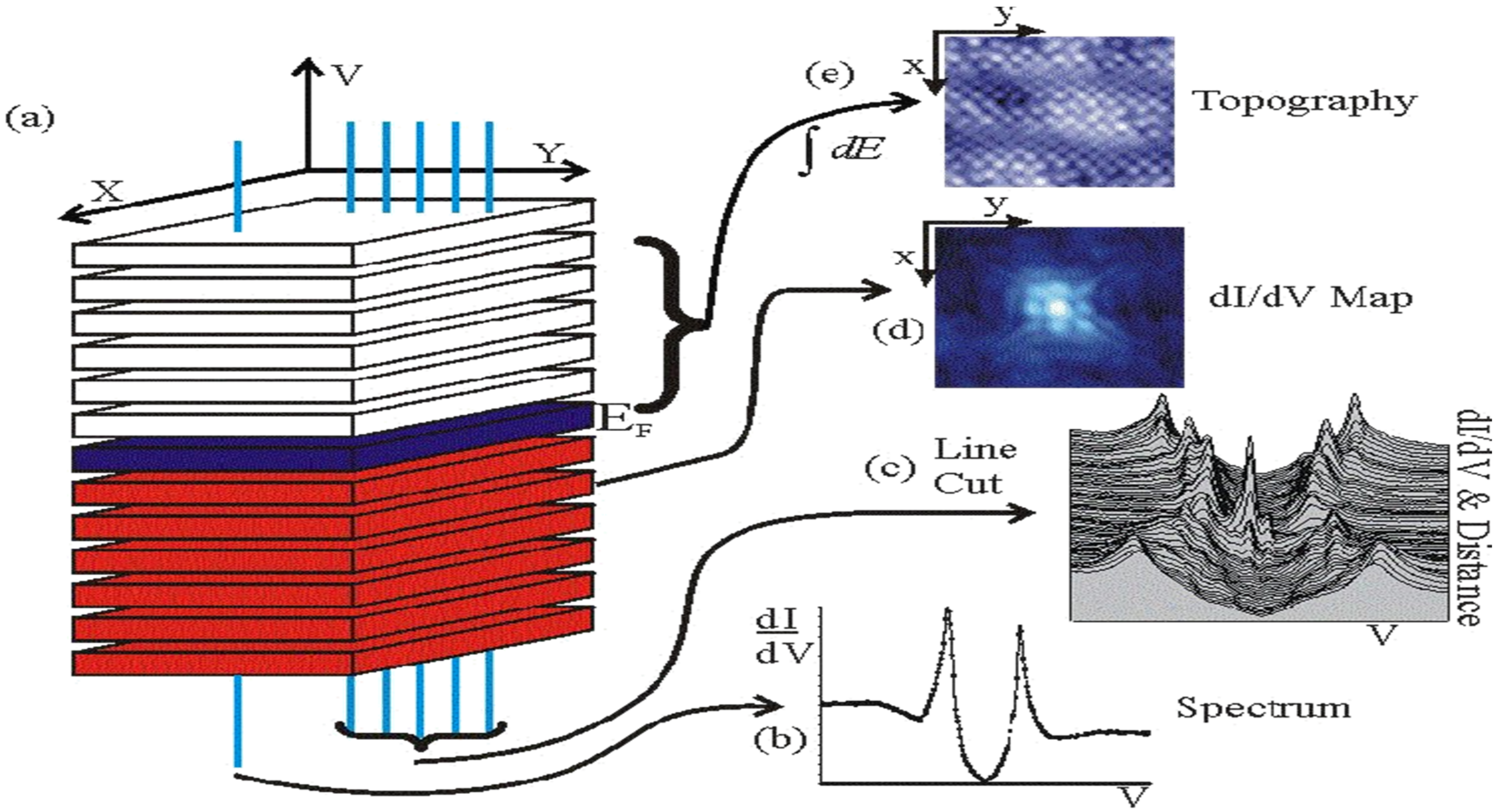
Here we image sample's "filled" state
If the sample bias is reversed, we image "empty" states



By applying a bias voltage to the sample with respect to the tip, we effectively raise the Fermi level of the sample with respect to the tip. Now we have empty states available for tunneling into.

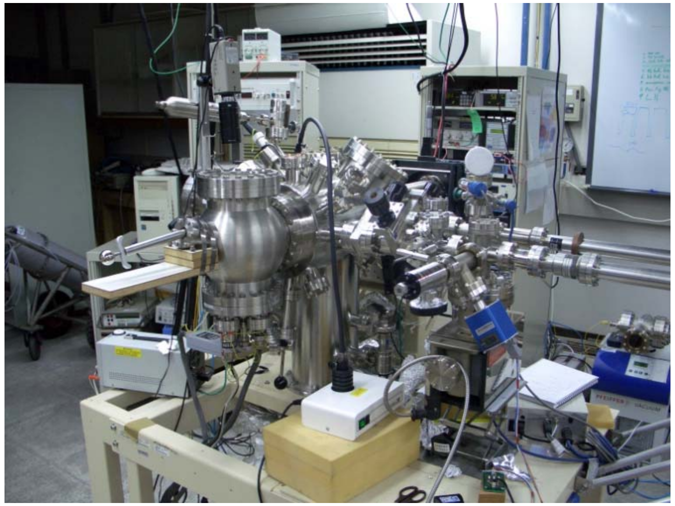
What an STM measures?------*local density of states*

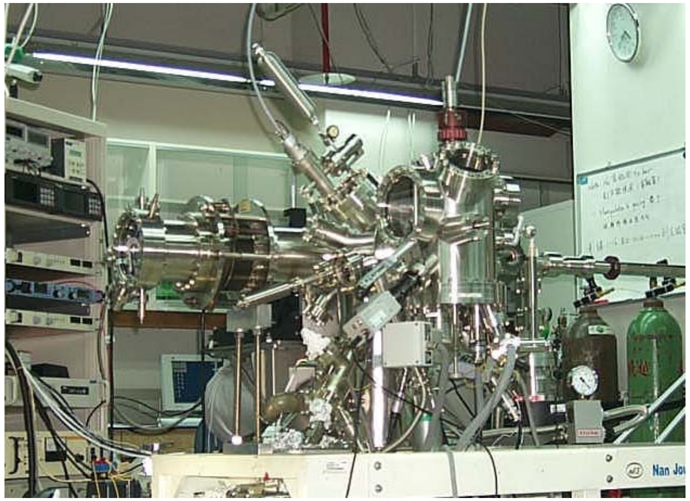
Each plane represents a different value of the tip-sample bias V, and the lateral position on the plane gives the x,y position of the tip. Filled states are given in red. The plane at the Fermi energy (V=0) is shown in blue.

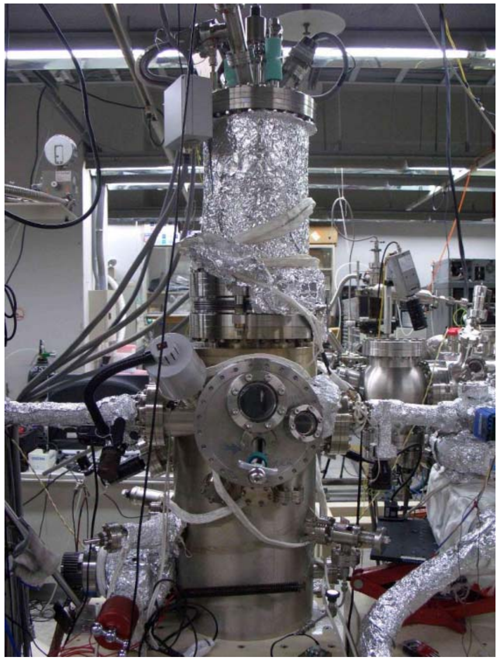


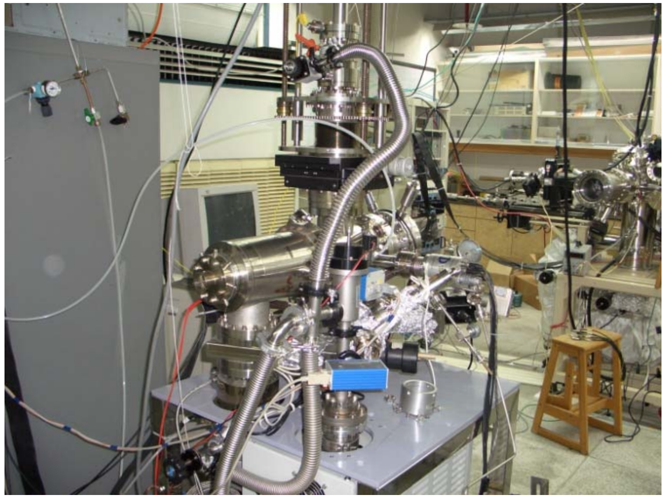
My laboratory setup: (takes time and care for smooth operation)

Room-temperature UHV STM/AFM (Omicron)
Variable-temperature UHV STM/AFM (Omicron)
Low-temperature STM (Omicron)
Temperature programmed desorption system (Hiden)
Ambient AFM (PSIA)









carbon materials : 0D, 1D, 2D, 3D

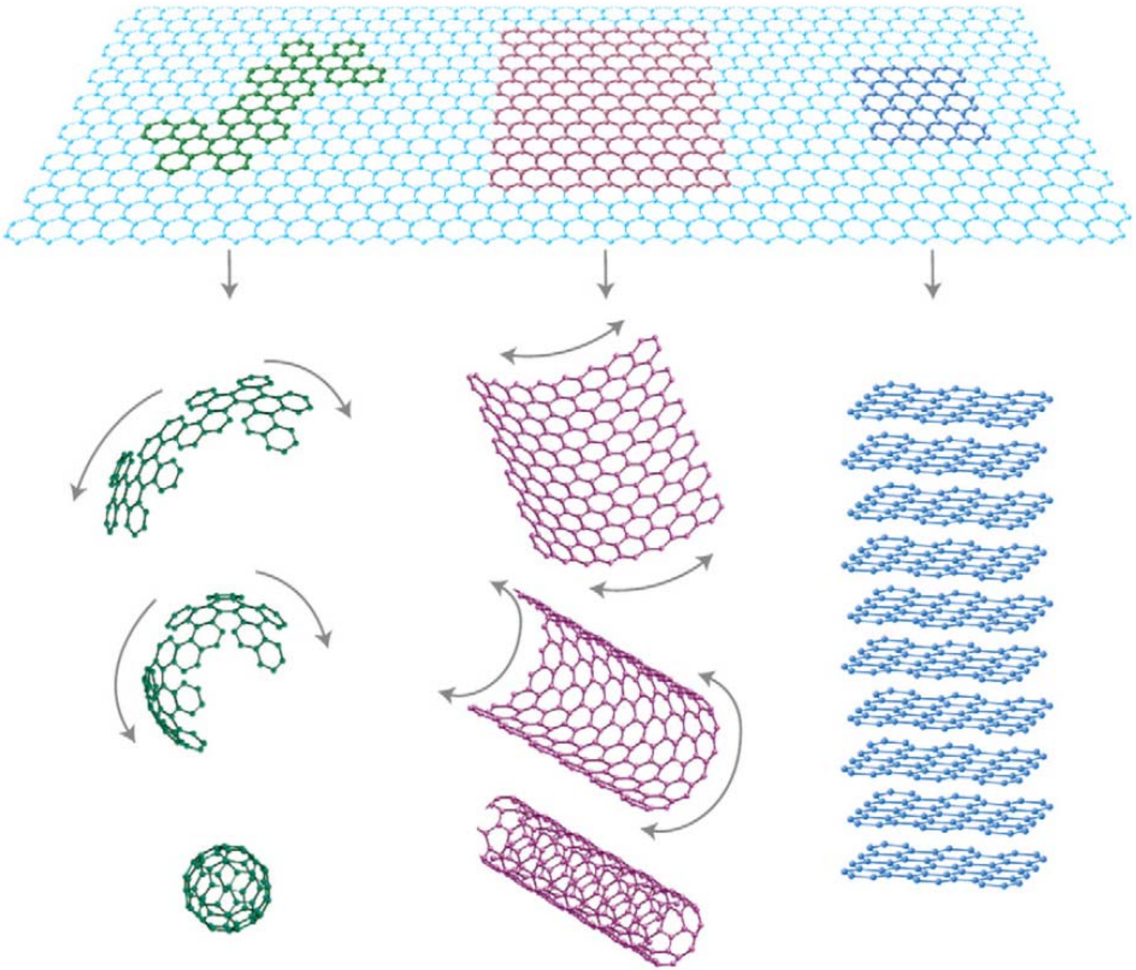
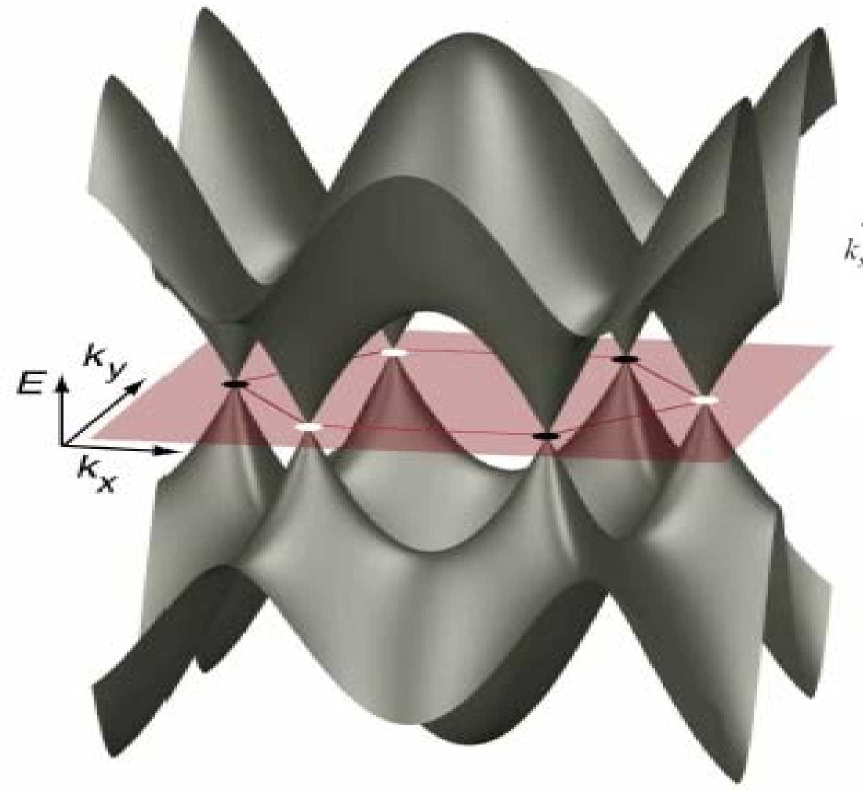
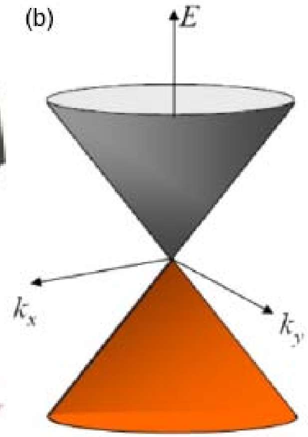
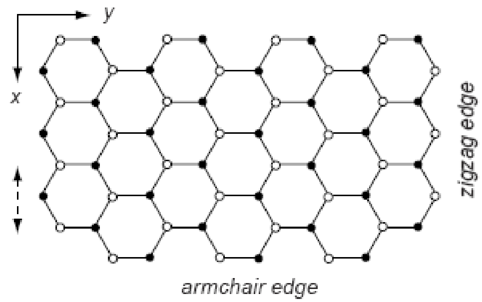


Fig. 1. Basis of all graphitic forms. Graphene is a 2D building material for carbon materials of all other dimensionalities. It can be wrapped up into 0D buckyballs, rolled into 1D nanotubes, or stacked into 3D graphite. (Reproduced with permission from [2].)

Graphene – a sheet of carbon atoms, with "Dirac" Fermion



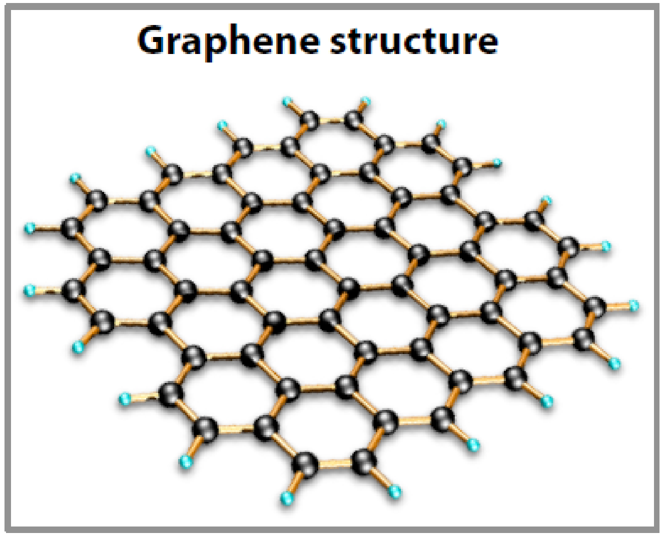


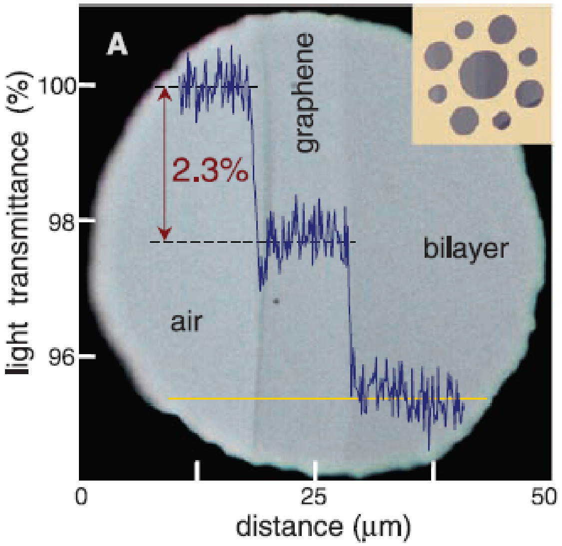


The spectrum is well described by the tight-binding Hamiltonian on a hexagonal lattice:

Fundamental properties of Graphene

- A single layer of carbon atoms densely packed in a honeycomb crystal lattice.





- Thermodynamic stable : ~ 1000 °C
- High in-plane thermal conductivity : ~ 5×10^3 W/mk

- Mechanically properties:
  (1) Incredibly strong and remaining flexible
  (2) Yield strength : 130 GPa (cf.: CNT : 53 GPa)
  (3) Young's modulus: 1 TPa
  (4) Shear modulus : ~ 280 GPa

- Charge carrier (n): ~ 10^{13} /cm^2
- High electron mobility : 15000 cm^2/Vs

- Coupling between light and relativistic electron fine structure constant:

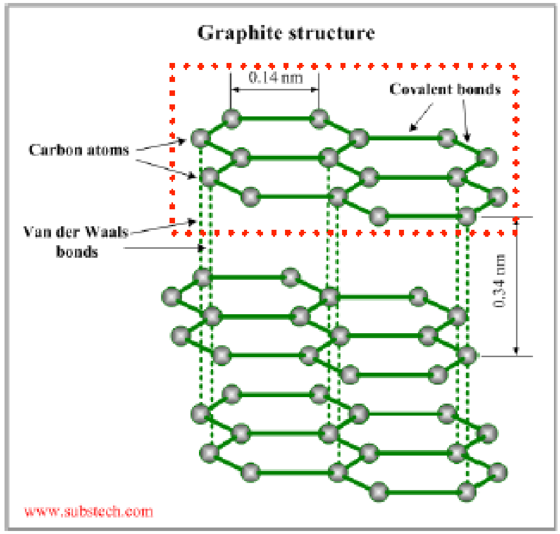
$$\alpha = \frac{e^2}{\hbar c} \approx \frac{1}{137}$$

Optical absorption : $\pi\alpha \approx 2.3\ \%$ (monolayer)

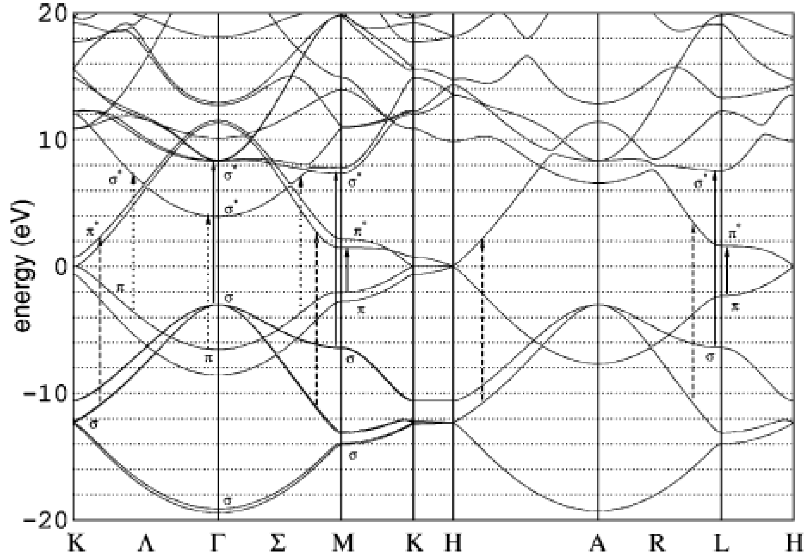
- Doping, n ~ 10^{14}/cm^2 (E_F ~ 1 eV) ⇒ Visible range

1. R. R. Nair, P. Blake, A. N. Grigorenko, K. S. Novoselov, T. J. Booth, T. Stauber, N. M. R. Peres and A. K. Geim. Science 320, 1308 (2008).

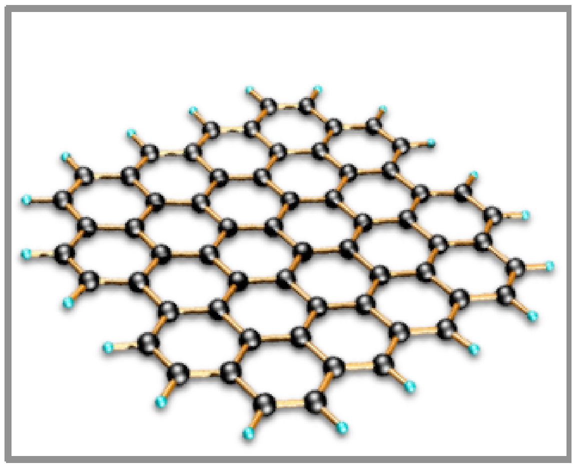
Crystal/Band structures : Graphite and Graphene

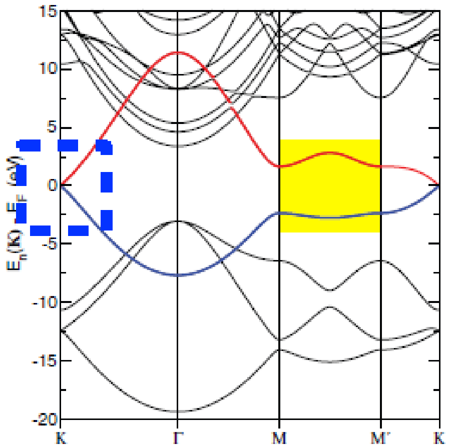


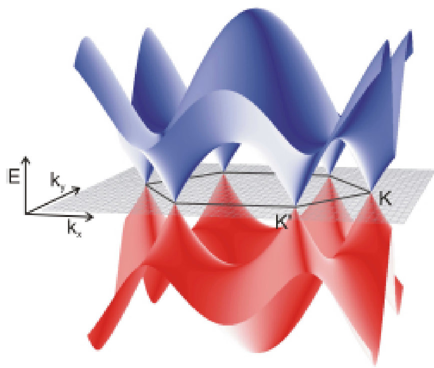
Graphite



Graphene





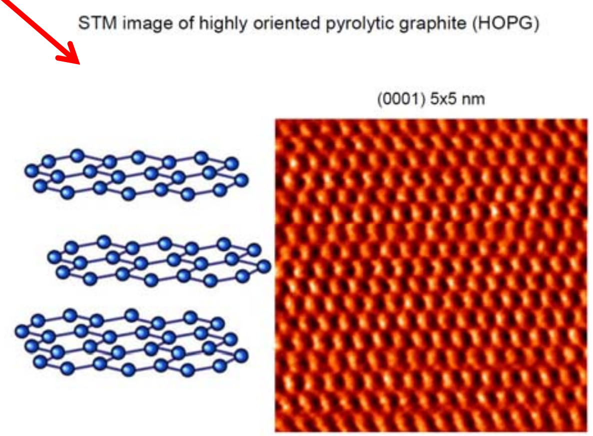


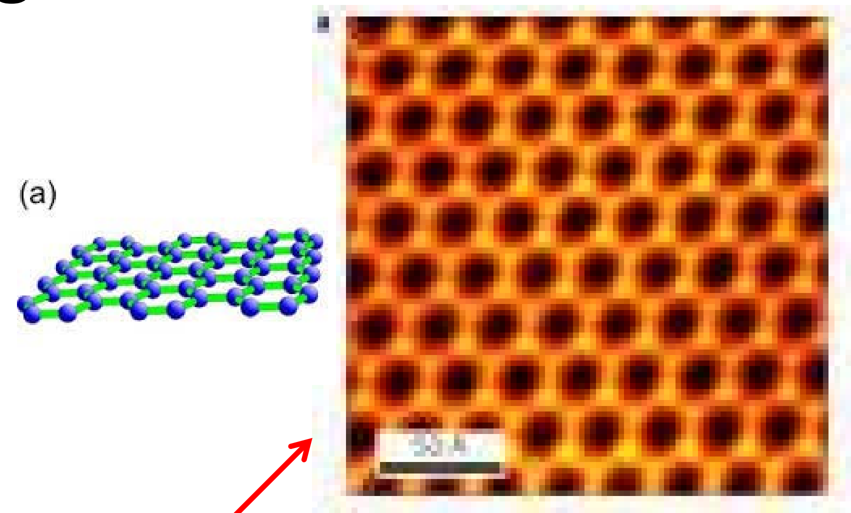
Dirac cone

- Around Dirac cone point (K point): Linear dispersion (zero gap)
- Strong absorption peak : ~ 4.5 eV (M point)

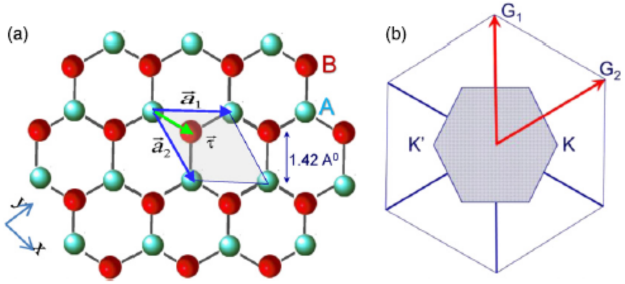
Basic characters of STM imaging on graphitic materials

- Graphite: AB sites are imaged differently, lattice appears as triangle



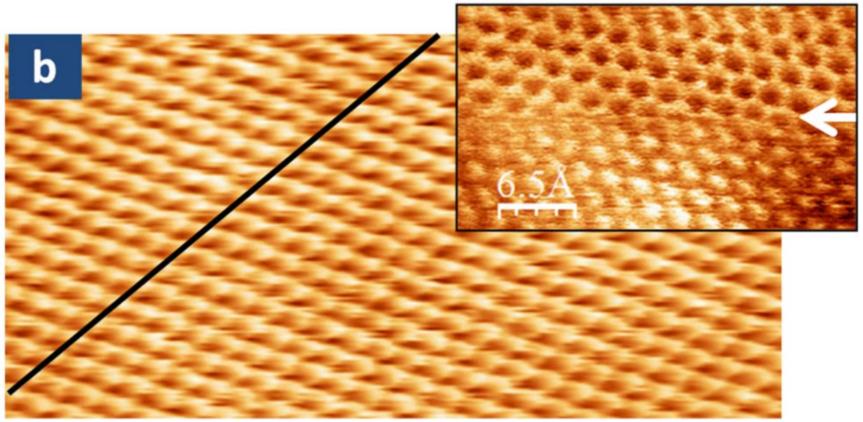


- Graphene: AB sites are symmetric, lattice appears as hexagonal

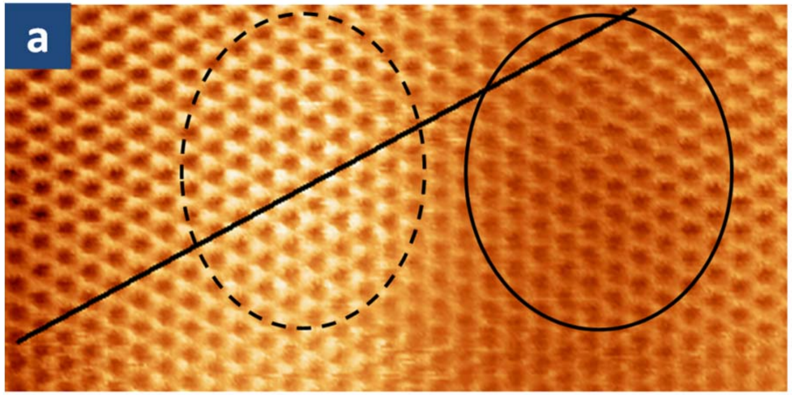


But, is it always true?

Lattice type changes when tip changes…



Lattice type changes even when there is no tip change… (curvature effect?)



suspended graphene

So, the imaging of graphene, especially on curved surface, remains puzzling

Graphene samples

- For STM studies

-- graphene grown on metal surfaces

-- graphene on SiC surface

-- transferred CVD graphene

-- exfoliated graphene

-- suspended graphene

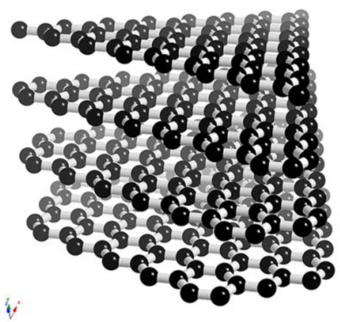
Preparation methods of graphene

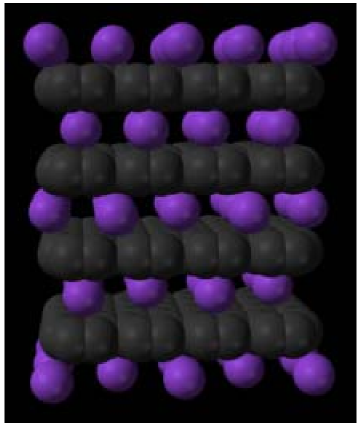
Top-down approach
(From graphite)

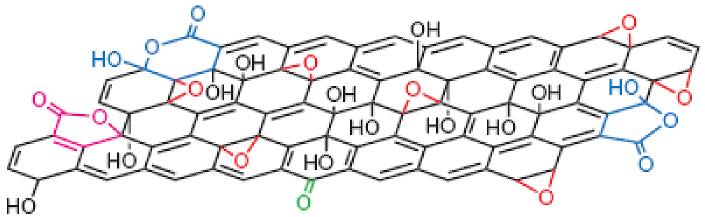
Direct exfoliation of graphite

Graphite intercalation compound

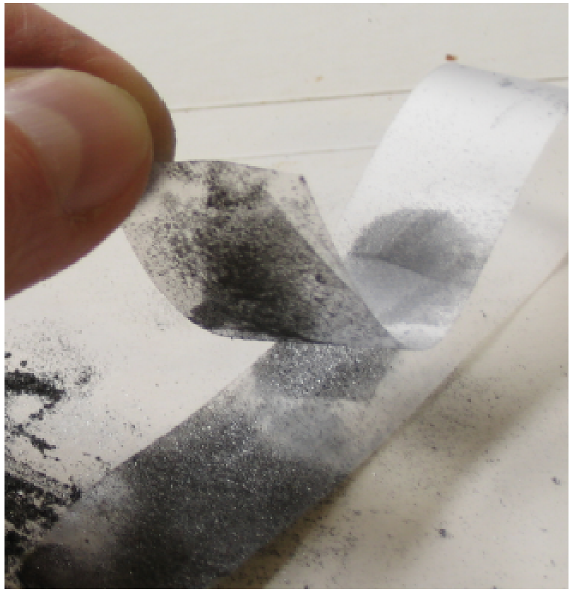
Graphite oxide method

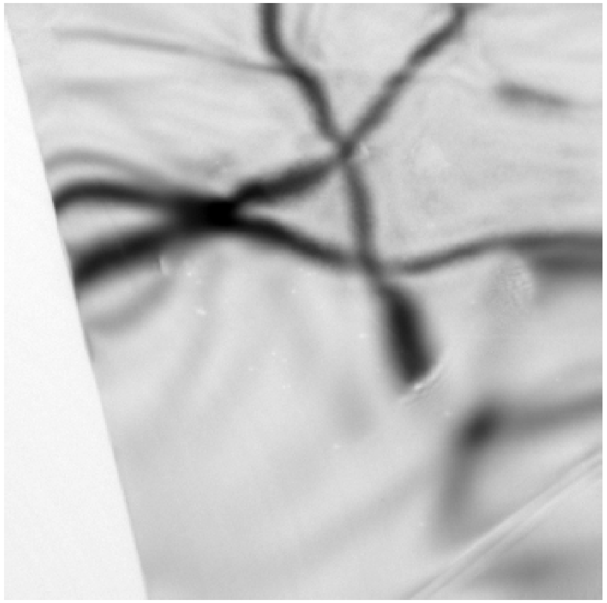






Preparation of Graphite - scotch tape

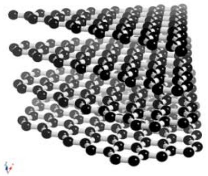




1. You put scotch tape on graphite or mica and peel the top layer.
   There are flakes of graphite that come off your tape.
2. Then you fold the tape in half and stick it to the flakes on top and split again.
   And you repeat this procedure 10 or 20 times.
   Each time, the flakes split into thinner and thinner flakes.
3. At the end you're left with very thin flakes attached to your tape.
   You dissolve the tape and everything goes into solution.

Graphene obtained from the reduction of graphene oxide (by heat, flash, chemistry etc.)

Graphite oxide method (Most common and high yield method)



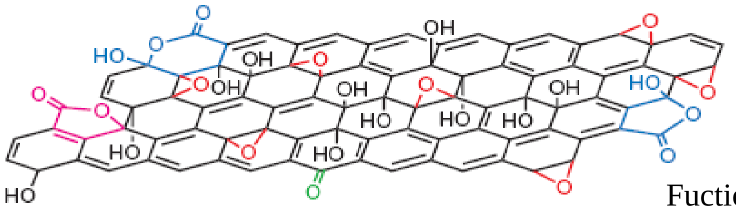
Graphite

Oxidation (Hummers'method)

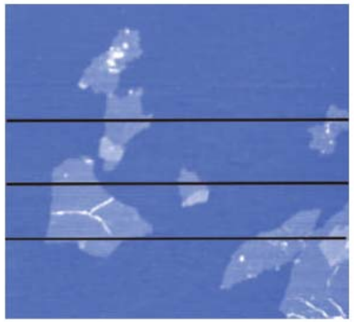
H_2SO_4/ $KMnO_4$
H_2SO_4/$KClO_3$
Or $H2SO_4$/HNO_3
…………………

Graphite Oxide

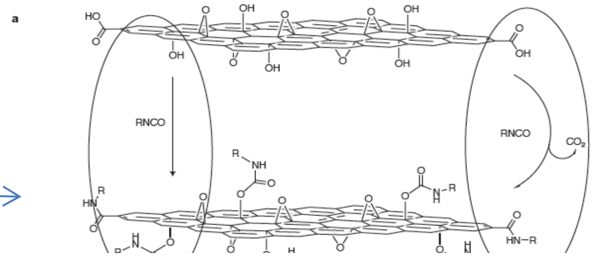
H_2O



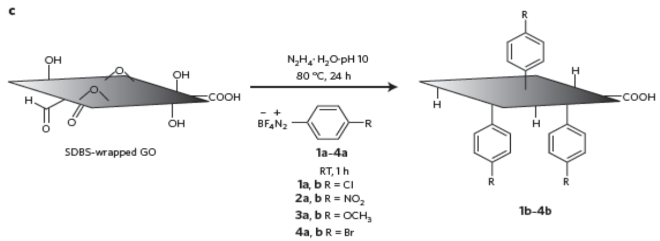
Graphene Oxide
monolayer or few layers



Ultrasonication (exfoliation)



Fuctionalization (for better dispersion)



Chemical reduction to restore graphitic structures

Making composite with polymers

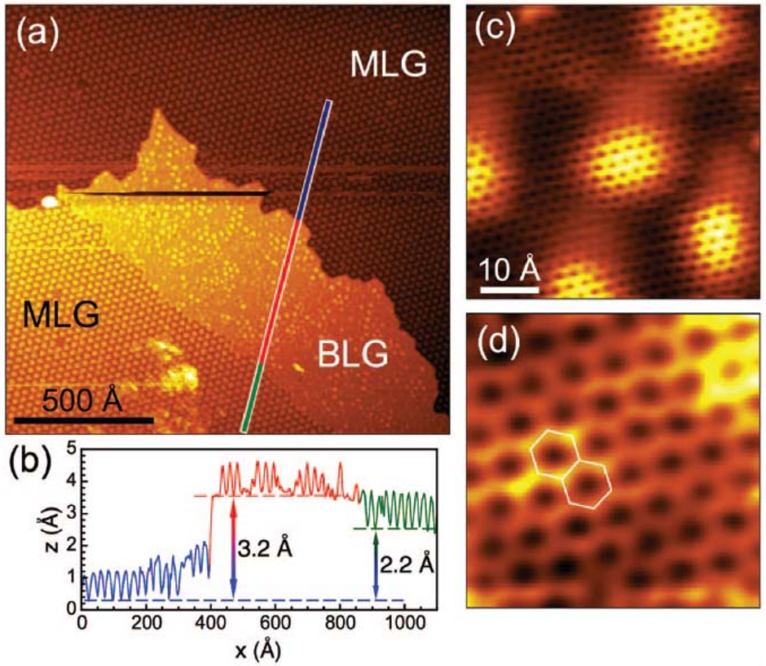
Graphene on metal surfaces

- Strong or weak graphene/metal interactions

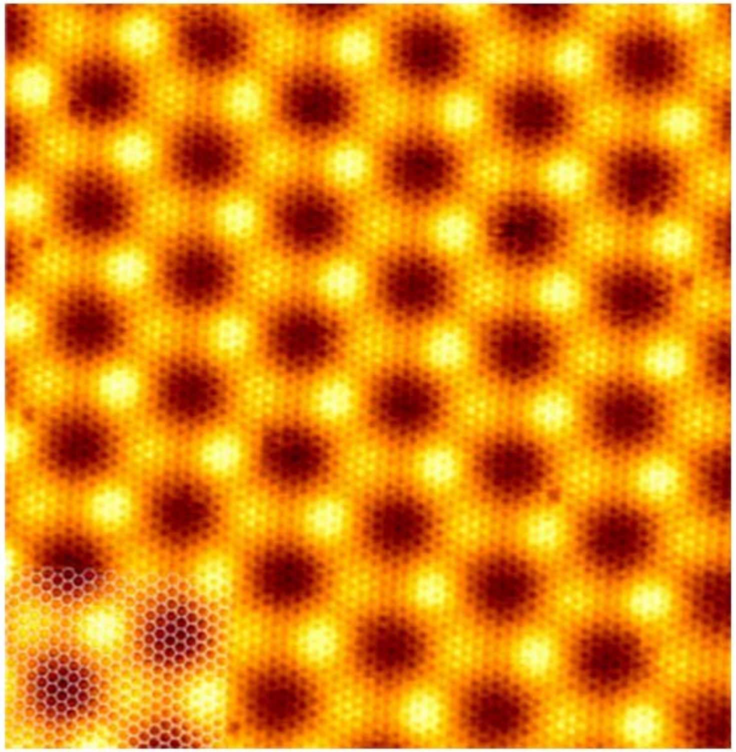
Weak: graphene on Ir(111), Pt(111)

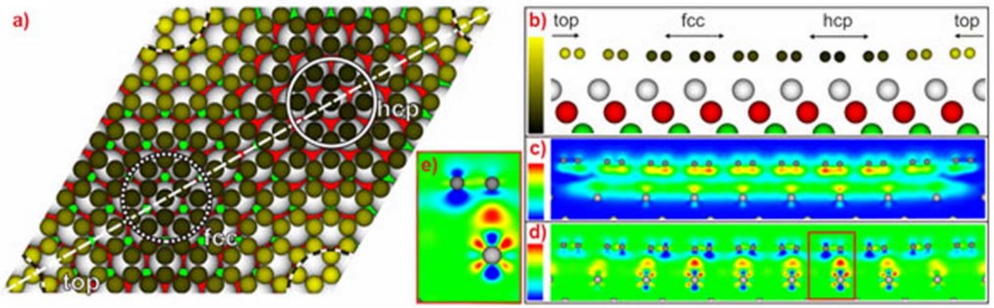
Strong: graphene on Rh(111), Ru(0001)

Moderate: graphene on Cu, Ni



Graphene/Ru(0001)

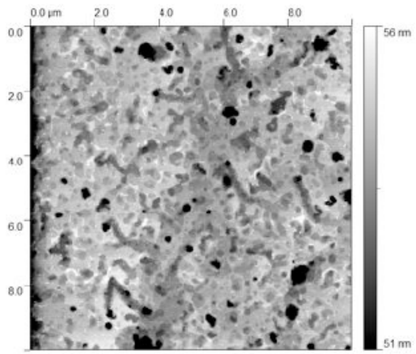




Graphene/Ir (0001)

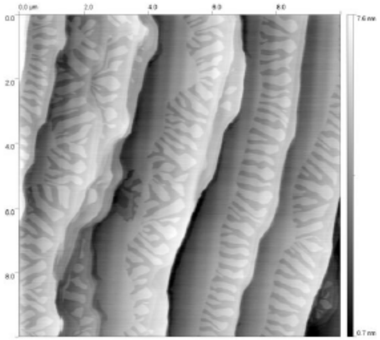
Epitaxial graphene on SiC surface

UHV Grown Si-Face



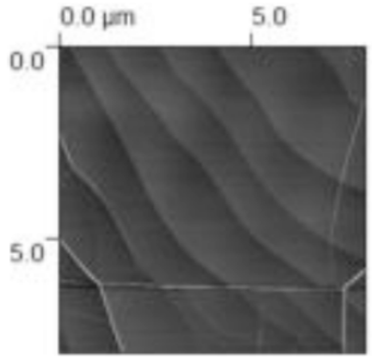
10X10 µm

Furnace Grown Si-Face



10X10 µm

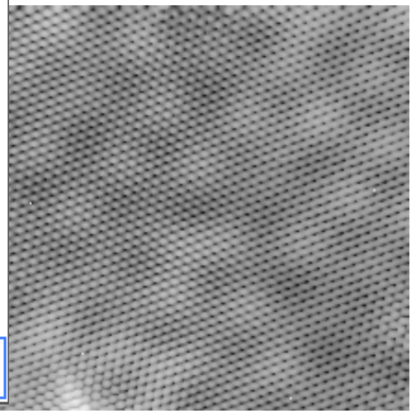
Furnace Grown C-Face



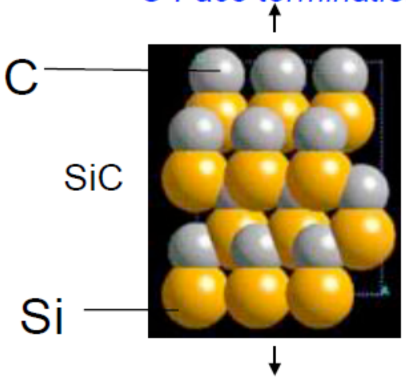
7.5X7.5 µm

Vacuum Furnace

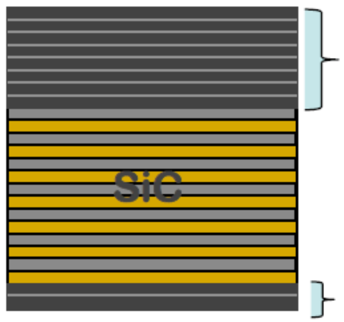
STM



C-Face termination



Si-Face termination



Thick graphene films
4 - 100 ML

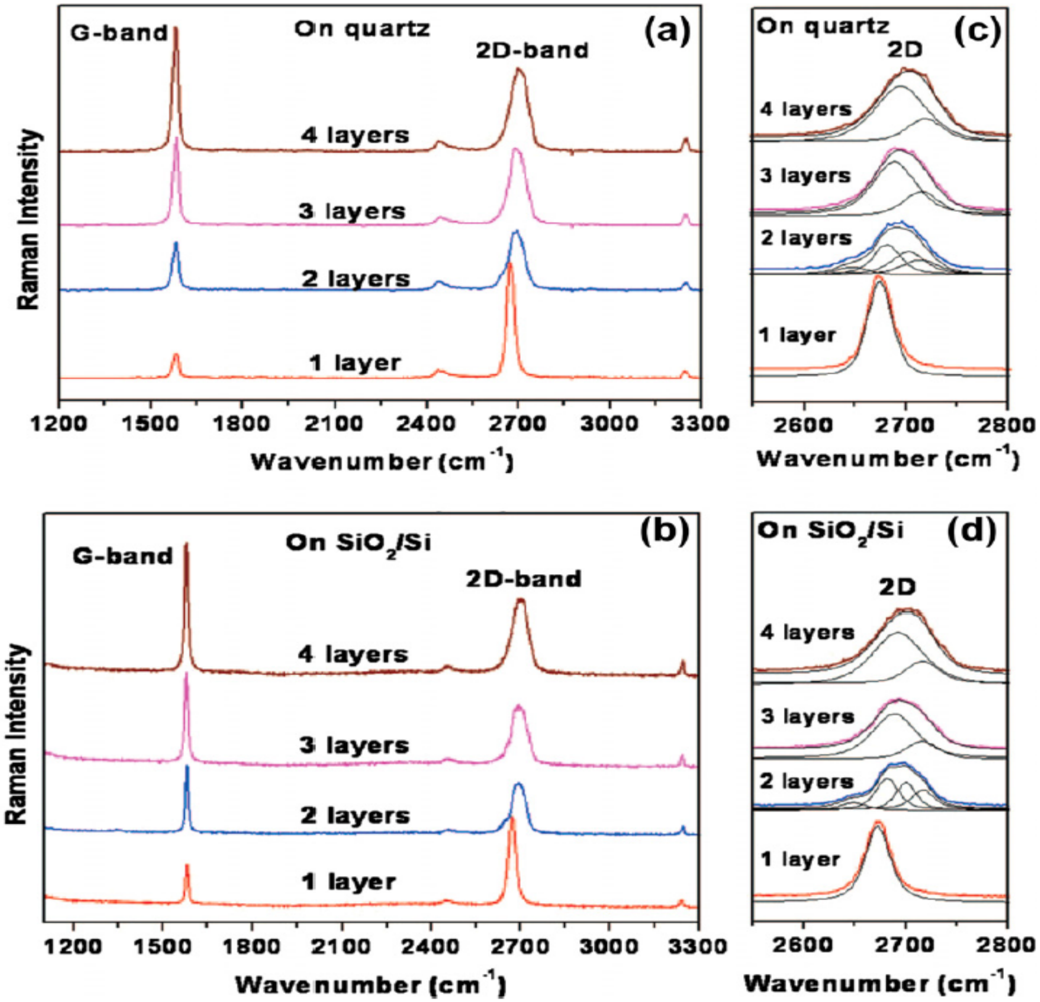
Thin graphene films
1 - 5 ML

J.Milan,L31.00010 U29.00001 Joanna Hass

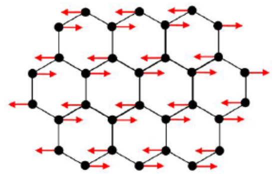
Basic ways of graphene structure characterization

- Raman
- AFM
- SEM
- STM
- TEM

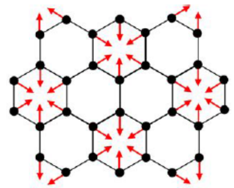
Raman characterization of graphene



G band:



Defect-induced D band:



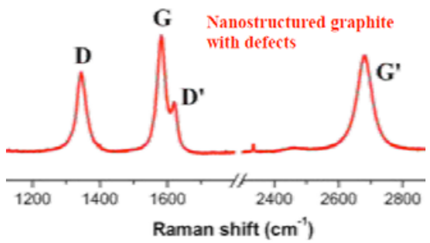
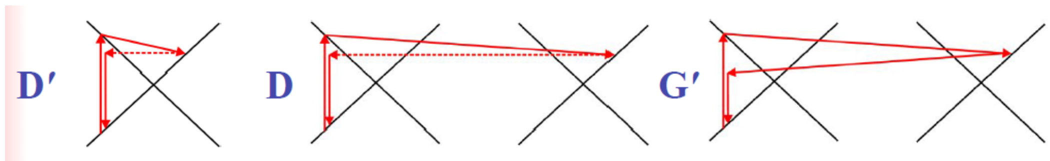


Fig. 10. The Raman spectra of monolayer, bilayer, tri-layer, and four-layer graphene on quartz (a) and SiO_2 (300 nm)/Si substrate (b). The enlarged 2D-band regions with the curve fit are shown in panels c and d. (Reproduced with permission from [58].)



Transfer of graphene to substrate (using resist)

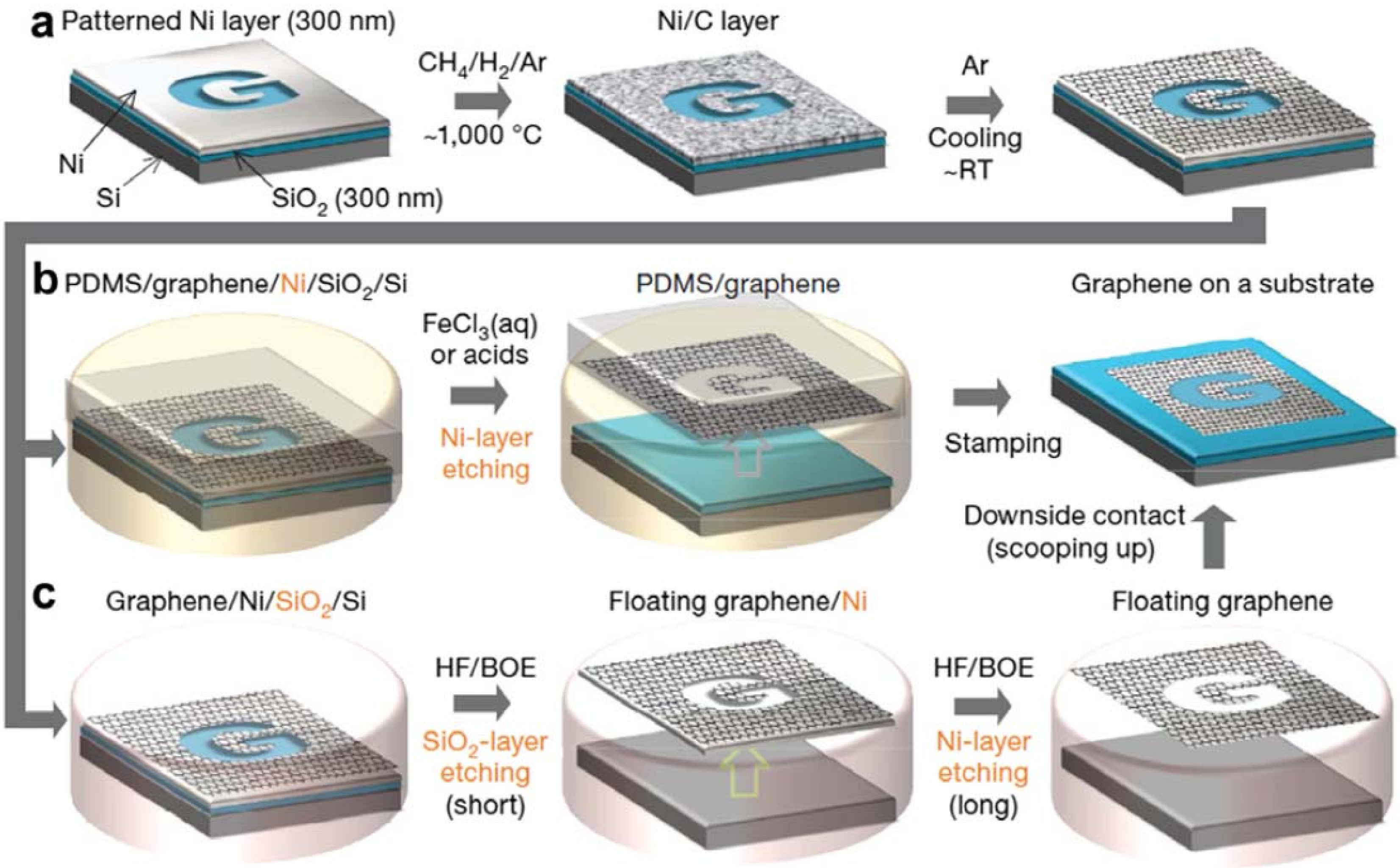
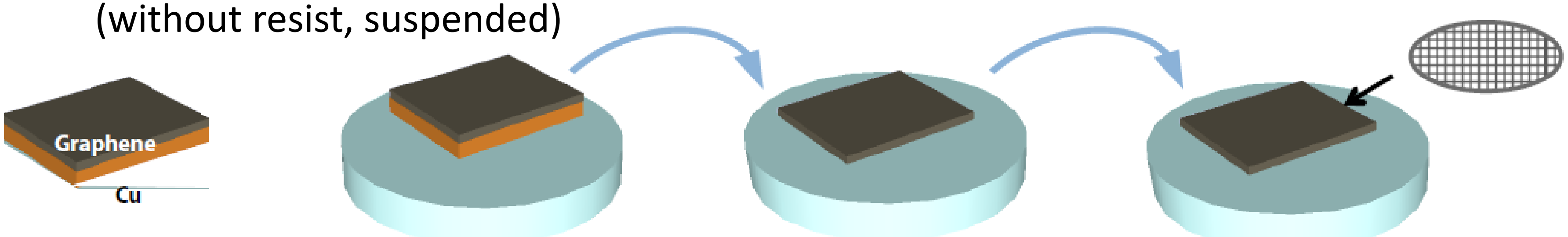
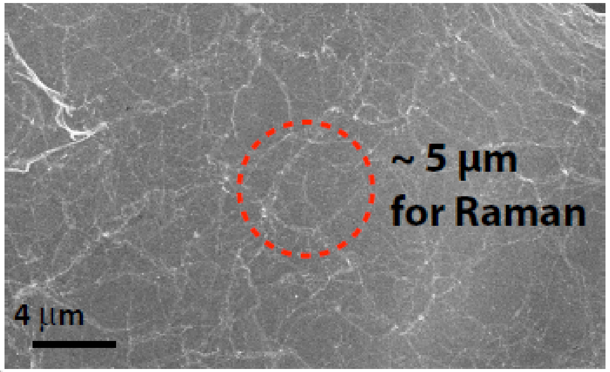


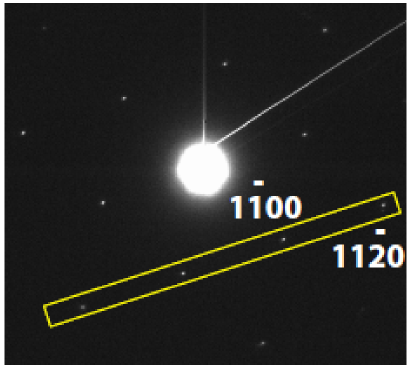
Fig. 2. Synthesis, etching, and transfer processes for large-scale and patterned graphene films: (a) Synthesis of patterned graphene films on thin nickel layers. (b) Etching using $FeCl_3$ (or acids) and transfer of graphene films using a PDMS stamp. (c) Etching using BOE or hydrogen fluoride (HF) solution and transfer of graphene films. (Reproduced with permission from [25].)

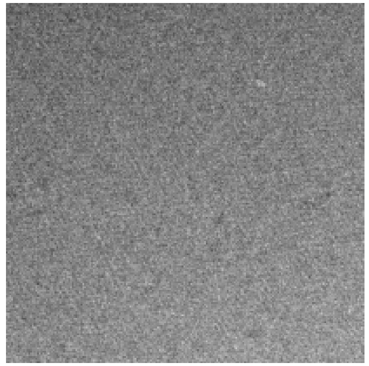
Preparation of Graphene - CVD growth

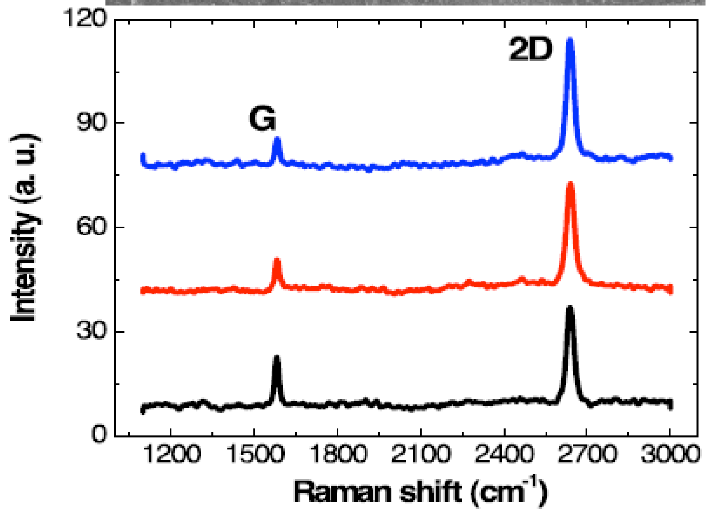
(without resist, suspended)

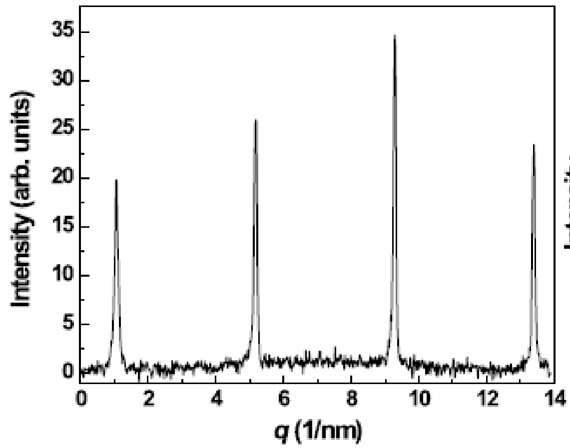


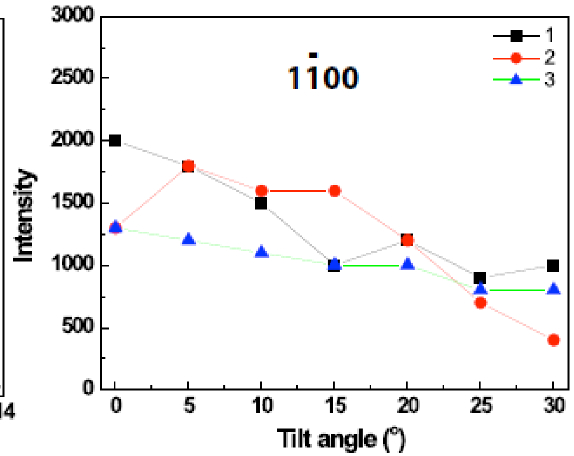






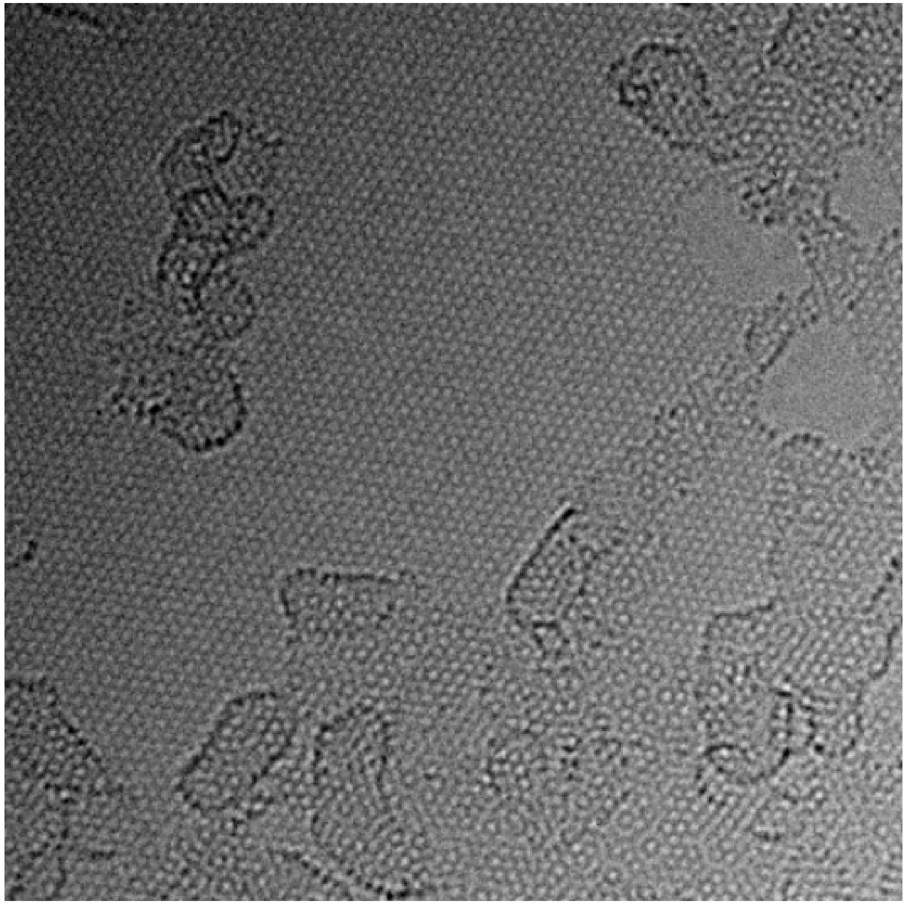




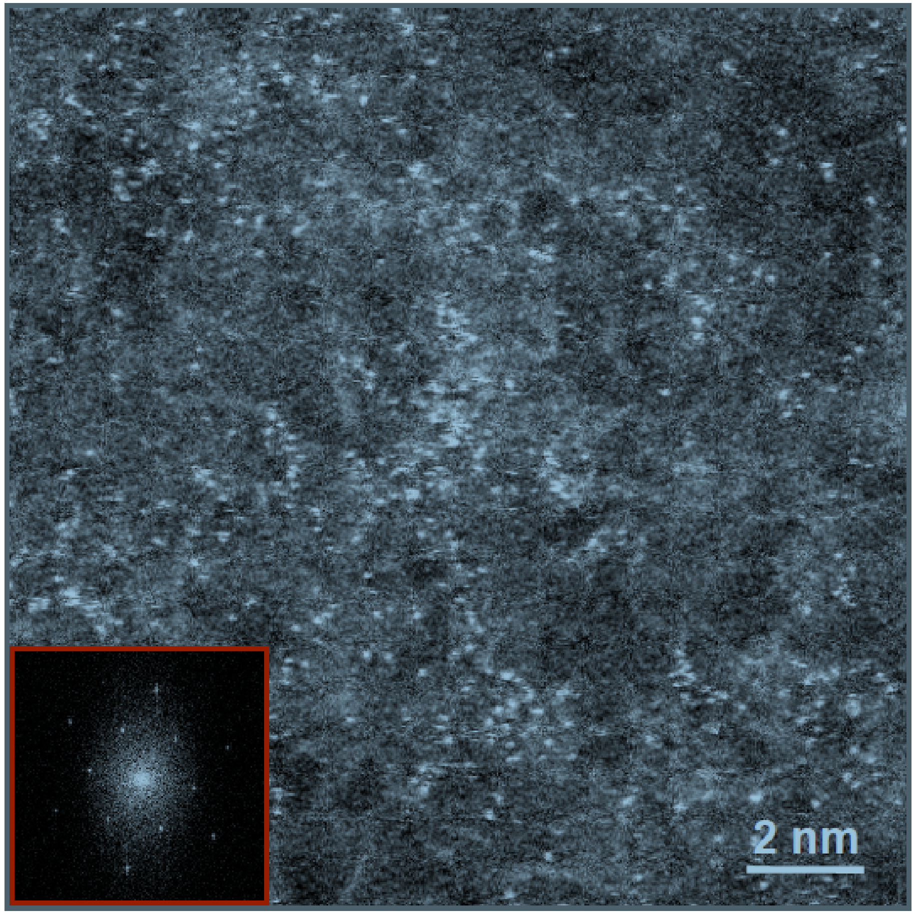


Graphene : Cs-(S)TEM HRTEM and HAADF images

Cs-TEM (80 kV)



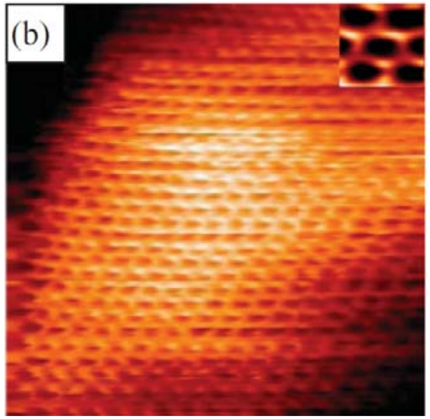
Cs-STEM (200 kV)



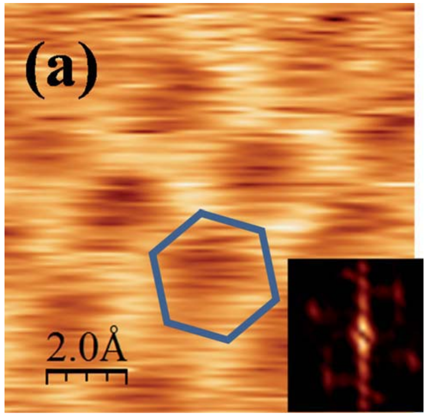
Cs-TEM Image courtesy: Ricolleau et al. (CNRS, Paris 7 University)
Advanced Electron Microscopy and Nano-Structures at Matérials and Quantum Phenomena Laboratory

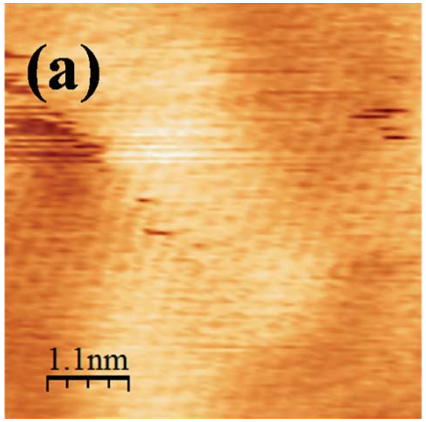
Reported STM images of suspended graphene

PHYSICAL REVIEW B **85** (2012)

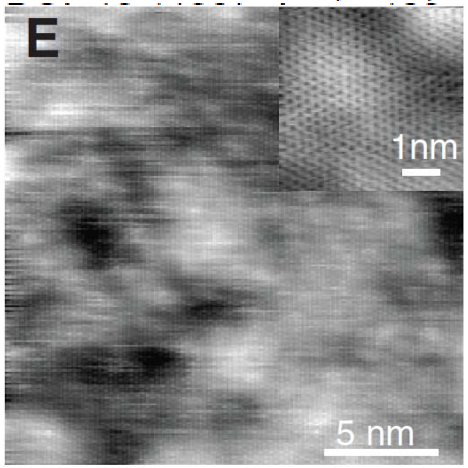


Nanoscale **4**, 3065-3068 (2012)

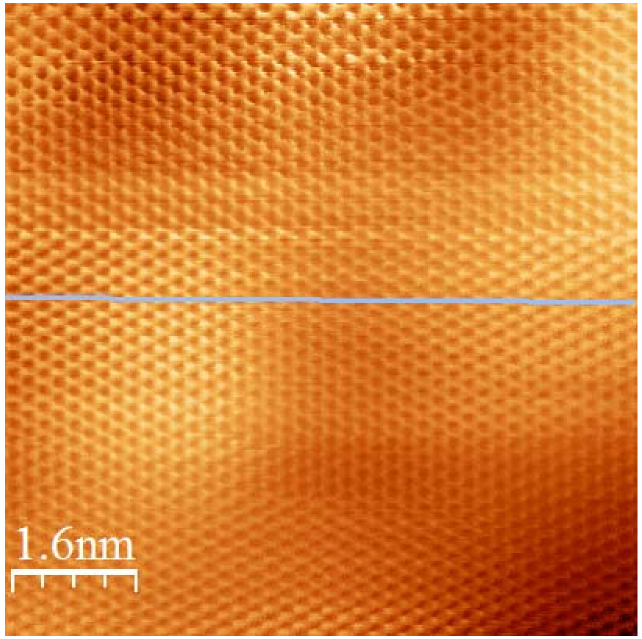




Science **336**, 1557 (2012)



try and error

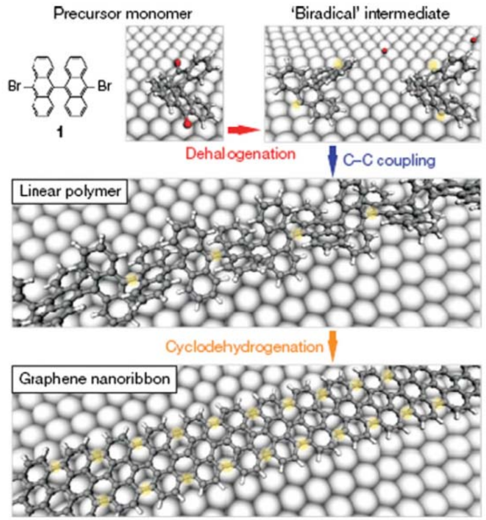


The present work

Tip-graphene interaction understood and controlled imaging

In-situ synthesis of graphene

- Synthesis of graphene nanoribbons from hydrocarbon molecules



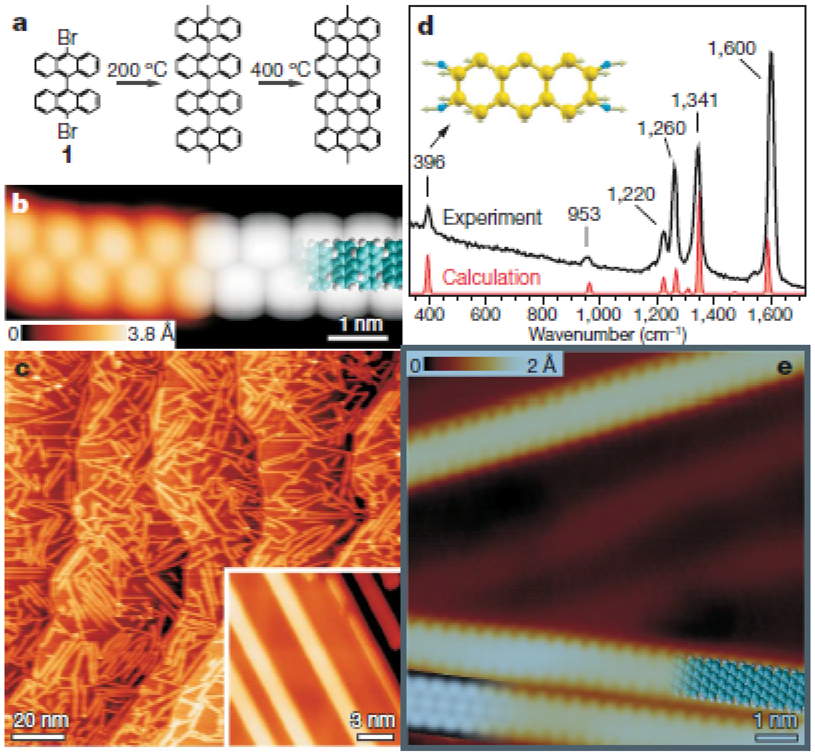


Figure 2 | Straight GNRs from bianthryl monomers. a, Reaction scheme

10,109-dibromo-9,99-bianthryl

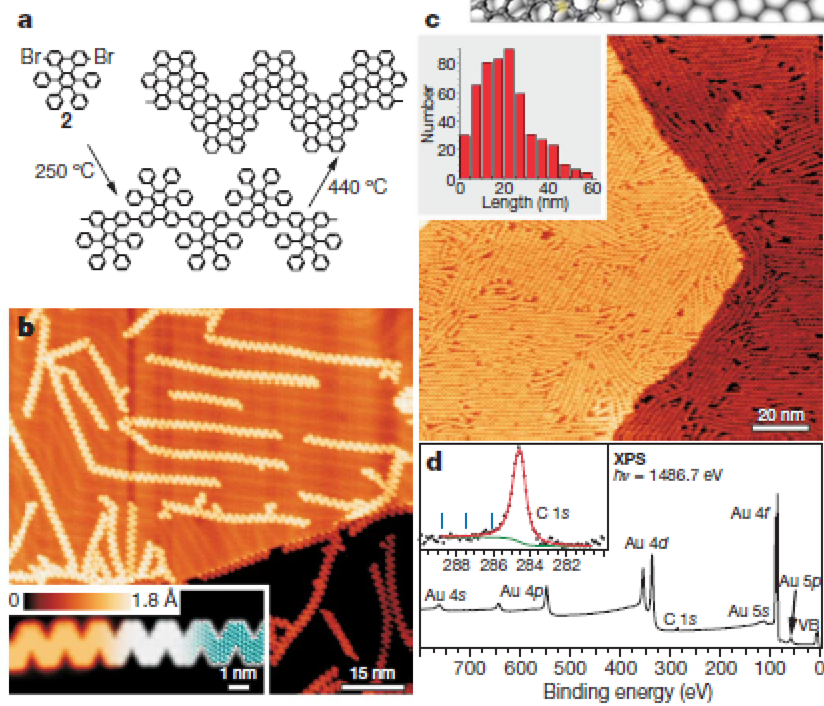
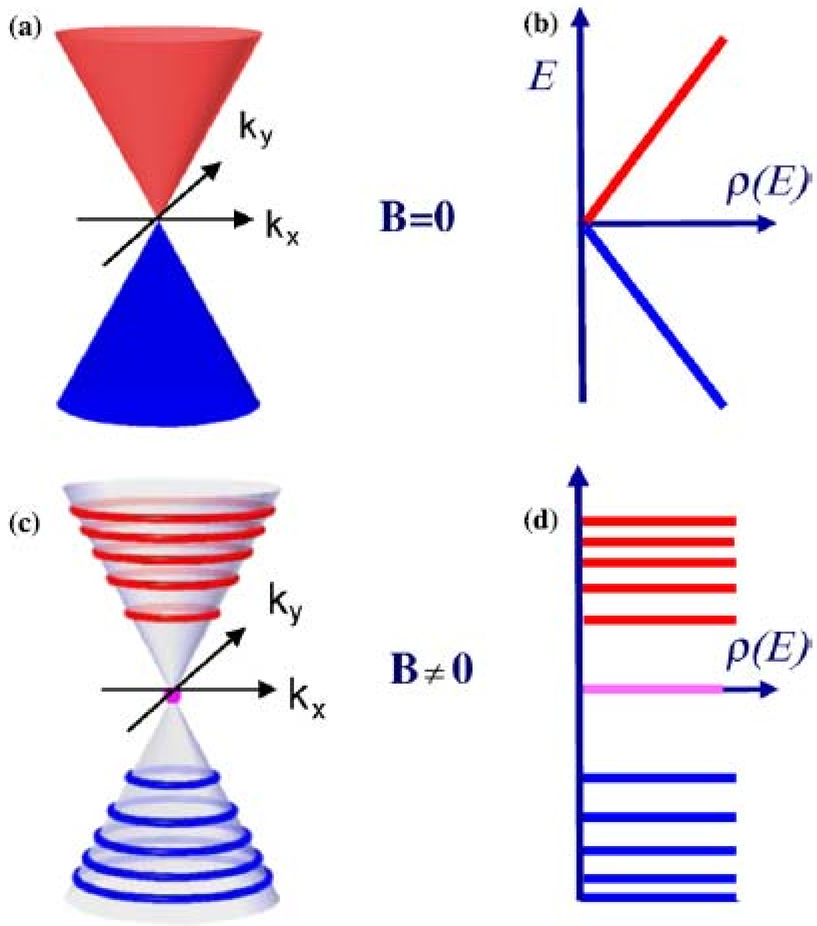
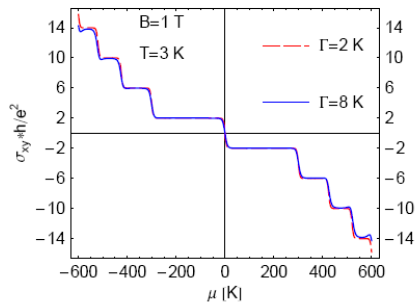


Figure 3 | Chevron-type GNRs from tetraphenyl-triphenylene monomers.
a, Reaction scheme from 6,11-dibromo-1,2,3,4-tetraphenyltriphenylene

Electronic property of graphene

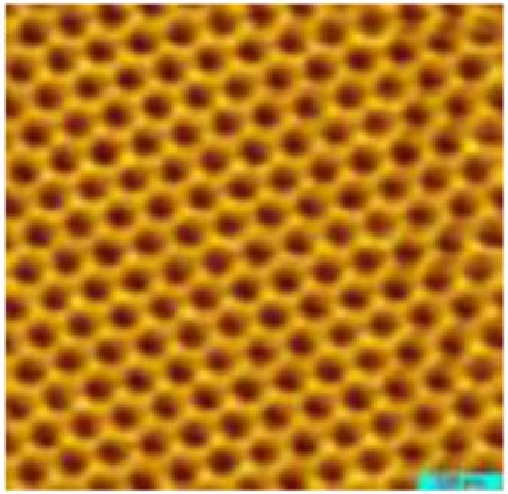




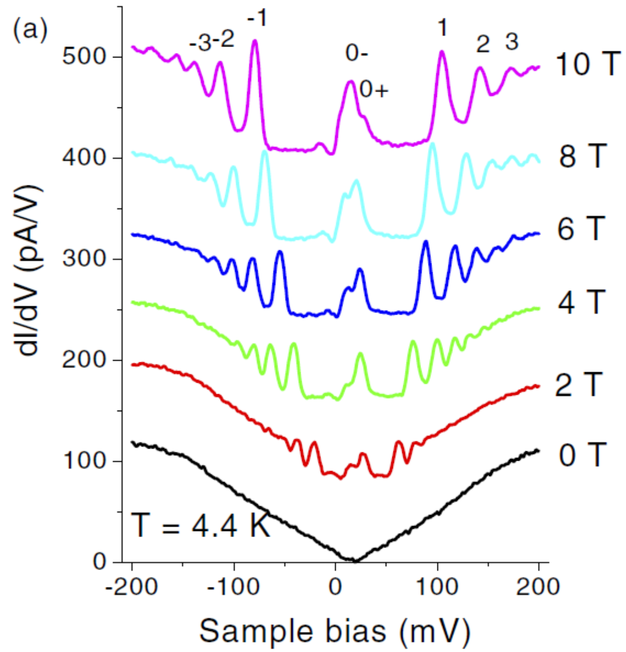
$$E_N = \hbar v_F q_F = \pm\sqrt{2e\hbar v_F^2 B|N|}, \qquad N = 0, \pm 1, \ldots \qquad \sigma_{xy} = 4(N + 1/2)\frac{e^2}{h}$$

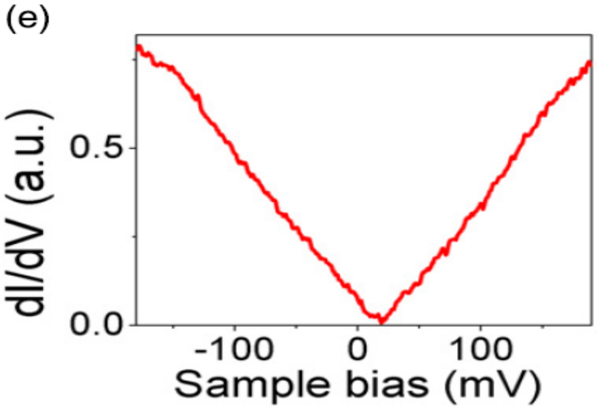
Hall effect of Graphene

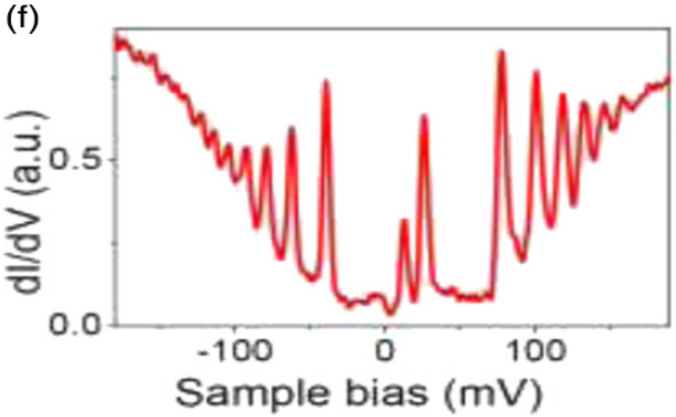
(d)



B= 4T, 4.2K

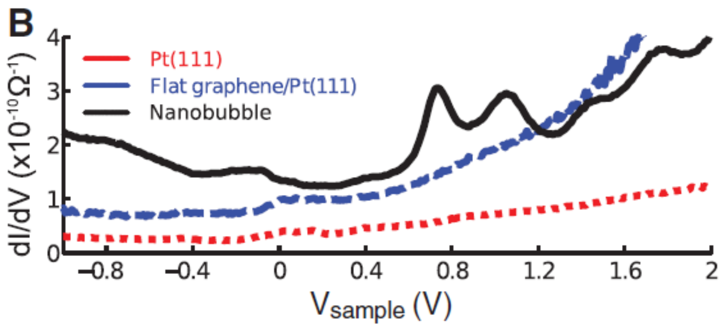


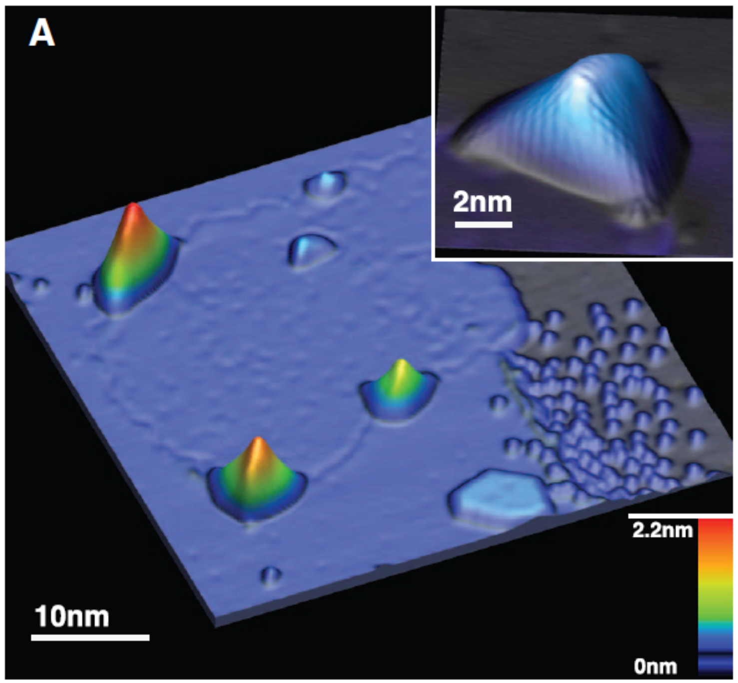


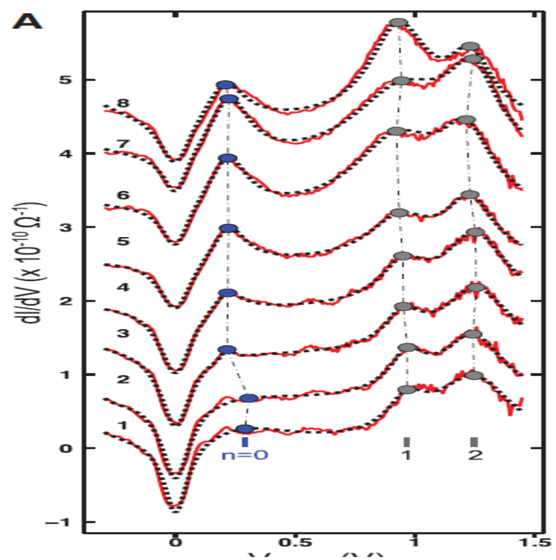


Electronic property of graphene

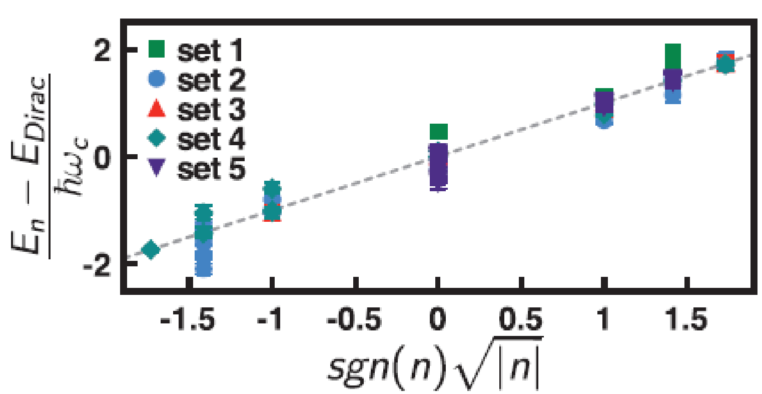
- Landau levels (strain-induced huge pseudo magnetic field)





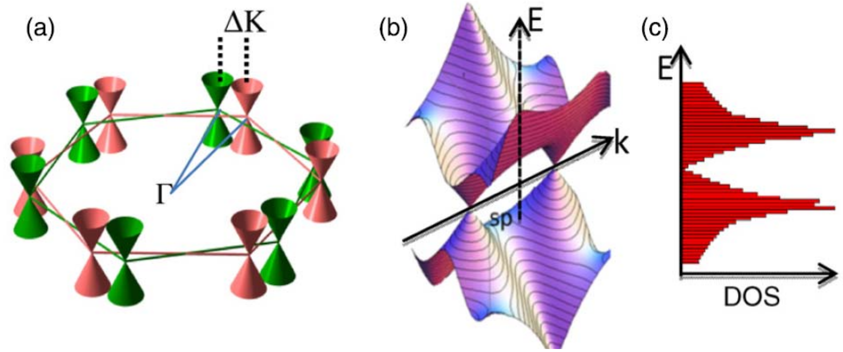


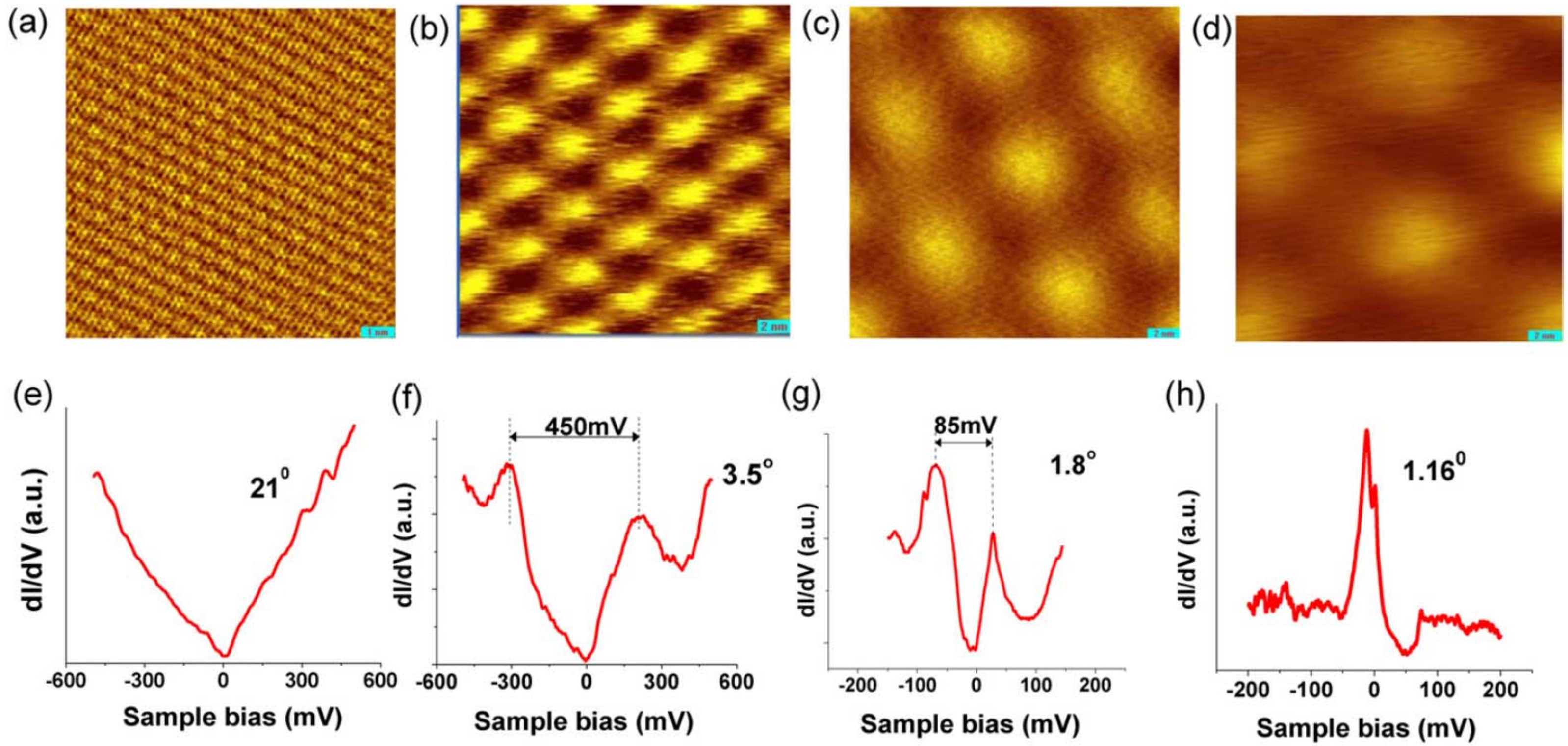
Over "300 T" effectively



Electronic property of graphene

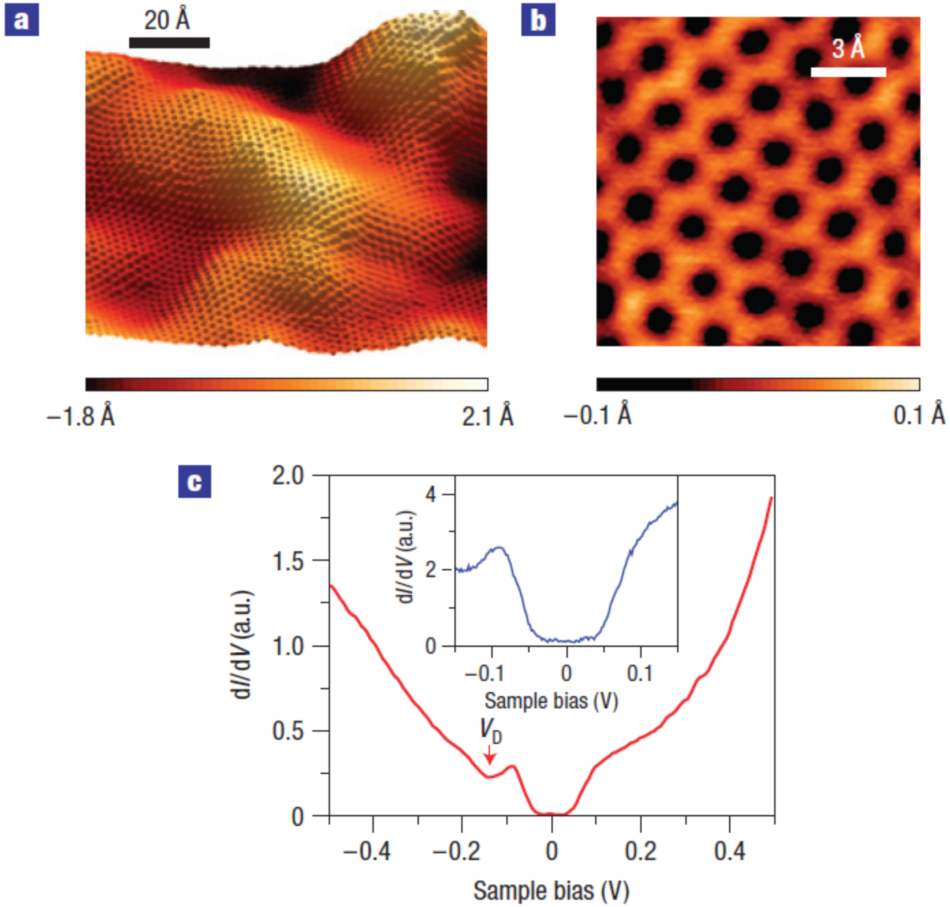
- Van Hove singularity

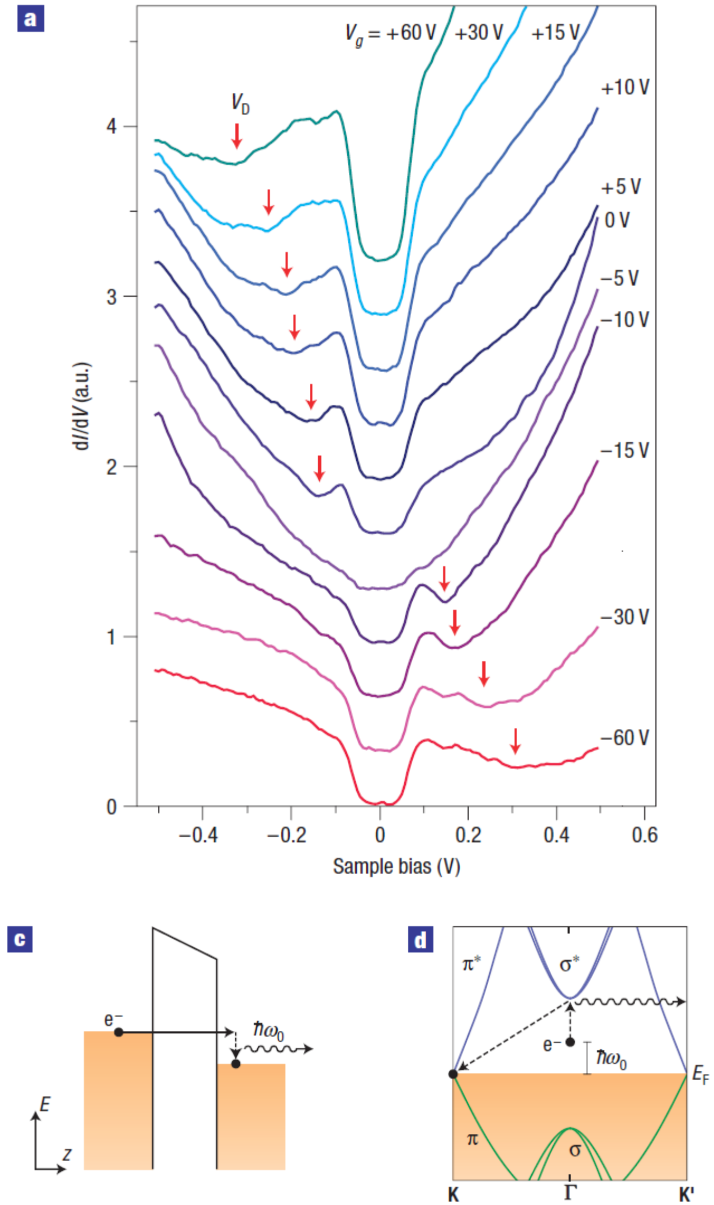




Scanning tunneling spectrum of graphene

- Phonon-assisted tunneling

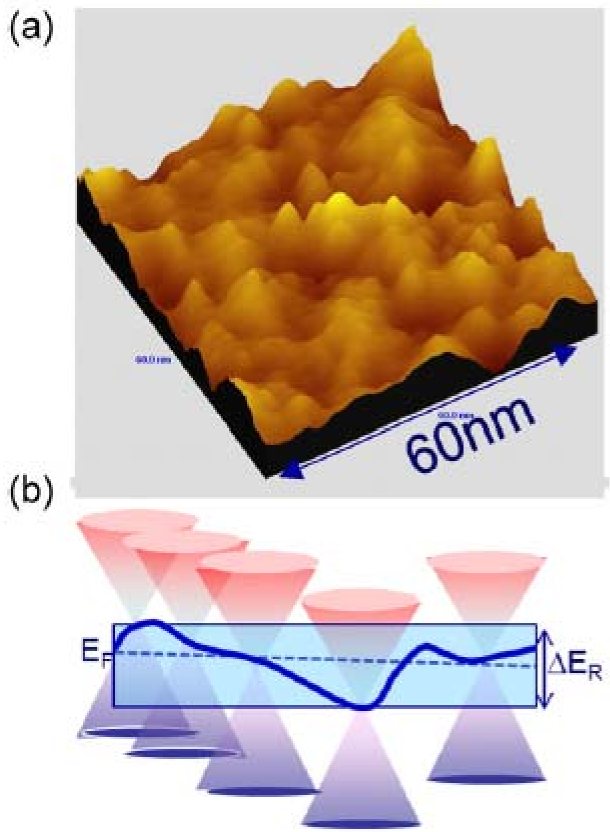




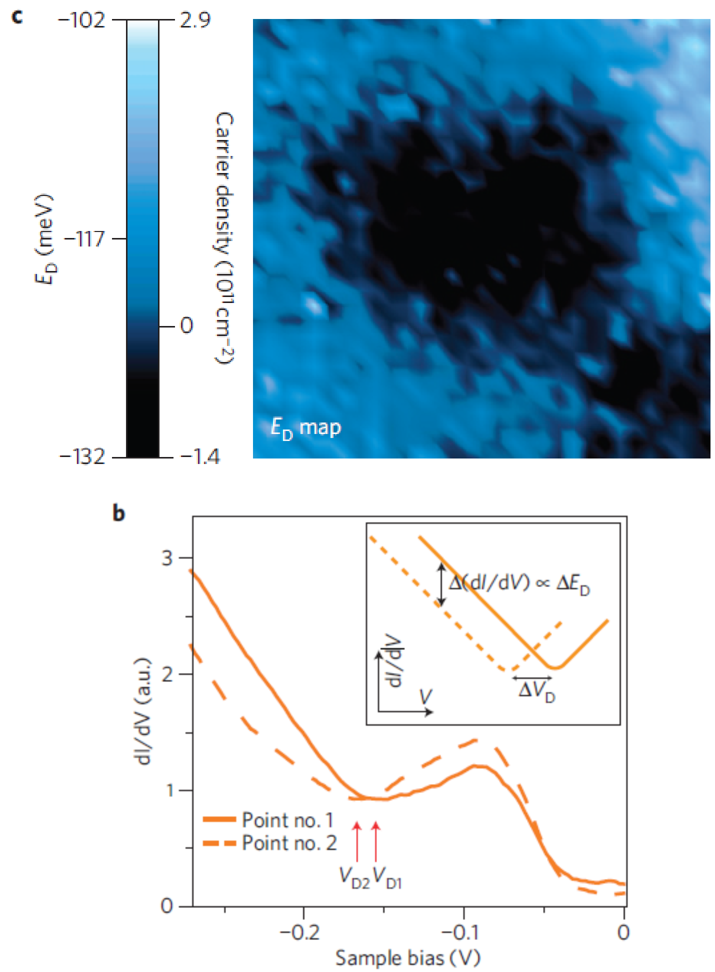
Electronic inhomogeneity (graphene with external potential, due to charges etc.)

Graphene on substrates (e.g., SiO2 etc.)

Electron-hole puddles/ local gating

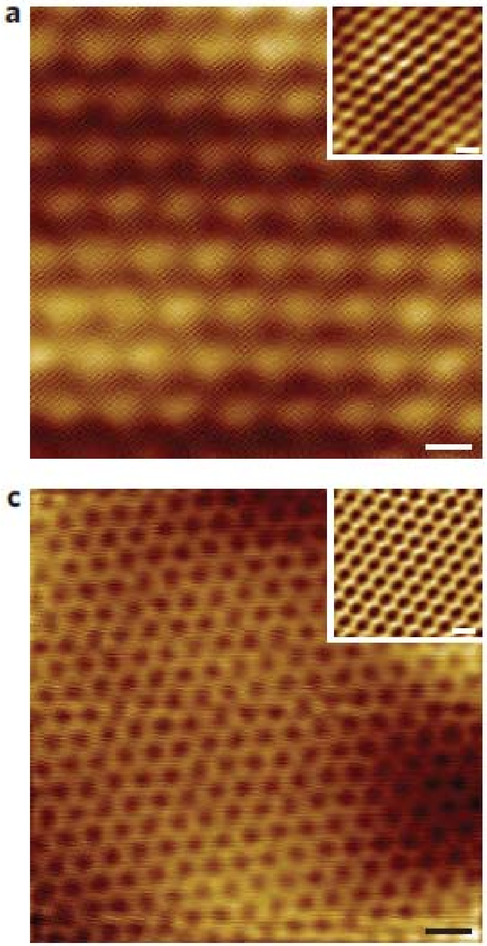


Variation of Dirac point energies

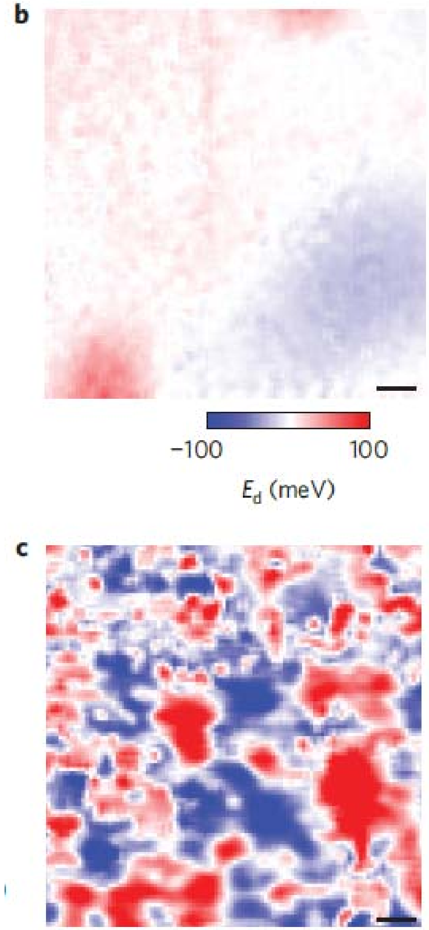


Electronic property of graphene

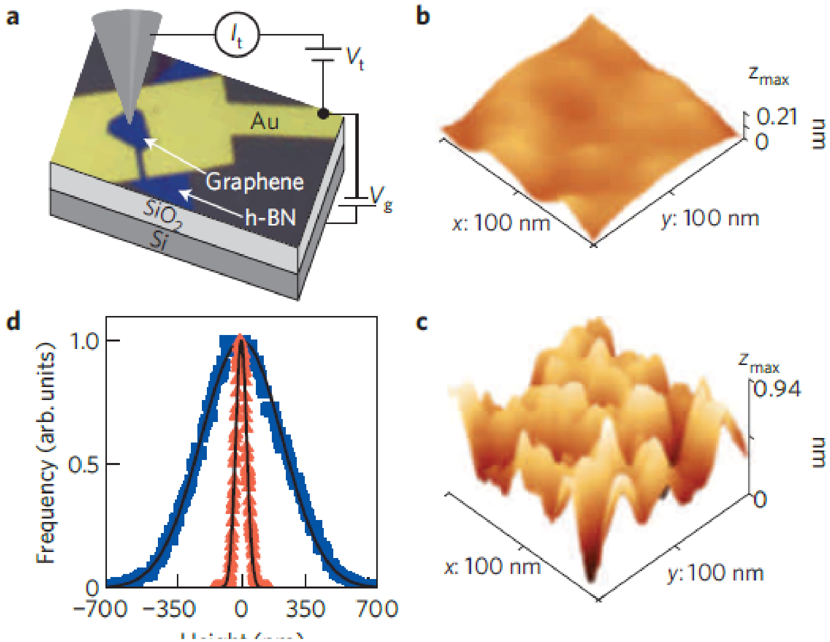
- Elimination of electronic inhomogeneity → using a flat and “charge-free” substrate, BN



Topography (Moire)



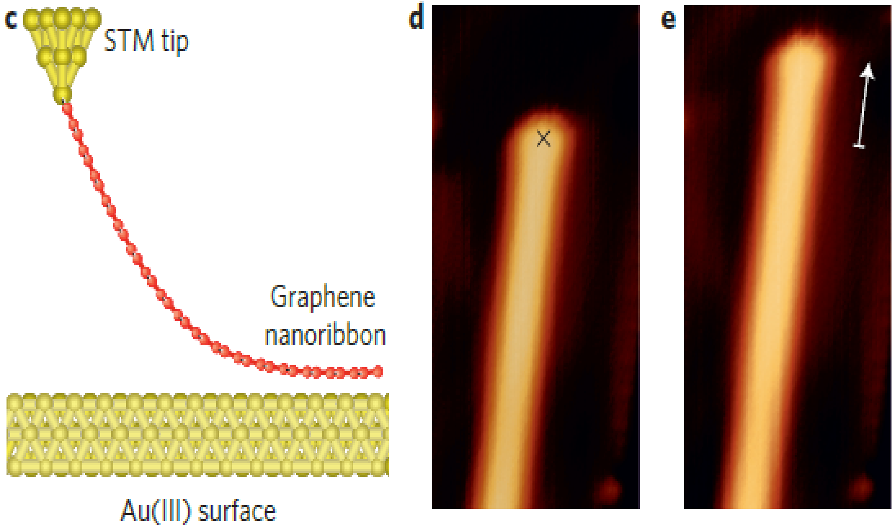
Dirac point variation
(top: G/BN, below: G)

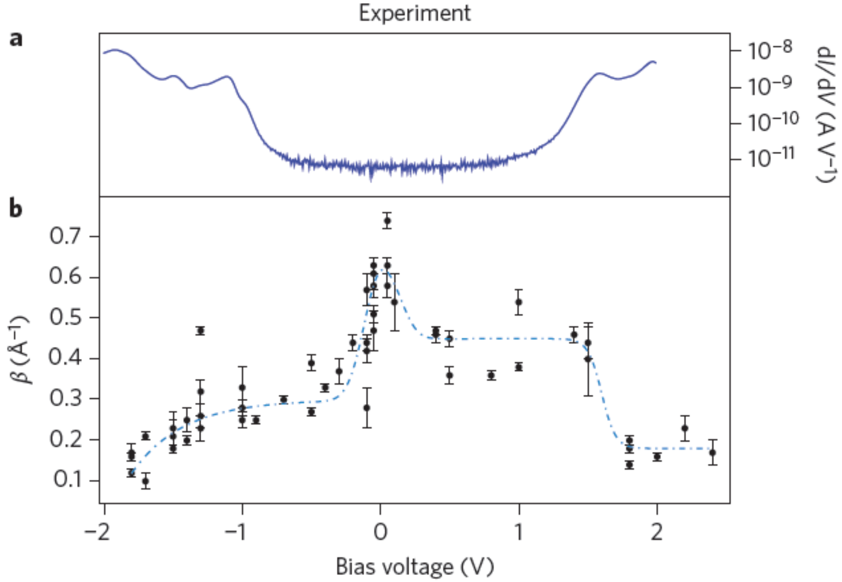


Sample preparation

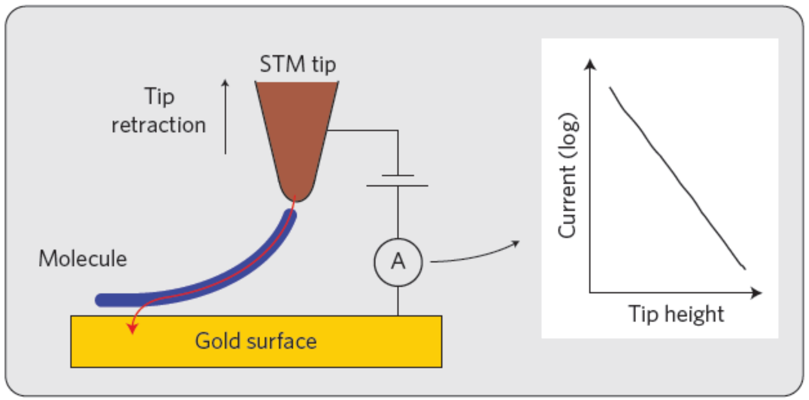
Electronic property of graphene

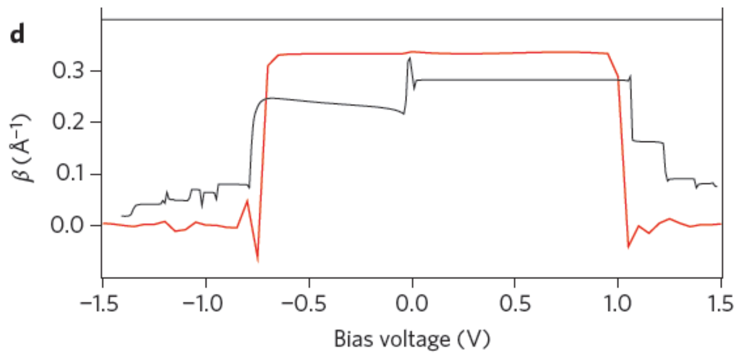
- Direct measurement of a graphene nanoribbon, “pick up” graphene





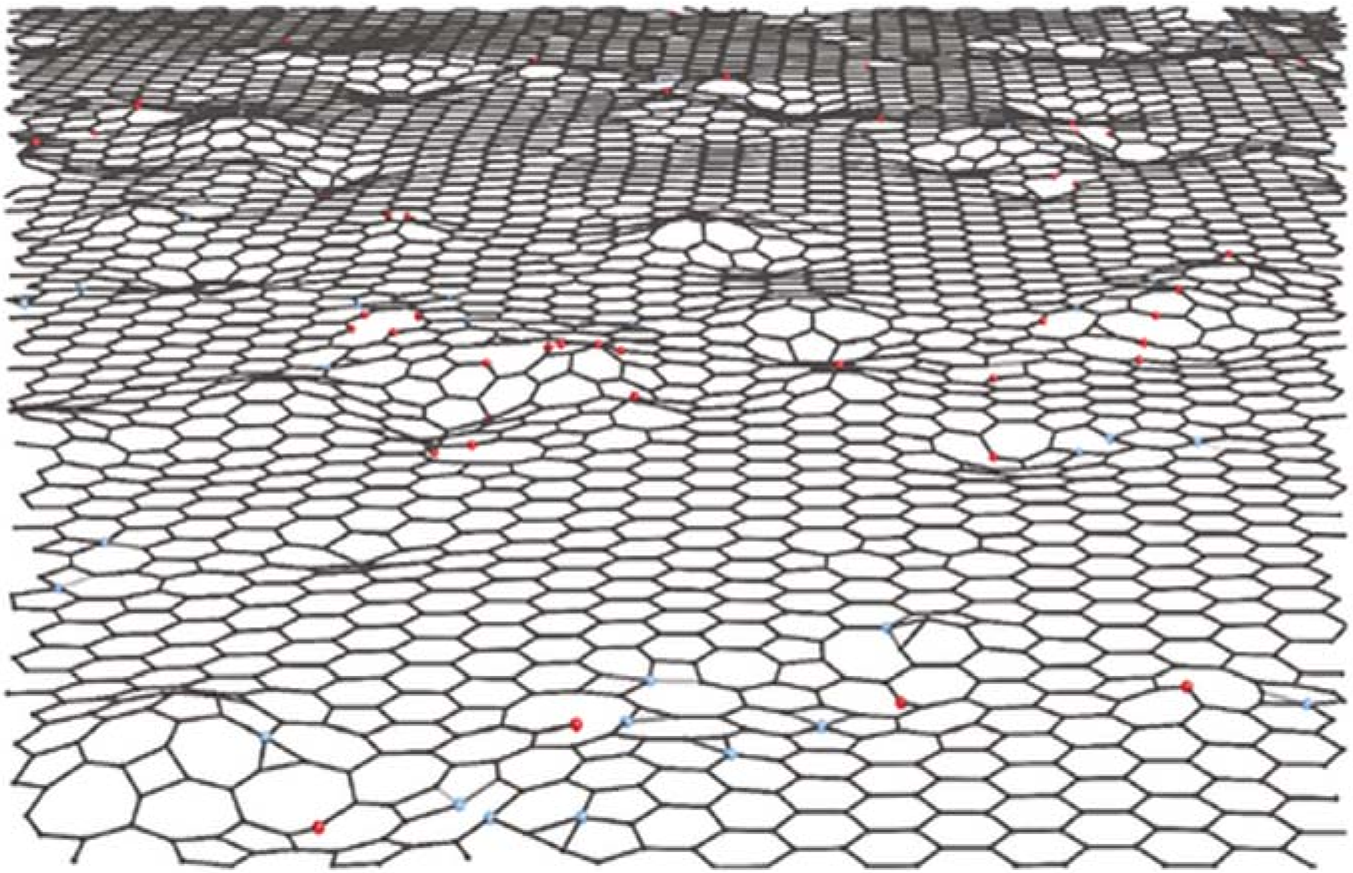
exp





theory

Defected graphene



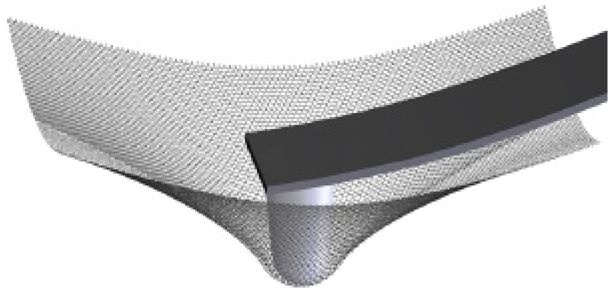
In contrast to pristine graphene, the highly defective sp^2 carbon sheets exhibit a high density of states at the charge neutrality point raising challenging questions concerning the electronic transport of associated charge carriers.

Much remained to be done, in terms of microscopy

Mechanical properties

- High Young's modulus (~1,100 Gpa)
High fracture strength (125 Gpa)

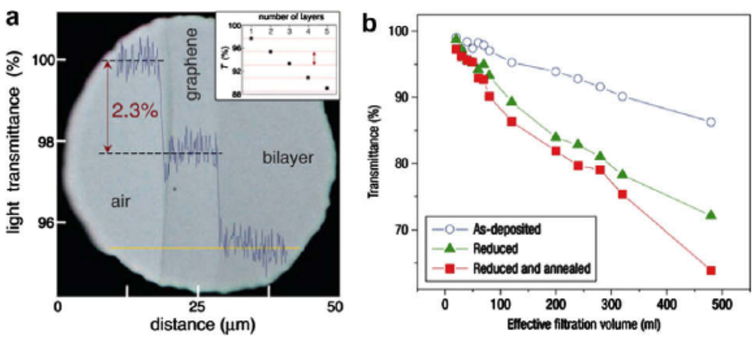
- Graphene is as the strongest material ever measured, some 200 times stronger than structural steel



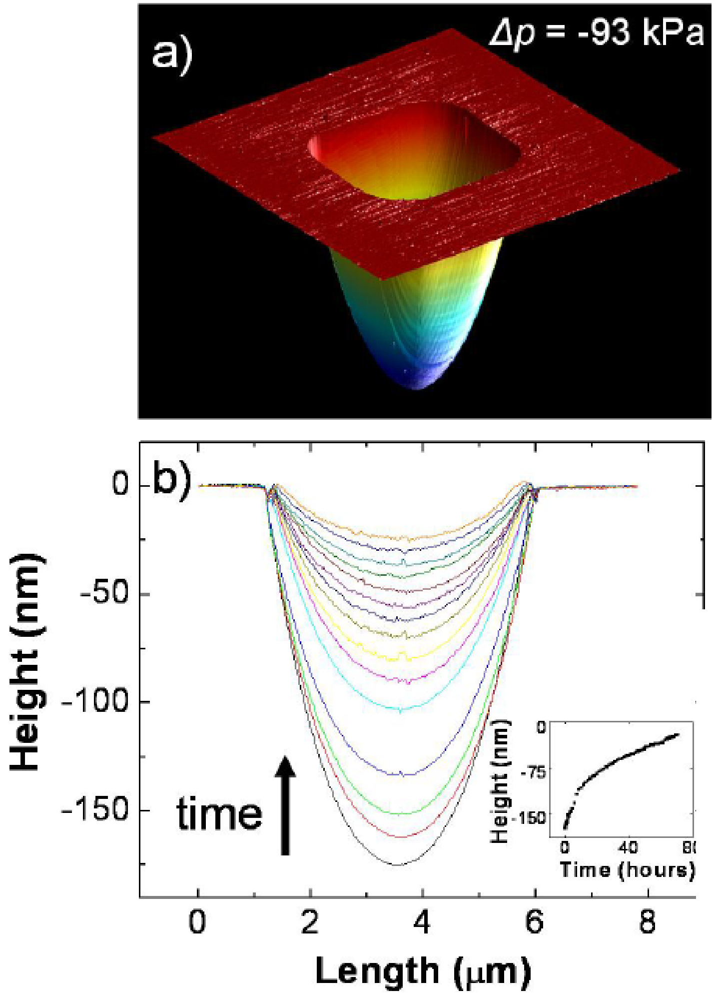
A representation of a diamond tip with a two nanometer radius indenting into a single atomic sheet of graphene *(Science*, **321** (5887): 385)

Optical properties

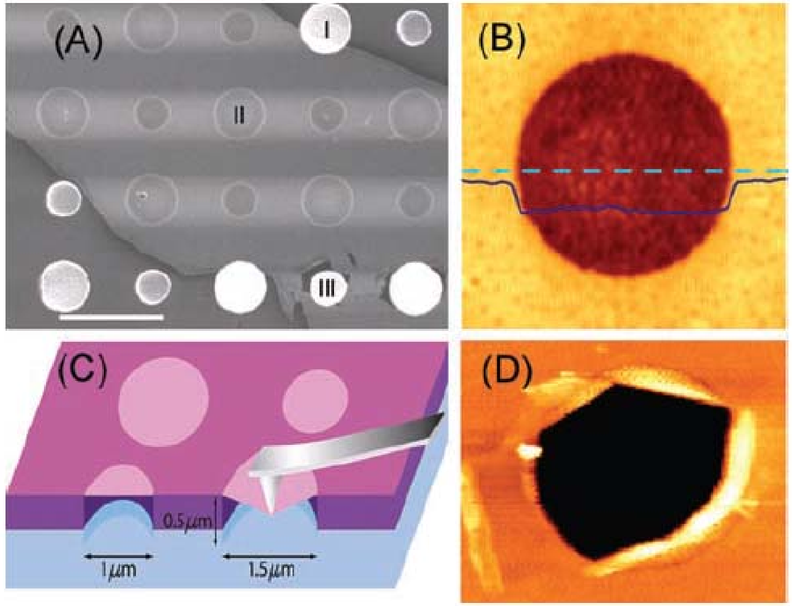
- Monolayer graphene absorbs $\pi\alpha \approx 2.3\%$ of white light (97.7 % transmittance), where α is the fine-structure constant.

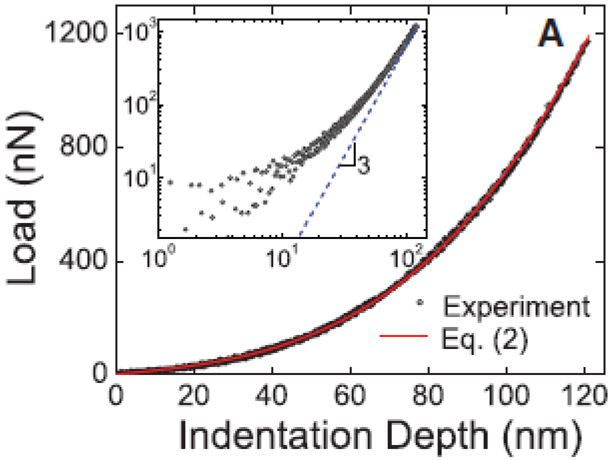


Mechanical property of graphene
-flexible yet very strong



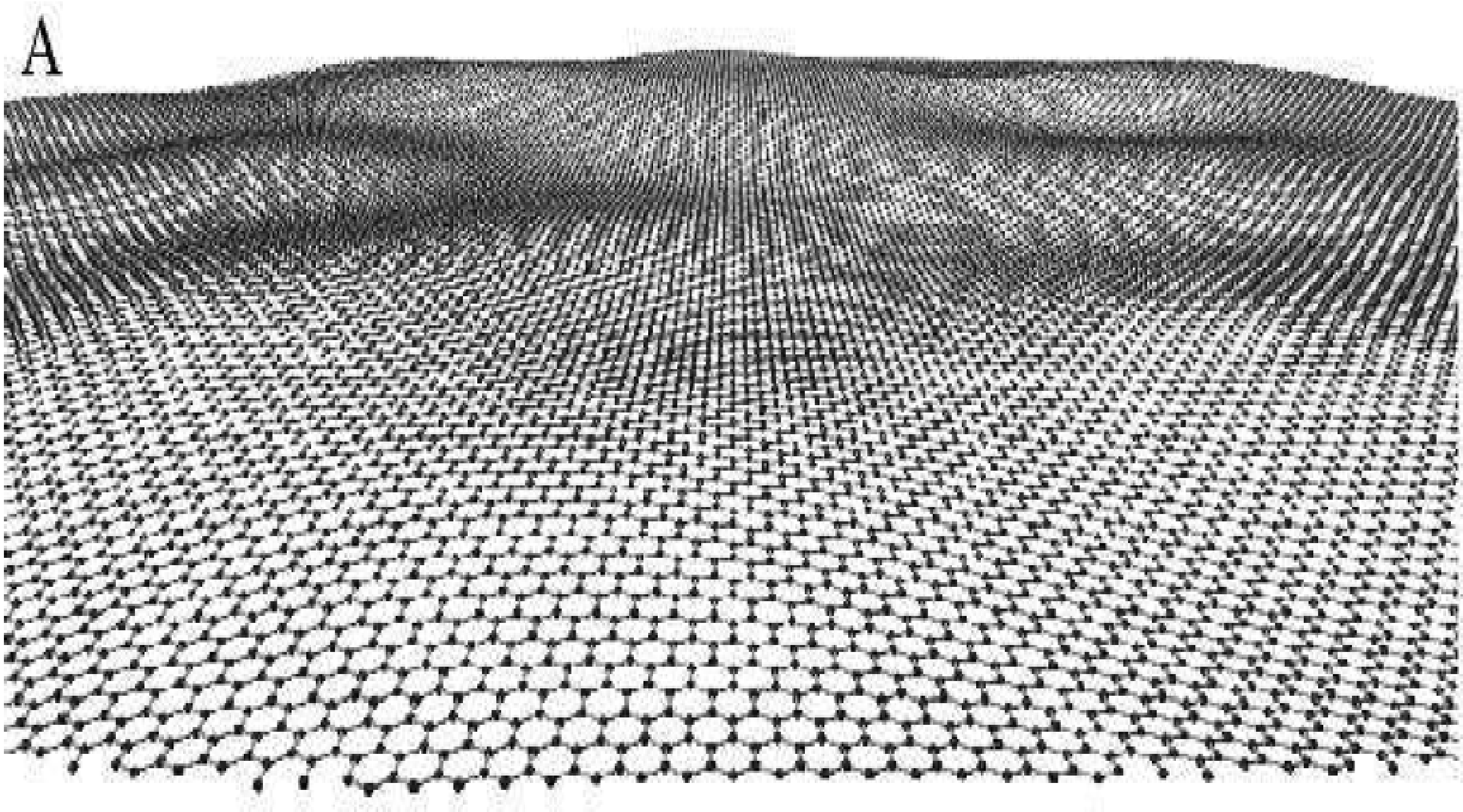
Impenetrable to almost all gases



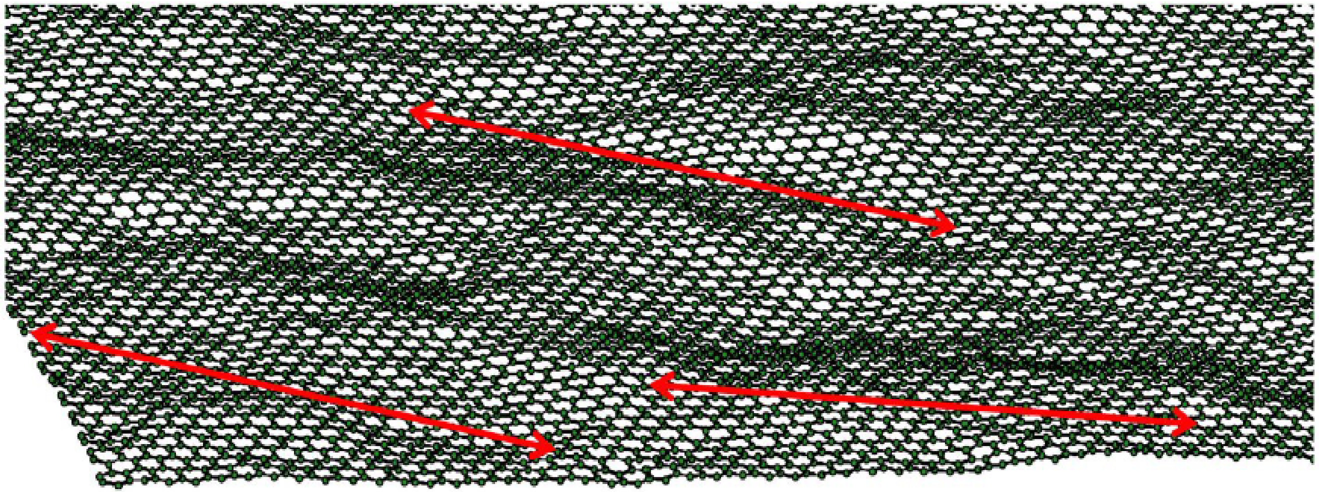


The breaking strength is 42 N m^{-1} and represents the intrinsic strength of a defect-free sheet. These quantities correspond to a Young's modulus of E = 1.0 terapascals

Crumpling of graphene sheet – the main source of disorder.



Lattice effects: Ripples in graphene

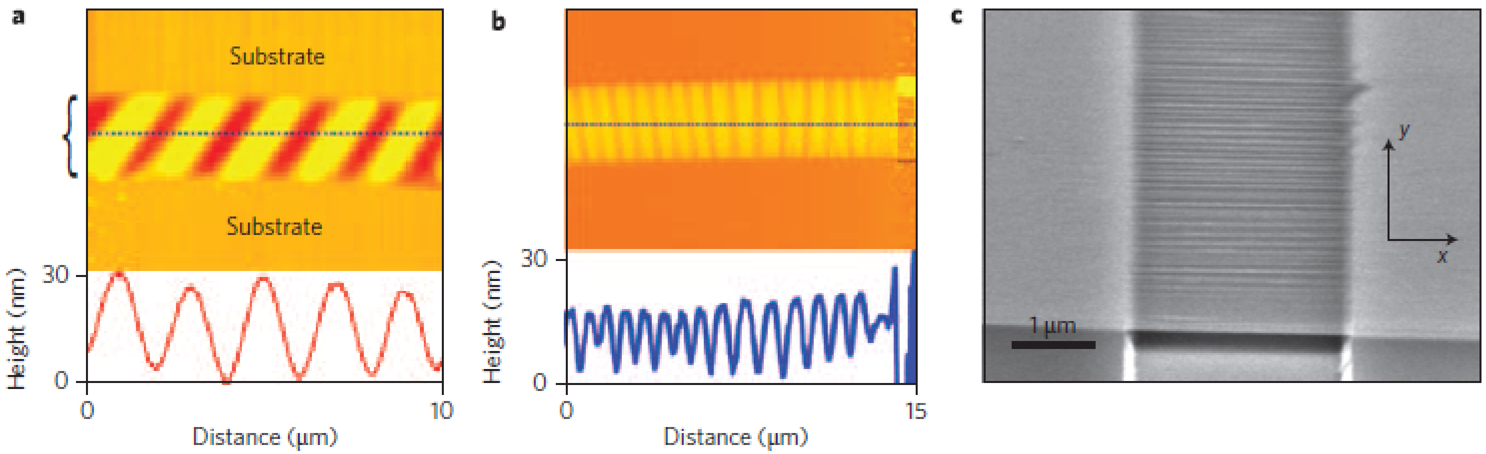


A typical snapshot of graphene at room temperature. The size of height fluctuations is comparable to the lattice size.

2D membranes embedded in 3D space have a tendency to get crumpled.
These dangerous fluctuations can be suppressed by an anharmonic coupling between bending and stretching modes. Result: the membranes can exist, but with strong height fluctuations.

Monte Carlo simulations (Katsnelson et. al. (2007)): disordered state with weakly T-dependent correlation length (70A at 300K and 30A at 3500K).

Ripples on graphene (micron and nano scales)



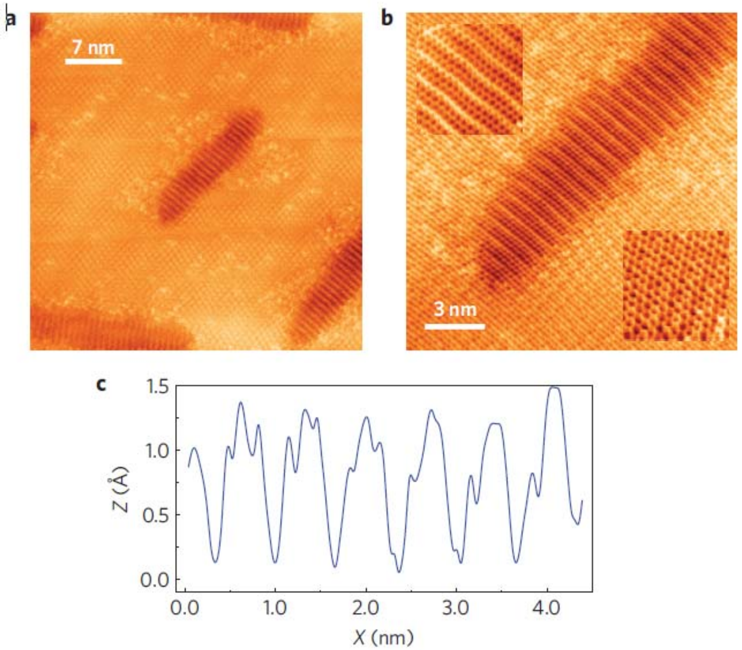
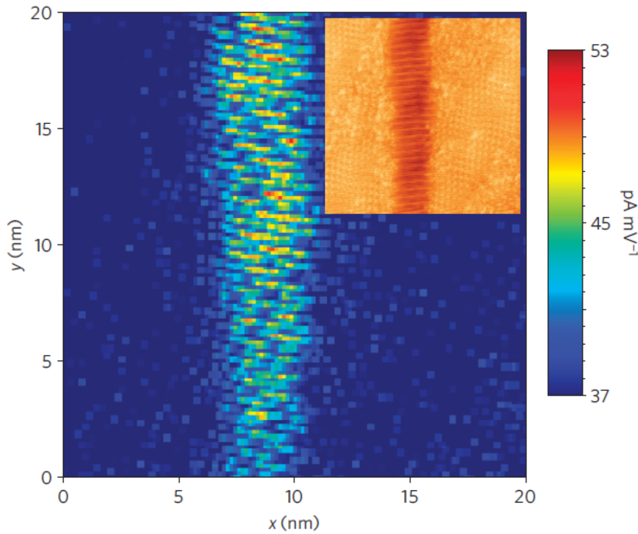


Figure 2 | Atomic-resolution STM images of graphene nanoripples.

Graphene grown on Cu(111)



STS: ripples affect electronic property

Figure 4 | Local electronic density of states map of graphene nanoripples. Spatially resolved differential tunnelling conductivity map (plotted at $U_{bias} = 48$ mV) exhibiting the periodic modulation of the local density of

Graphene functionalization

Functionalization of graphene: for the purposes in the areas of polymer nanocomposites, super-capacitor devices, drug delivery systems, solar cells, memory devices, transistor devices, biosensors etc.

- Covalent

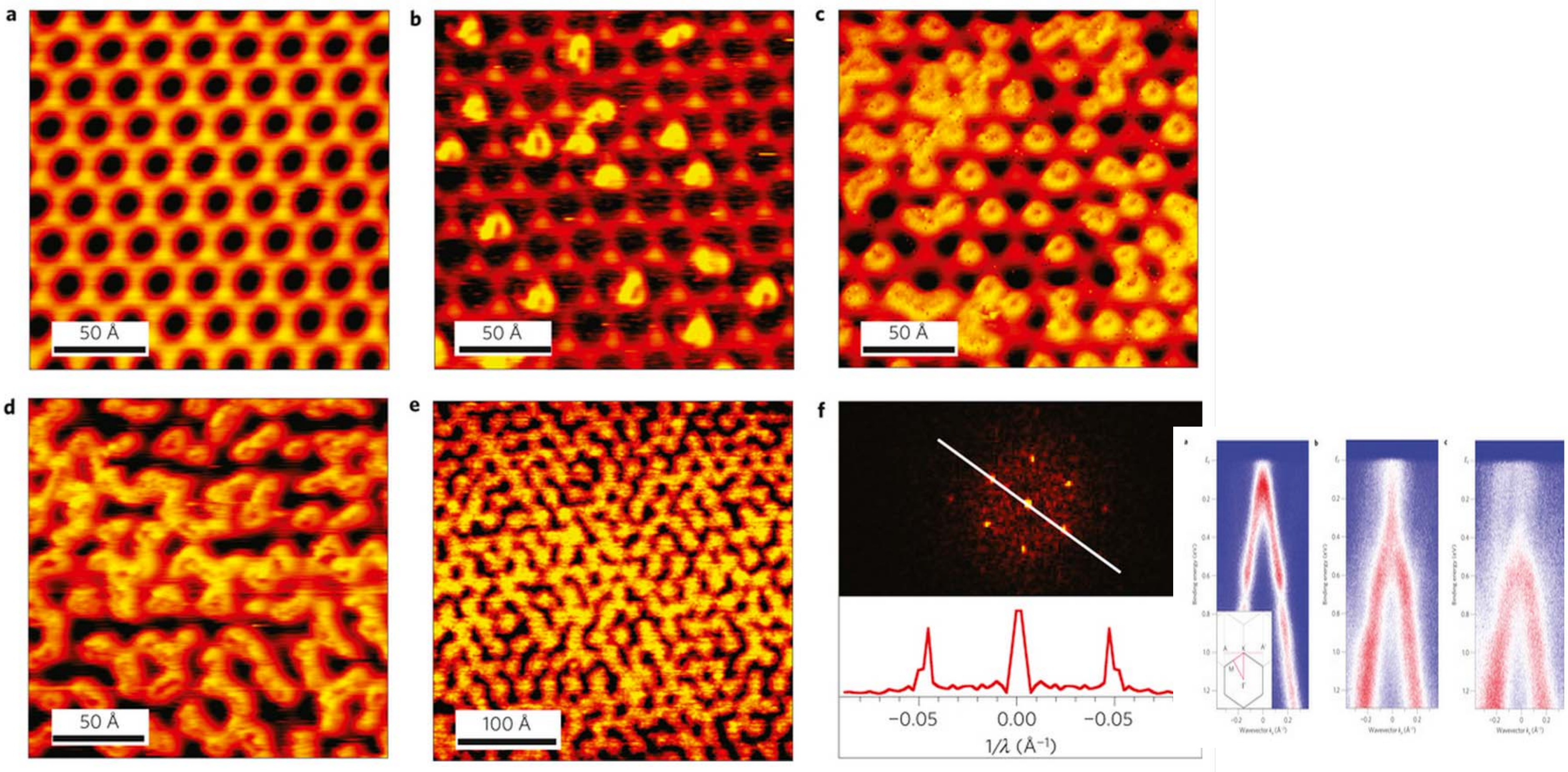
-OH, -COOH, -NH2, -O-, -H, -N etc

Non-covalent

Pi-pi interaction, vdw, hydrogen bonding, electrostatic etc.

Graphene functionalization (simple atomic species)

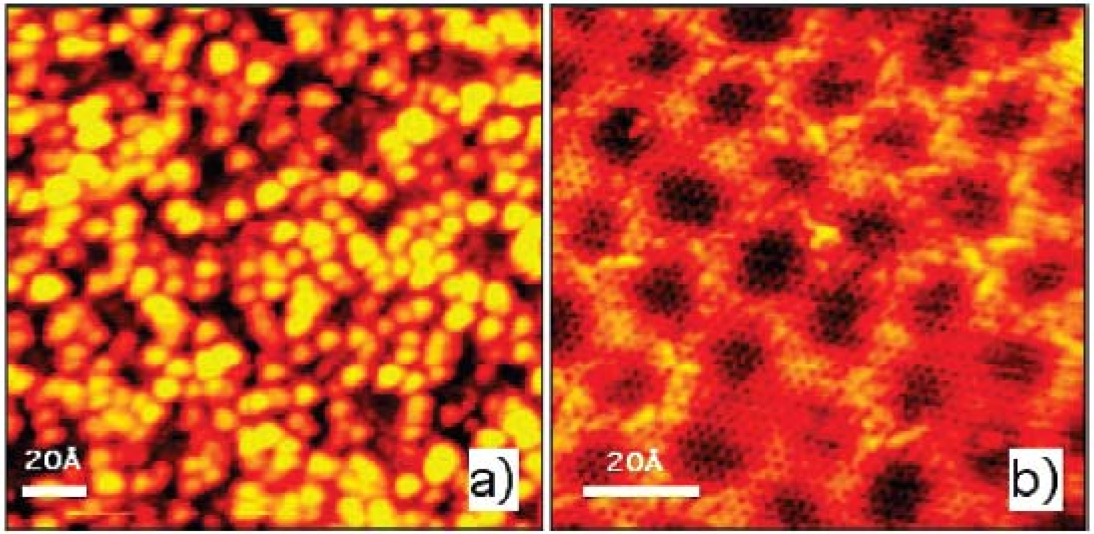
- H: graphane



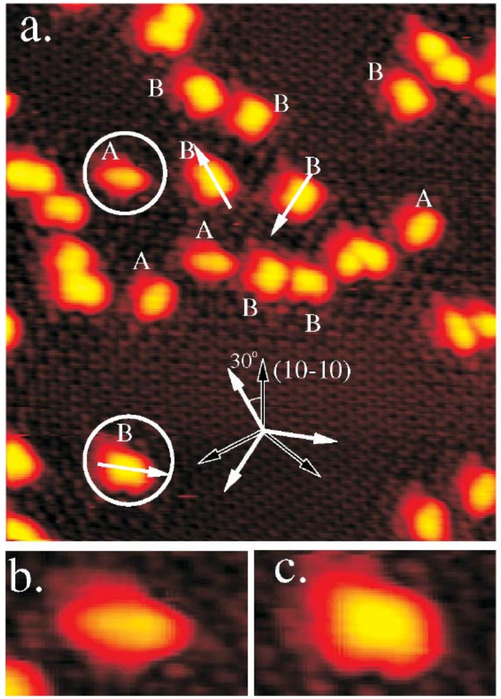
Patterned H adsorption on G/Ir(111) → band gap opening

Graphene functionalization (simple atomic species)

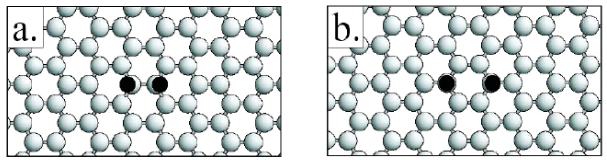
- H: graphane



Patterned H adsorption on G/SiC



H on HOPG

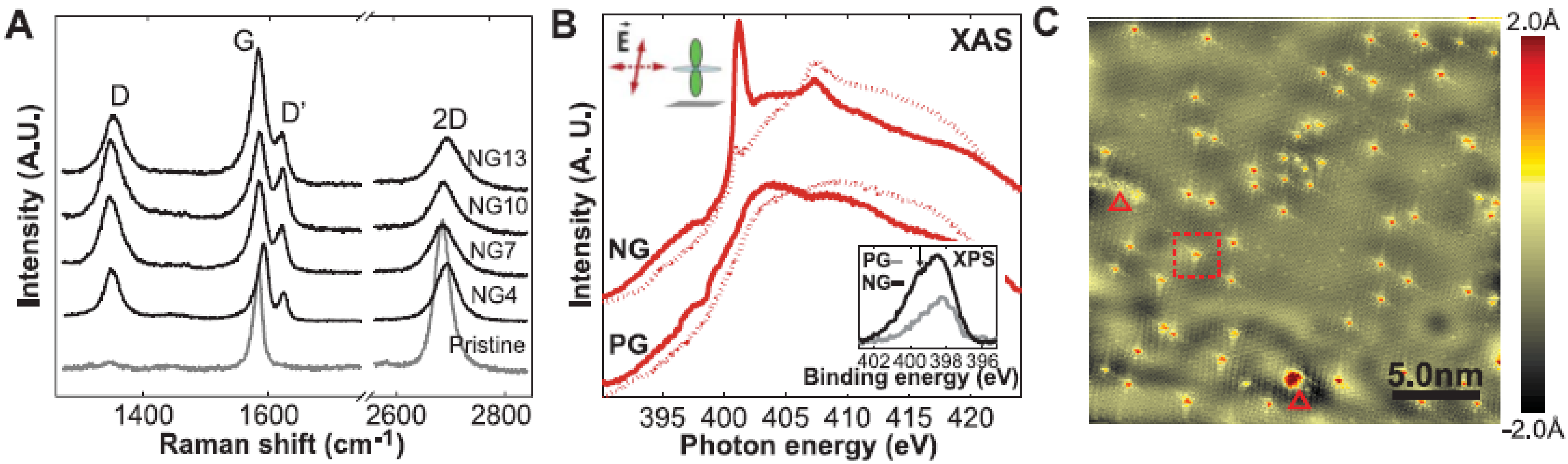


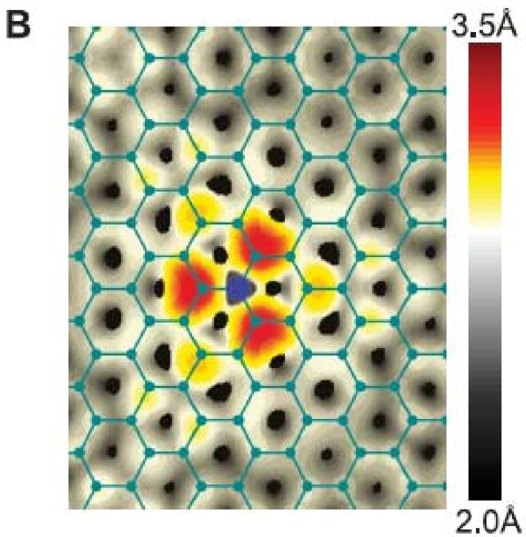
Pretty disordered
→ Due to single-side adsorption, geometric structure frustration

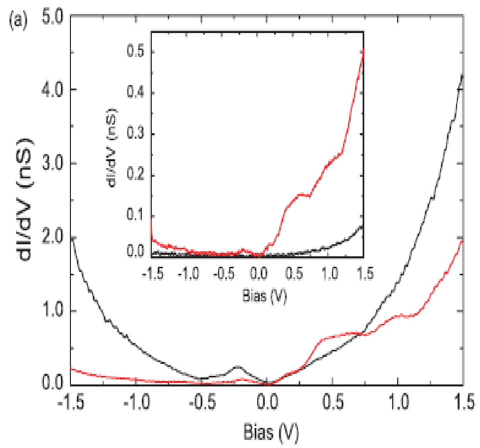
How to form ordered structure?
→ double-side adsorption → forming graphane? (Not done yet)

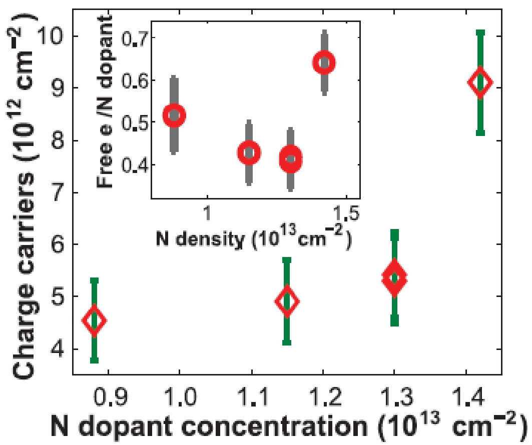
Graphene functionalization (simple atomic species)

- N-doped graphene: useful as an oxygen reduction reaction catalyst



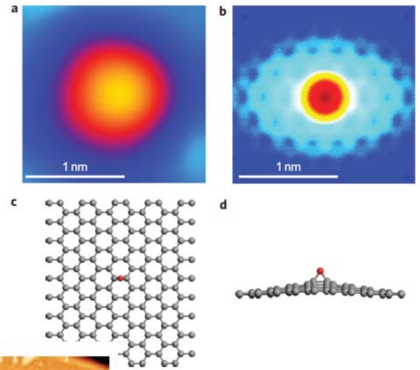


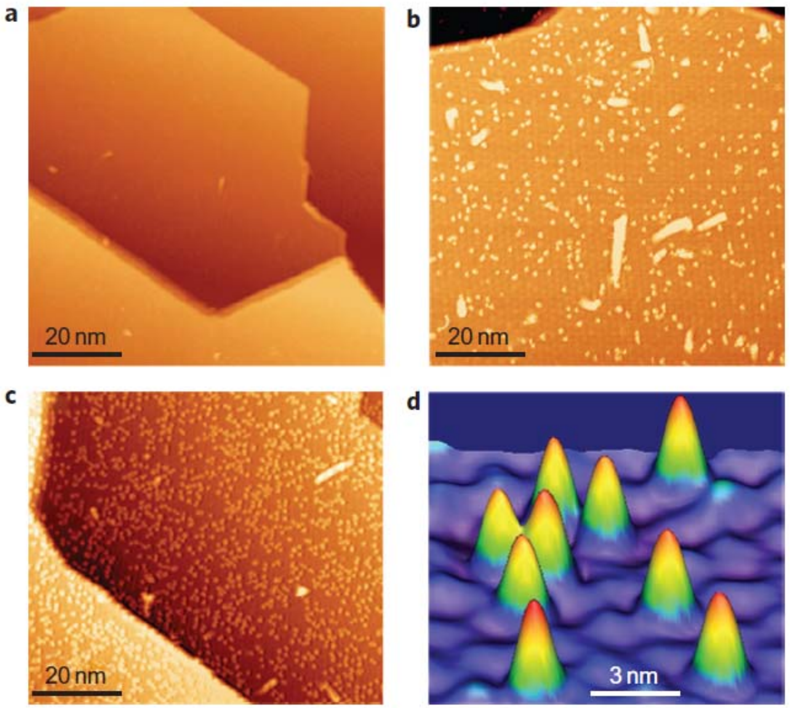


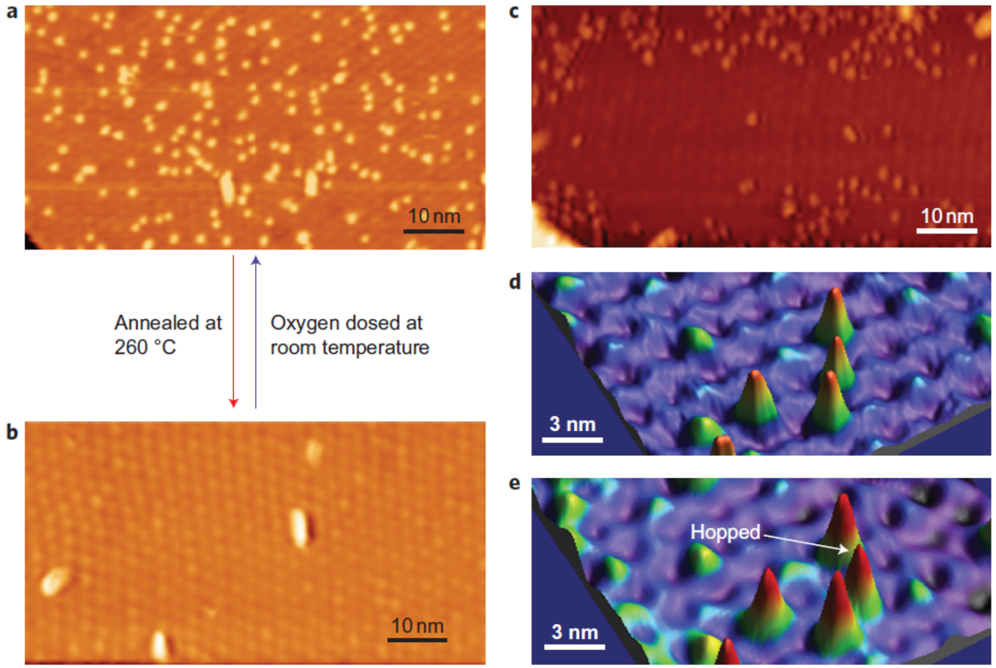


Graphene functionalization (simple atomic species)

- -O-: epoxide group







On SiC, reversible ; Atomic O in UHV

Temperature and tip-induced desorption of O

Graphene functionalization (simple atomic species)

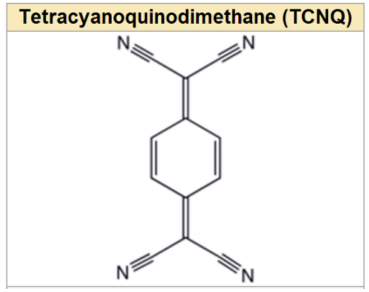
- Some others that should be characterized:

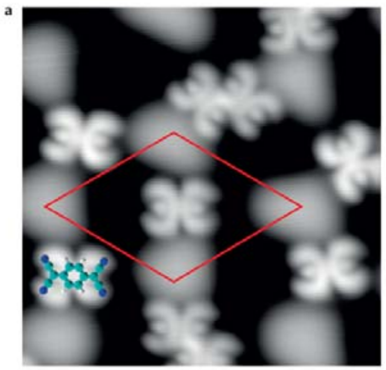
B, P, F, and metals

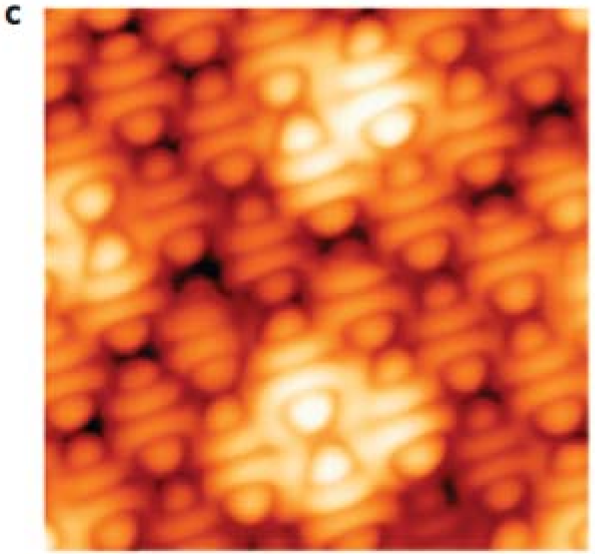
More to be done here.

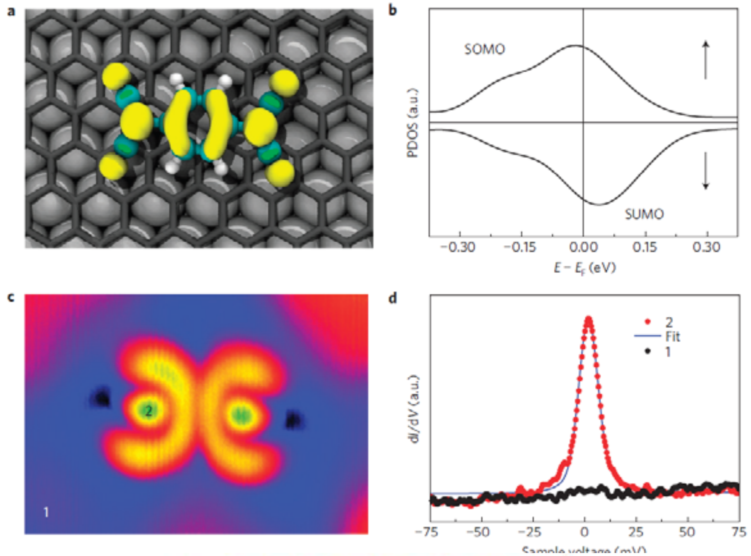
Graphene functionalization

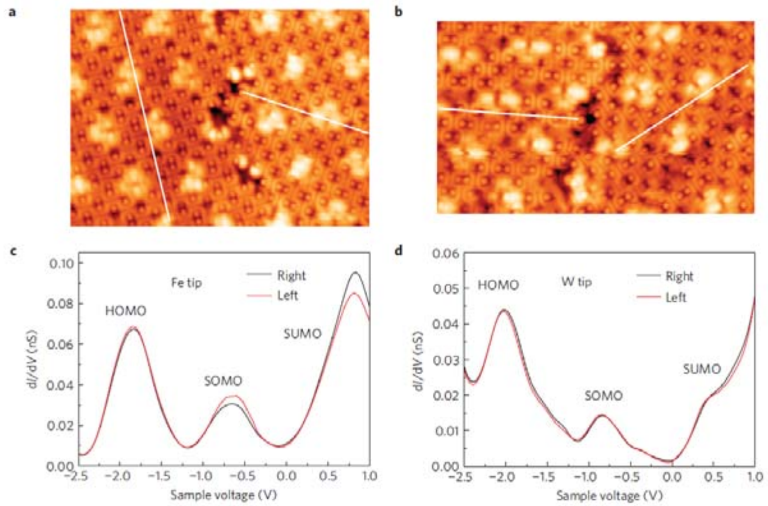
- Magnetic flavor : A magnetic molecular overlayer







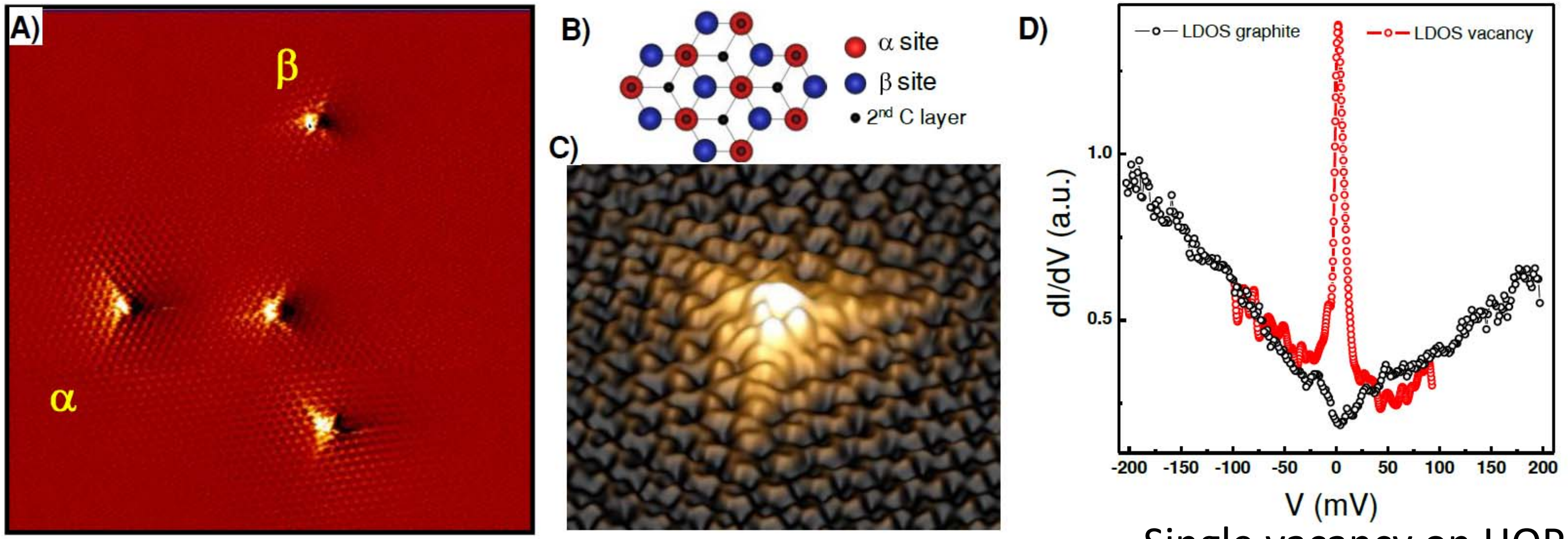




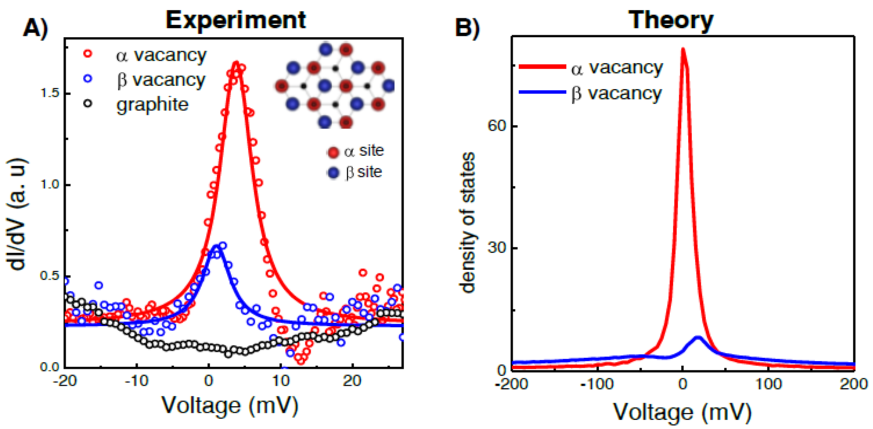
Herewe showthat isolated TCNQ deposited on graphene epitaxially grown on Ru(0001) acquire charge from the substrate and develop a magnetic moment of 0:4 B per molecule. The magnetic moment survives even when the molecules form into a dimer or a monolayer, with a value of 0:18 B permolecule for the monolayer.

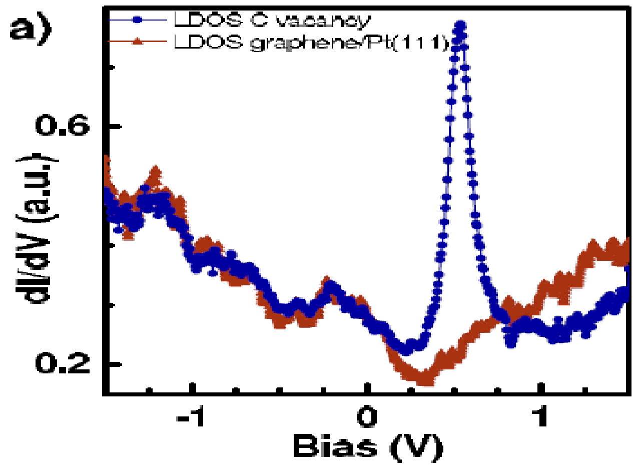
Graphene with magnetism

- Magnetic flavor: Magnetic moments from structural defects or adsorbates



Single vacancy on HOPG

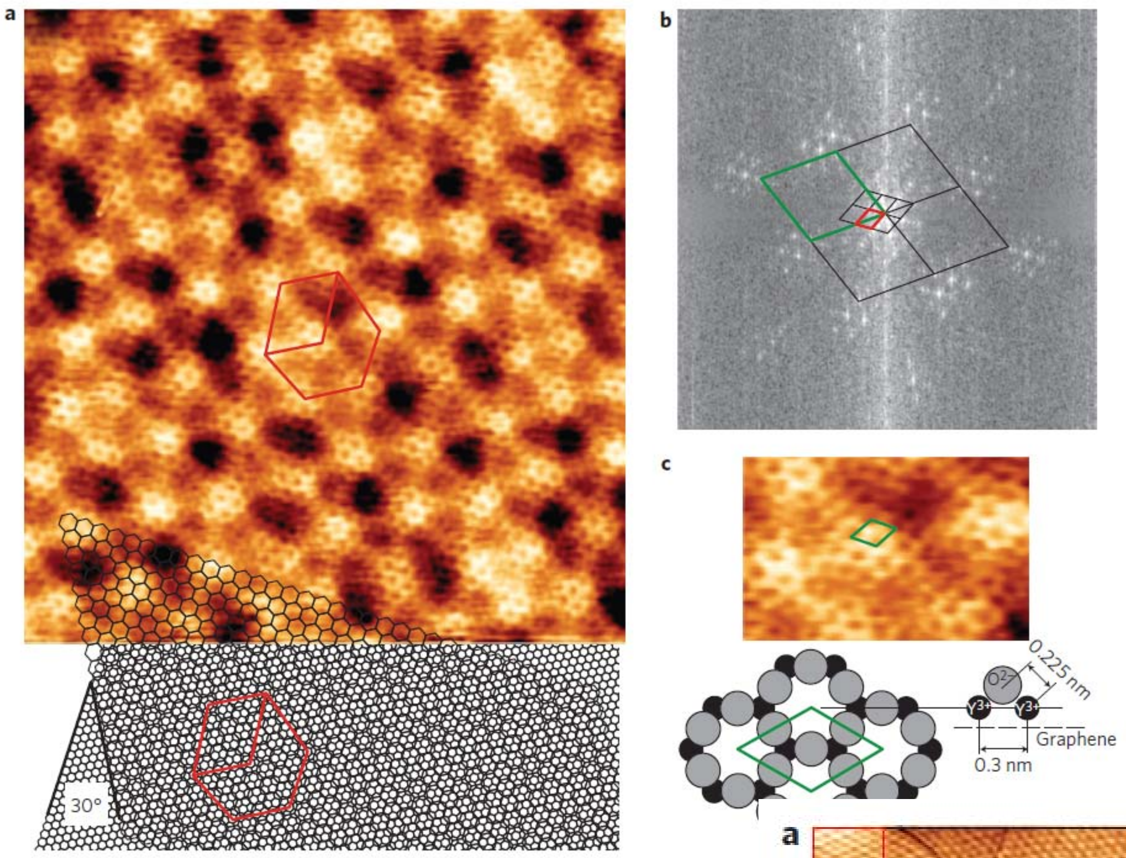


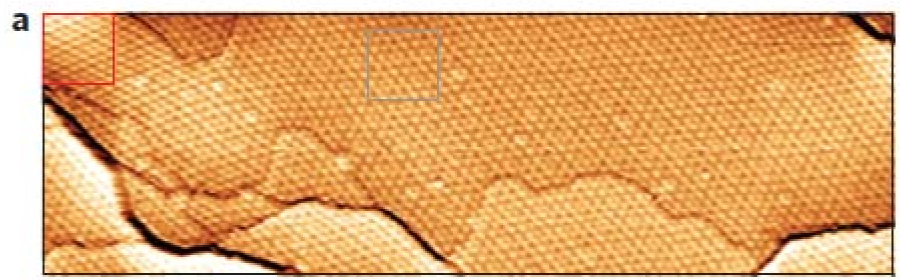


Similarly, on G/Pt(111)

- **Graphene covered with dielectrics** (important for future devices)

  yttria (Y_2O_3)—a high-k dielectric—can form a complete monolayer on platinum-supported graphene. Possibly works for other metal supports too .





Graphene functionalization via intercalation

- GIC (graphene intercalated compounds): superconductivity etc..
- Imaging of molecules under graphene

conclusion

- Interest in graphene (and other 2D materials, e.g., MoS2 etc.) remains strong.
- Good STM experiments on graphene are not easy.
- STM (SPM)/TEM gives unprecedented microscopic details of 2D materials. STM is particularly suited for studying low energy excitation phenomena
- There remain many new possibilities for STM studies of graphene (defects and its effect, double-side adsorption, nano transport, strain effect etc..)