

Outline

- 1- Graphene: a single layer of carbon atoms
- 2- Why graphene can be a revolution for future technology?
- 3- The roadmap of the graphene flagship



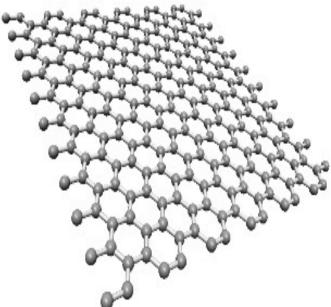
4-Graphene for the future technology: few examples

5-Is it easy to grow graphene?

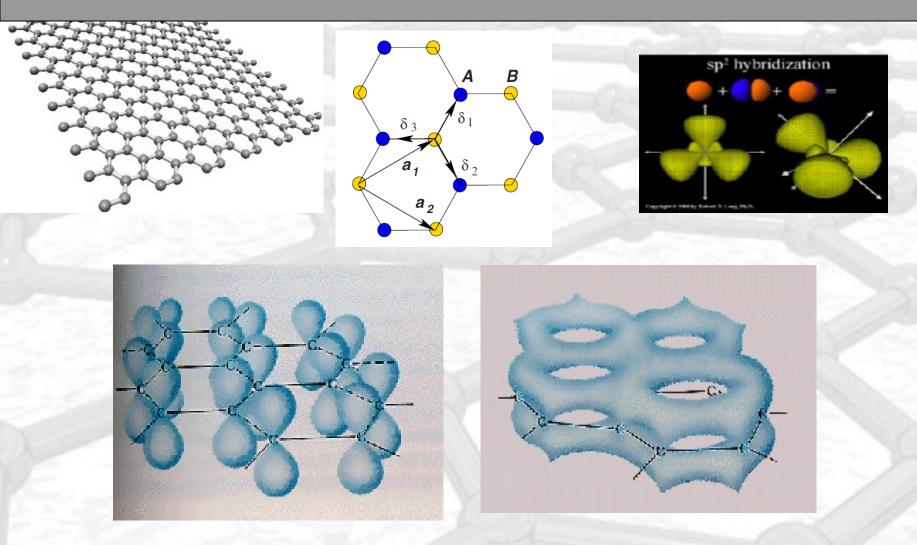
6-How to control and design the graphene properties?

7-Three examples:

- i) graphene: metal or semiconductor?
- ii) graphene a buffer layer for spintronics
- iii) graphene for energy storage and Li batteries

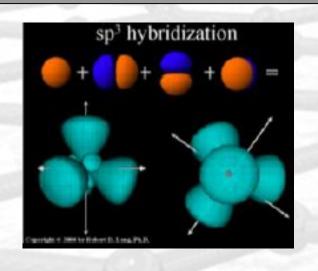


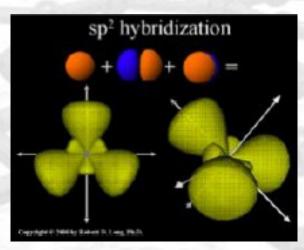
Graphene: a single layer of carbon atoms

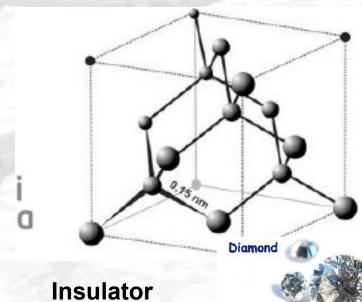


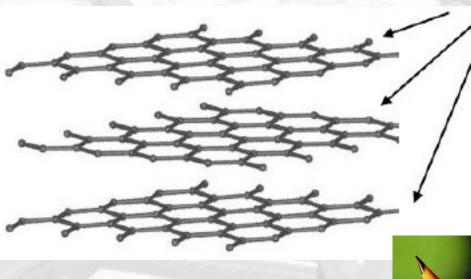
3 electrons to bind to other 3 atoms and keep one to share with everybody: METALLIC STATE and GOOD CONDUCTOR IN THE PLANE

Hybridization of carbon atoms



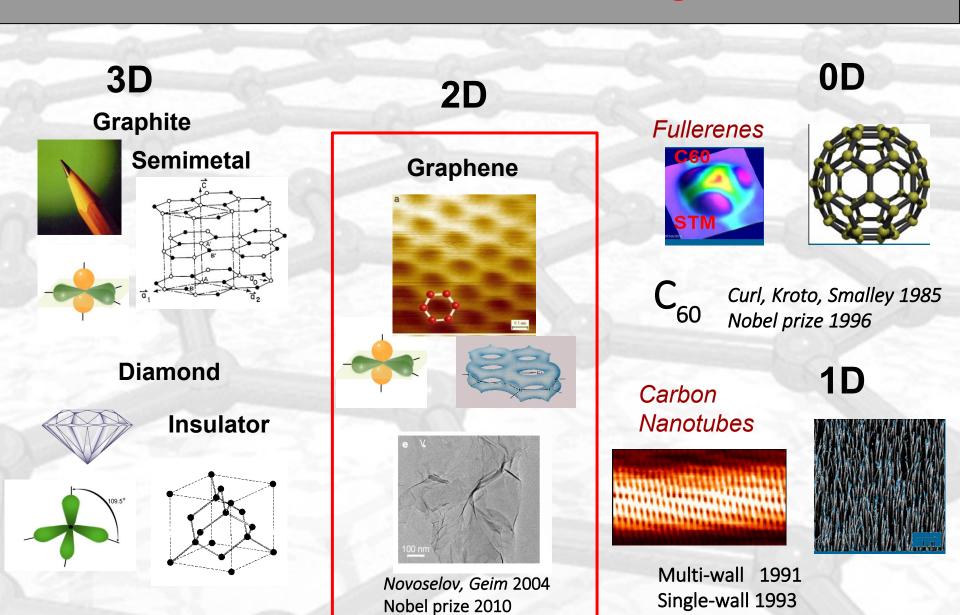






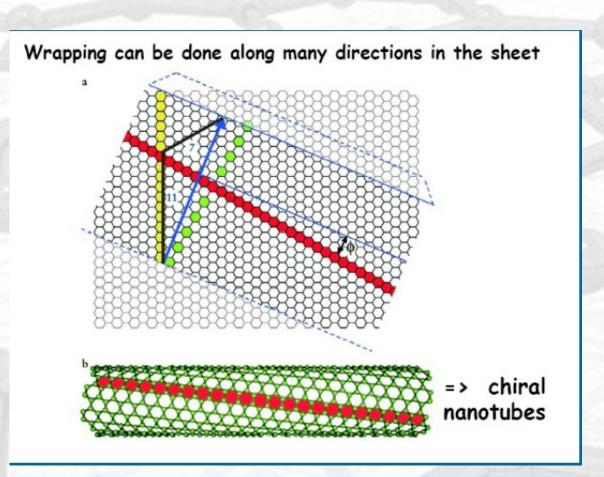
SemiMetal

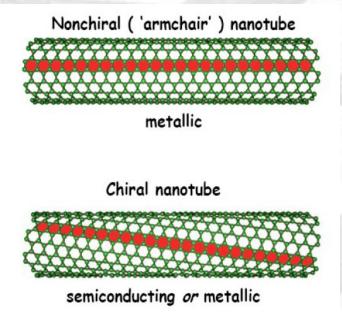
Carbon: OD, 1D, 2D and 3D configurations



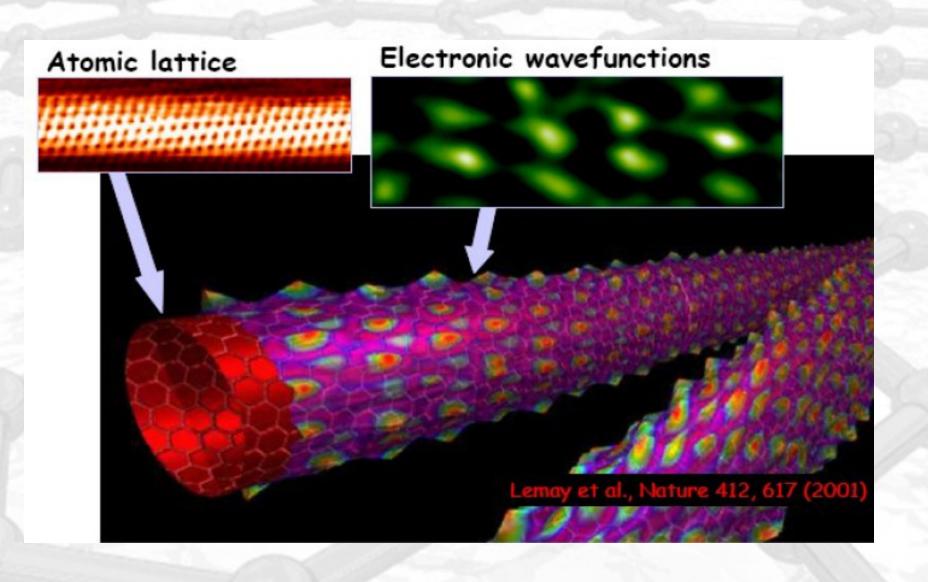
Metal or semiconductor

Carbon nanotubes: metallic or insulator?





Carbon nanotubes: metallic or insulator?



Why graphene for the future technology?

1- High Electrical conductivity

Sheet conductivity of a 2D material

 $\sigma = en\mu$

The mobility is μ =15.000*-200,000 cm^{2/}Vs with a carrier density of n=10¹² cm^{-2.}

2D sheet resistivity = 31Ω

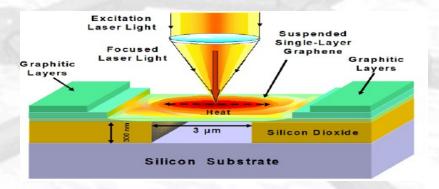
The resistivity is dominated by impurity scattering (independet from temperture 10-100K) and limited by acoustic phonons scattering

*Geim Novoselov Nat. Mat (2007) 6, 183

2- High Thermal conductivity

Thermal conductivity of graphene is 1500-5300 W/m K*

Copper thermal conductivity is 401 W/mK.



A.A. Balandin, S. Ghosh, W. Bao, I. Calizo, D. Teweldebrhan, F. Miao and C.N. Lau, *Nano Letters*, **8**: 902 (2008).

^{*} Balandin et al Nanoletters 8 902 (2009)

Why graphene for the future technology?

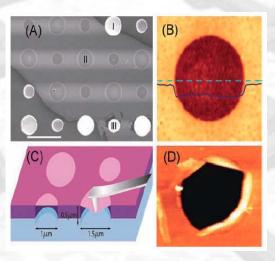
3- Mechanical strength

Graphene is the strongest material ever tested!
Tensile strength of 130GPa and Young modulus 1TPa

The spring constant of graphene has beem measured by Atomic Force Microscope K=-5N/m

Thus graphene is more than 100 times stronger than steel.

Mechanical strength



Young's modulus

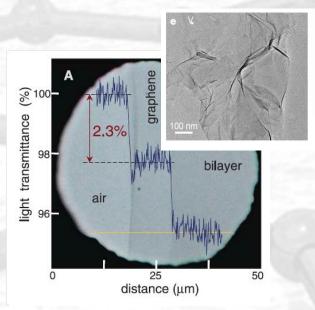
1 TPa

C. Lee et al, Science 321, 385 (2008)

Why graphene?

4- Trasparency

Nearly trasparent

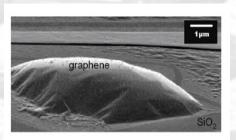


R. R. Nair et al. Science 320, 1308 (2008).

Red light absorption 2.3% R. Nair Science 320, 1308 (2008)

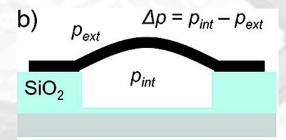
5- Impermeable

<u>Impermeable</u> <u>membrane!</u>



$$SiO_2 + 4HF \xrightarrow{\text{water}} SiF_4 + 2H_2O$$

One-atom thick impermeable membrane even to He!



Why graphene?

2- Electrical, thermal conductivity, mechanical strength and flexibility

Graphene, on flexible substrates, is mechanically robust and has the smallest bending radius among all flexible trasparent conductors

Bae, S. H. et al. ACS Nano 7, 3130–3138 (2013).

We expect that the market for flexible electronics will become larger than that for non-flexible electronics in about 10 years.





Figure 1 | Graphene-based multi-touch screen showing excellent flexibility (left)⁷ and possible applications in bendable or foldable mobile devices (right)

Why graphene?

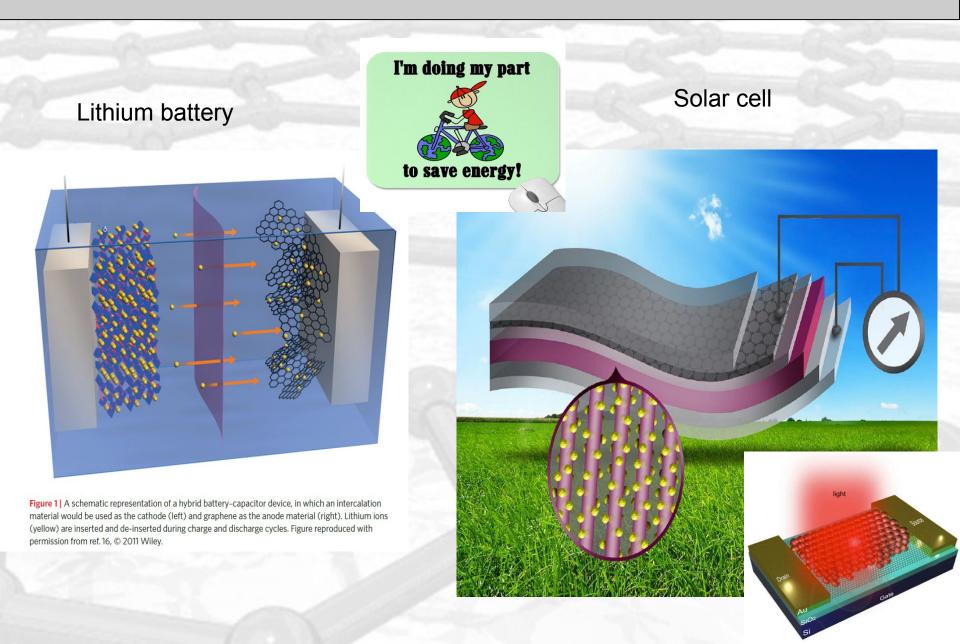




Electrifying inks with 2D materials

Nature Nanotechnology, 9, 737 (2014)

Graphene for energy

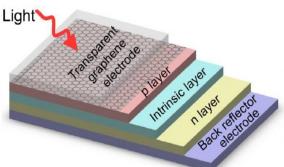


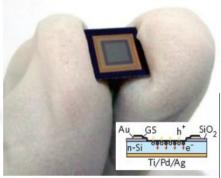
Graphene for energy

Graphene for photovoltaic devices

Inorganic solar cell

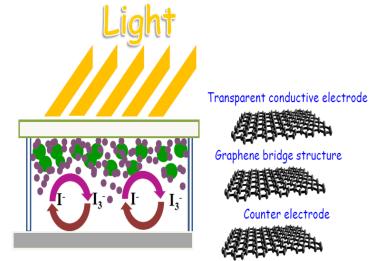
Graphene TC films can be used as window electrodes in inorganic solar cells



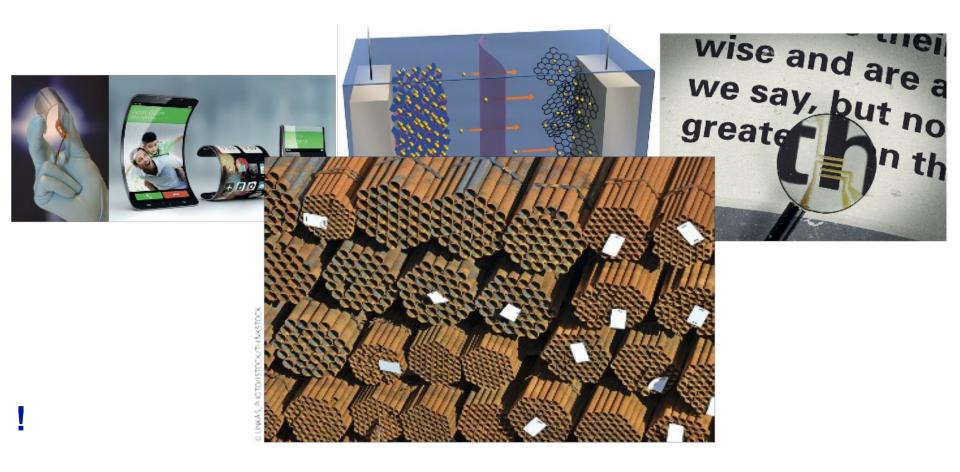


Schottky junction solar cell n ≈ 1.7%

Graphene in Dye Sensitized Solar Cell

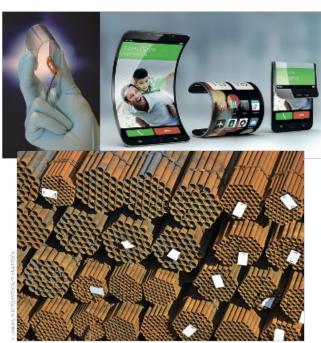


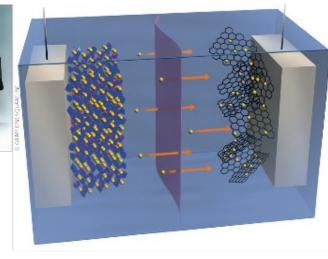
Graphene against corrosion



Nature Nanotechnology, 9, 737 (2014)







High electrical conductivity
High Thermal conductivity
Mechanical strength
Trasparency
Impermeability
Biological compatible



Flexible electronics
Energy devices
Sensors
Smart textile
Smart windows

.

The roadmap of the graphene flagship?

The European Union has identified graphene as future material for translational nanotechnology and the Graphene Flagship, a 1 billion euro venture, has been launched on October 10th 2013. The mission of the Graphene Flagship is "to take graphene and related layered materials from academic laboratories to society, revolutionize multiple industries, and create economic growth and new jobs in Europe".

http://graphene-flagship.eu/

http://graphene-flagship.eu/

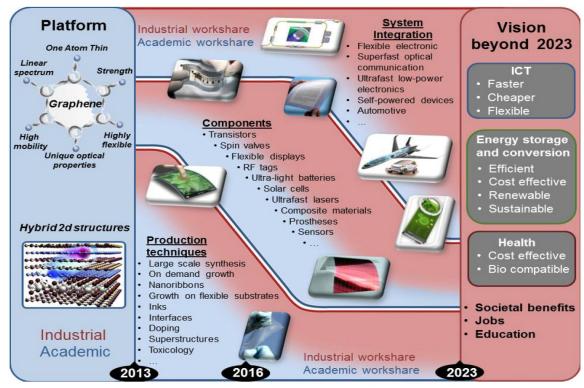


Figure 1-7: European graphene roadmap for the period of 2013-2023 and beyond for exploitation of graphene for a wide range of applications in ICT, energy, materials and beyond. In a black and white printout, the darker color indicates industrial workshare and the lighter color indicates the academic workshare. As the technology matures, industrial participation will take the lead.

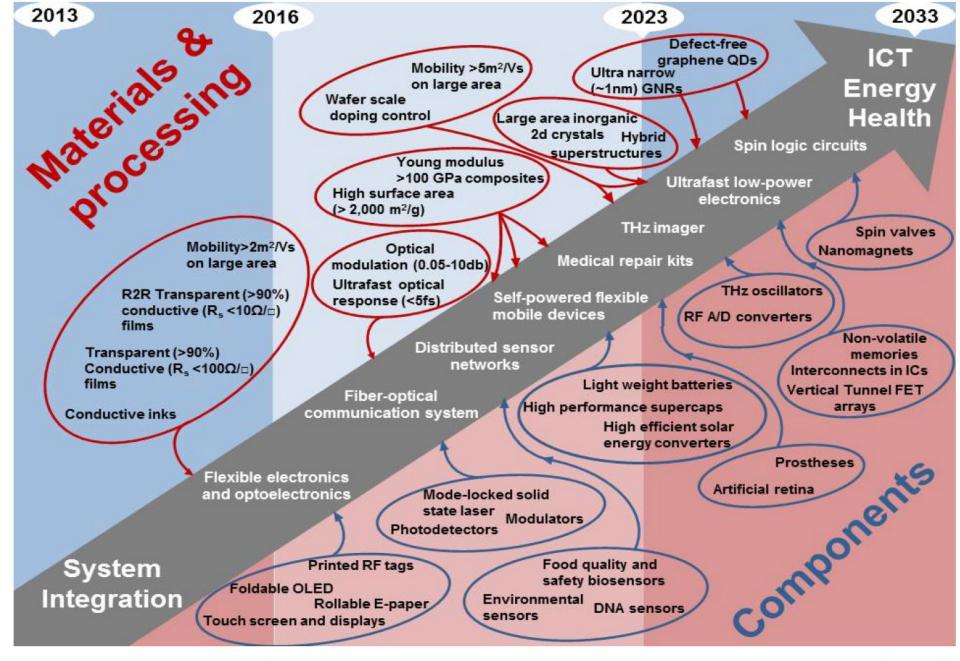
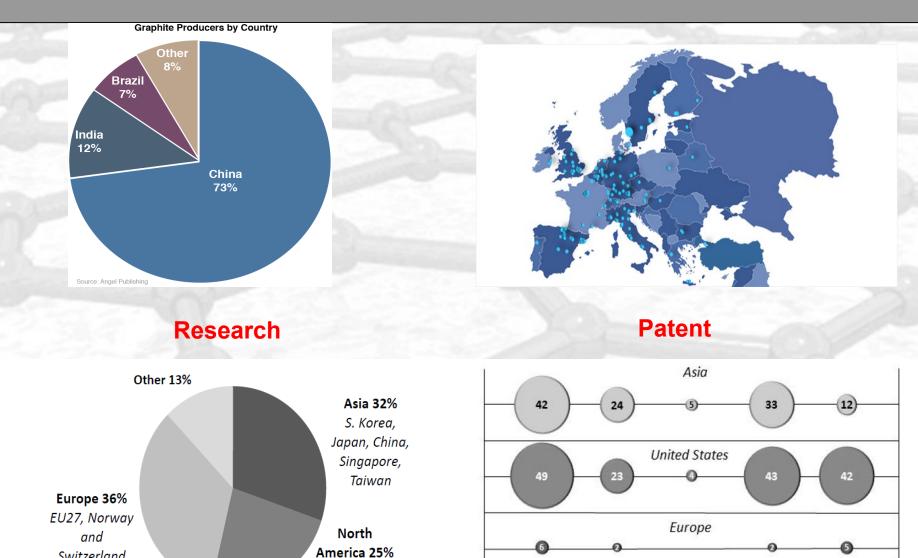


Figure 1-8: Illustration of the detailed European graphene roadmap for the period of 2013-202 beyond for the development of materials and processes needed for a wide range of component and in the action and the action to be into the component of the action to the action to the component of the action to the a

The roadmap of the graphene flagship?



Synthesis

Energy

US and

Canada

Figure 1-2 Geographical distribution of scientific publications on graphene.

Switzerland

Figure 1-3 Geographical distribution of graphene-based patent applications in specific fields.

Display

Nano-

devices

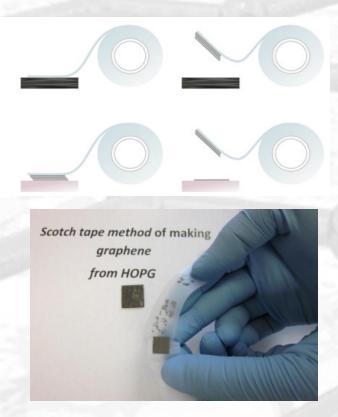
Composites

Is it easy to grow graphene?

Preparation methods

Top-down approach ∠ (From graphite)





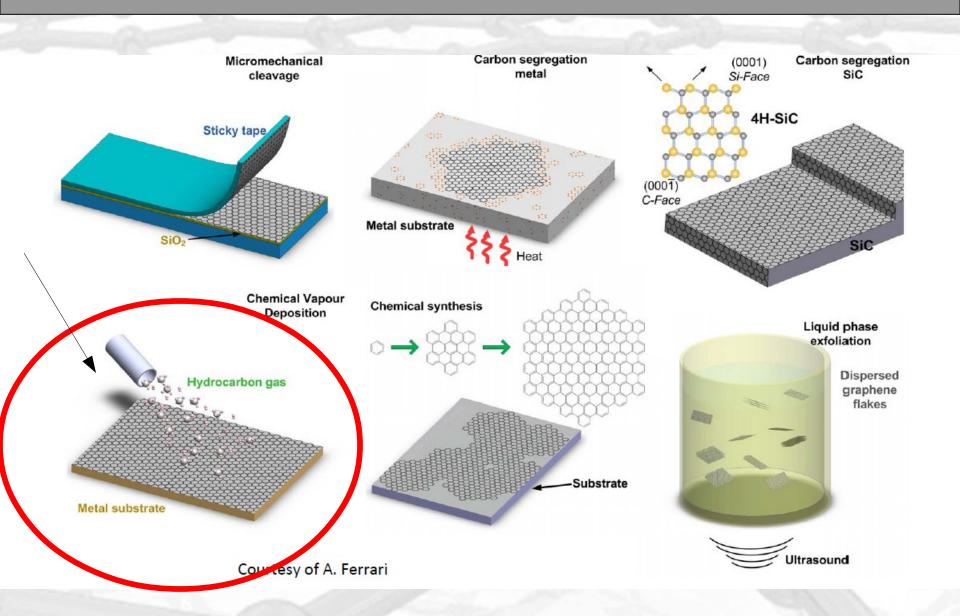
Carbon segregation from metals
Crvstals of 1cm²,imperfections ar Linteracting substrate ...

Dissolved carbon atoms

Metal film

Nan L. et al., Nano lett., 11,297 (2011)

Is it easy to grow graphene?



Is it easy to grow graphene? Yes

Preparation methods

Top-down approach ∠ (From graphite)

Flakes with limited size $(5-10\mu)$

Ripples

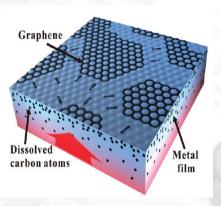


Bottom up approach (from carbon precursors)

Large graphene area

Regular Corrugation-Interaction with the substrate

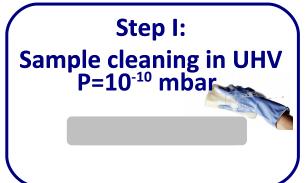
Carbon segregation from metals

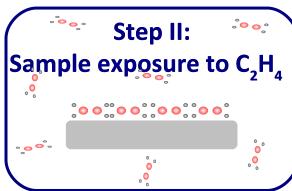


Nan L. et al., Nano lett., 11,297 (2011)

Graphene on metal substrates

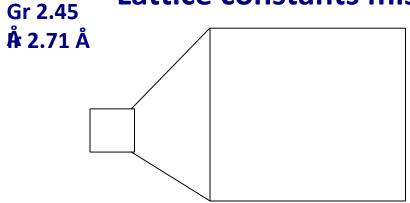
Catalytic hydrocarbon decomposition

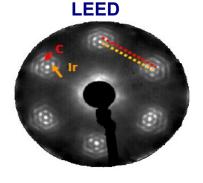




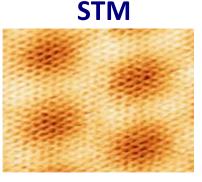


Gr/Ir(111) Lattice constants mismatch: moiré pattern!



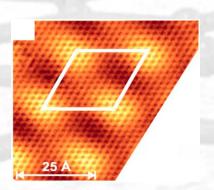


Betti et al., J. Nanopart. Res., **13**, 6013 (2011)



Pletikosic et al., *Phys. Rev.* **102**, 056808 (2009)

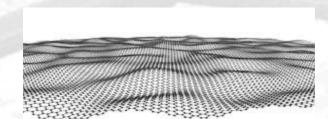
Graphene on transition metals



Hydrocarbons decomposition

<u>High quality monolayer graphene</u>

Alpha T. N'Diaye, et al. PRL 97, 215501 (2006)



Transition metal surfaces:

- 5d Ir(111), Pt(111)
- 4d Ru(0001), Rh(111)
- 3d Ni(111)

Increase of the interaction strenght

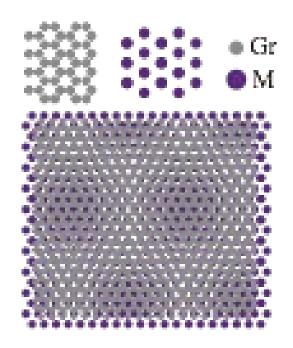
- less C / TM distance
- π d hybridization

Preobrajenski et al., Phys. Rev. B 78, 073401 (2008)

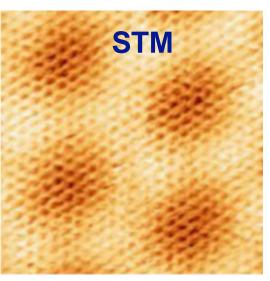
Graphene on Ir(111)

Low interaction

Slight corrugation (moiré effect)



Metal	a
Gr	2.46Å
Co(0001)	2.51 <i>A</i>
Ni(111)	2.49 À
Pt(111)	2.77Å
Ir(111)	2.72Å
Ru(0001)	2.71 Å
Rh(111)	2.69 <i>À</i>

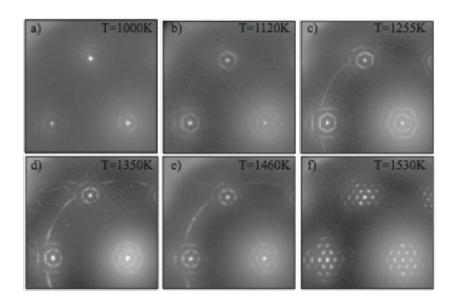


Pletikosic et al., *Phys. Rev. Lett.*

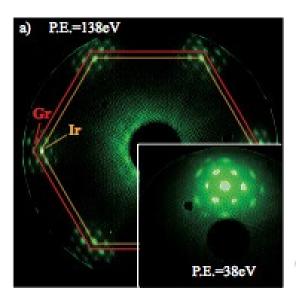
102, 056808 (2009

Graphene on Ir(111)

High quality and long range ordered sheets

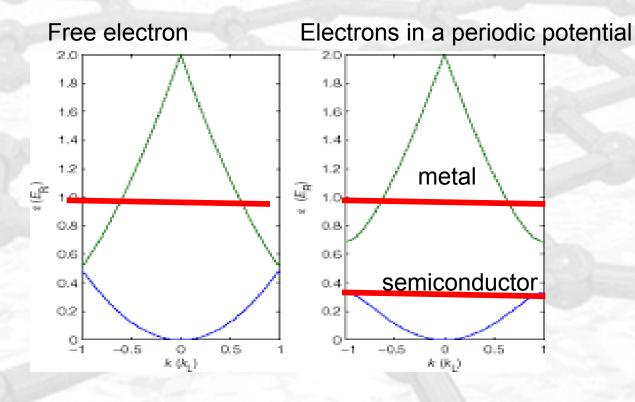


LEED diffraction pattern from Hattab, H. et al., Apple. Phys. Lett. 98 141903 (2011)

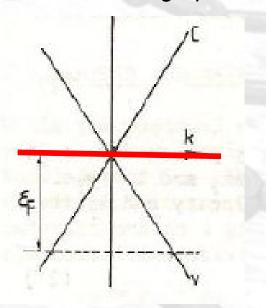


LEED diffraction pattern In LOTUS lab

Electrons in graphene: velocity



Electrons in graphene

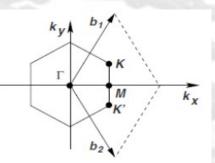


$$E=v_F k$$

Electronic properties

Tight binding solution for energy dispersion in the whole Brillouin zone

$$E(\mathbf{k}) = \sqrt{1 + 4\cos\left(\sqrt{3}ak_y/2\right)\cos(ak_x/2) + 4\cos^2\left(ak_x/2\right)}$$



Close to the K point

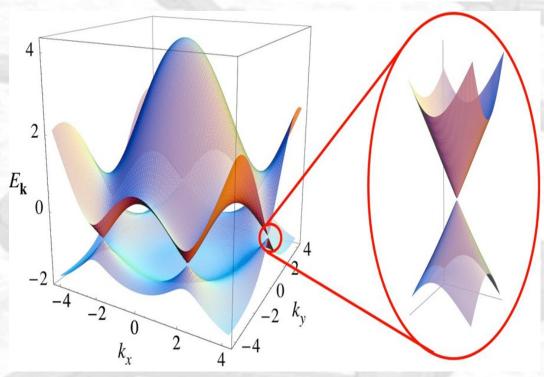
$$E(\mathbf{k}) = \nu_f K$$

$$H = \begin{pmatrix} 0 & \nu(k_x - ik_y) \\ \nu(k_x + ik_y) & 0 \end{pmatrix}$$

$$H = v\vec{p}\vec{\sigma}$$



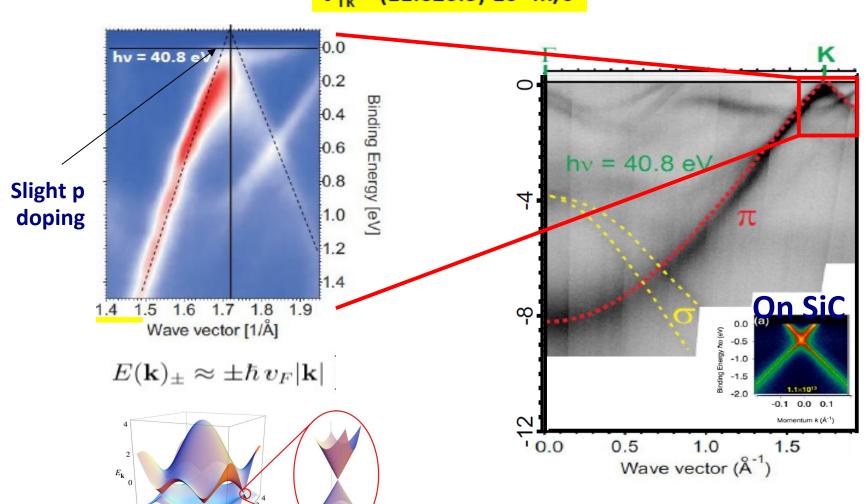
2D massless Dirac particles Hamiltonia with $v \sim 10^6$ m/s



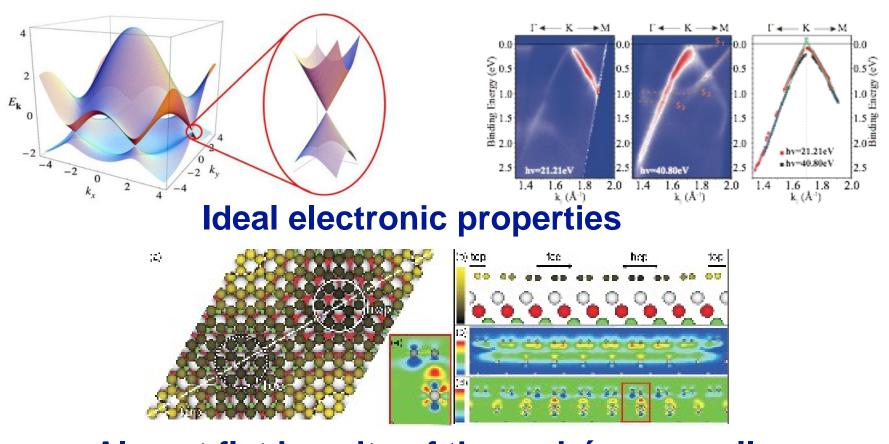
High quality graphene with low interaction with the substrate

Fermi velocity measurements!!!!!

 $V_{\Gamma K} = (11.6 \pm 0.5) \cdot 10^5 \text{ m/s}$



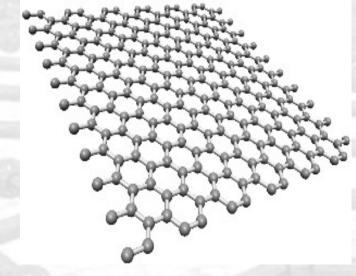
High quality graphene with low interaction with the substrate



Almost flat in spite of the moiré supercell

High quality graphene with low corrugation

Outline



5-Is it easy to grow graphene? YES, we can

6-How to control and design the graphene properties?

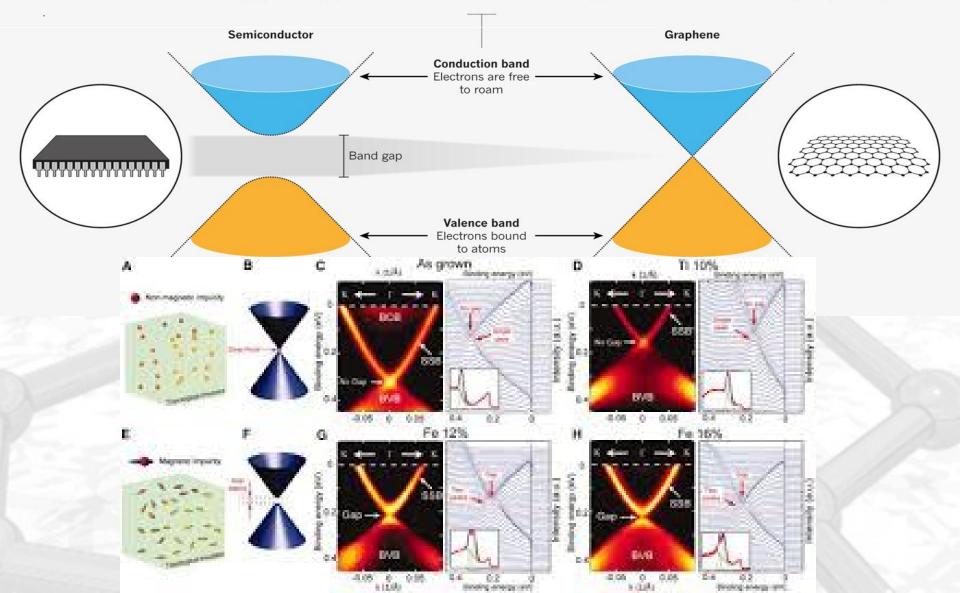
7-Three examples:

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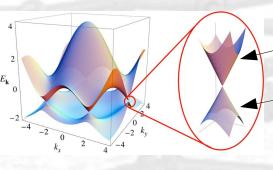
Mind the gap

MIND THE GAP

Electrons in a solid are restricted to certain ranges, or bands, of energy (vertical axis). In an insulator or semiconductor, an electron bound to an atom can break free only if it gets enough energy from heat or a passing photon to jump the 'band gap', but in graphene the gap is infinitesimal. This is the main reason why graphene's electrons can move very easily and very fast.



Why open a gap?



Conduction band

Valence band

Absence of a band gap in graphene limits seriously any electronic application

Tuning the energy gap is fundamental to control the optical response and electronic and optoelectronic devices

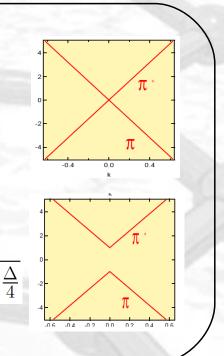
2x2 Tight Binding Hamiltonian in K point

$$H = \begin{pmatrix} 0 & \nu(k_x - ik_y) \\ \nu(k_x + ik_y) & 0 \end{pmatrix} \longrightarrow E(\mathbf{k}) = \pm \nu k$$

Introducing asymmetry in electric potential

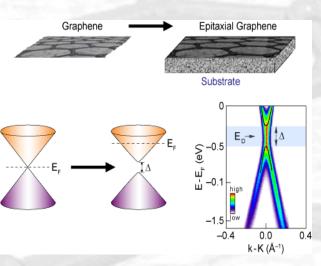
$$H = \begin{pmatrix} \frac{\Delta}{2} & \nu(k_x - ik_y) \\ \nu(k_x + ik_y) & -\frac{\Delta}{2} \end{pmatrix} \longrightarrow E(\mathbf{k}) = \pm \sqrt{\nu^2 k^2 + \frac{\Delta}{4}}$$

E.McCann, arXiv:1205.6953v1



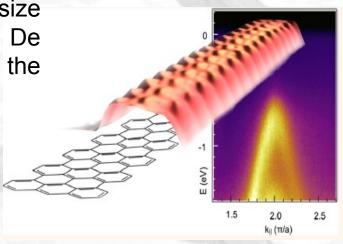
How to open a gap?

Two strategies to open a gap in a graphene sheet



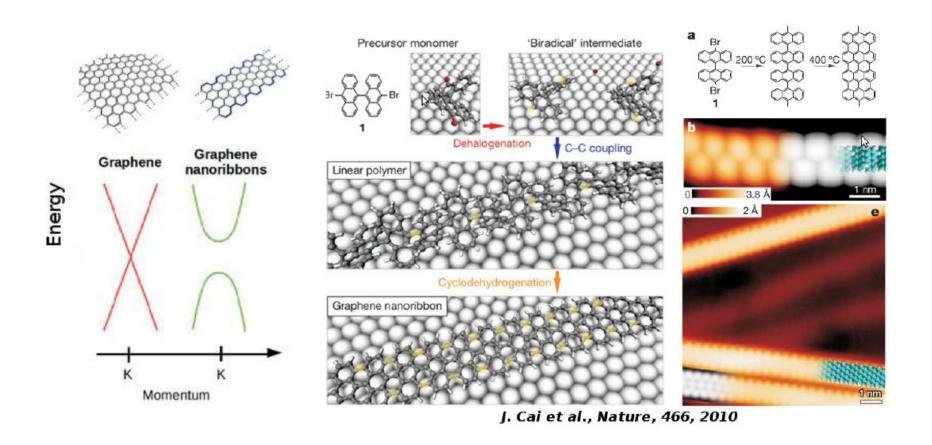
1- Move from sp² to sp³ hybridization induced by the substrate

2- Confine the electrons in a nanoribbon with a lateral size comparable with the De Broglie wavelength of the electrons

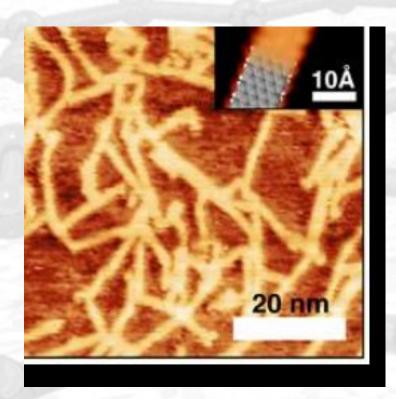


Graphene nanoribbons (GNRs)

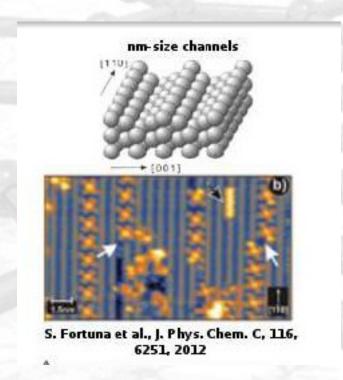
The covalent self-assembly of 10,10-dibromo-9,9-bianthryl (DBBA) monomer precursor into 7-AGNR on the Au(111) surface



Graphene nanoribbons



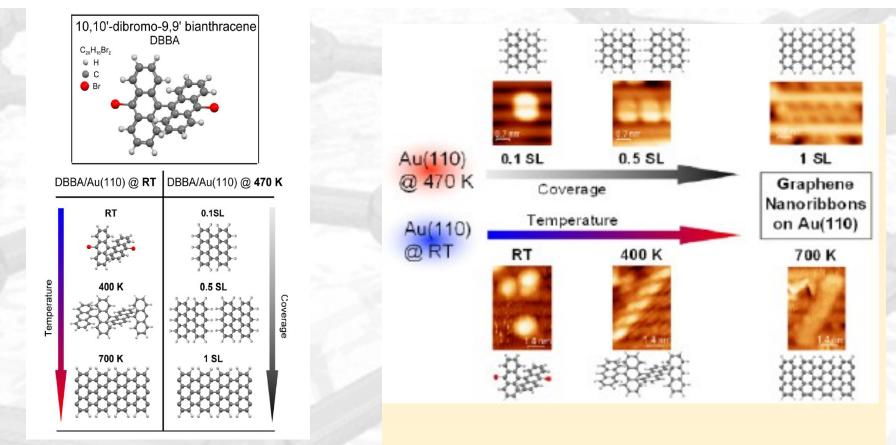
Graphene nanoribbons are disordered on the Au(111) surface!



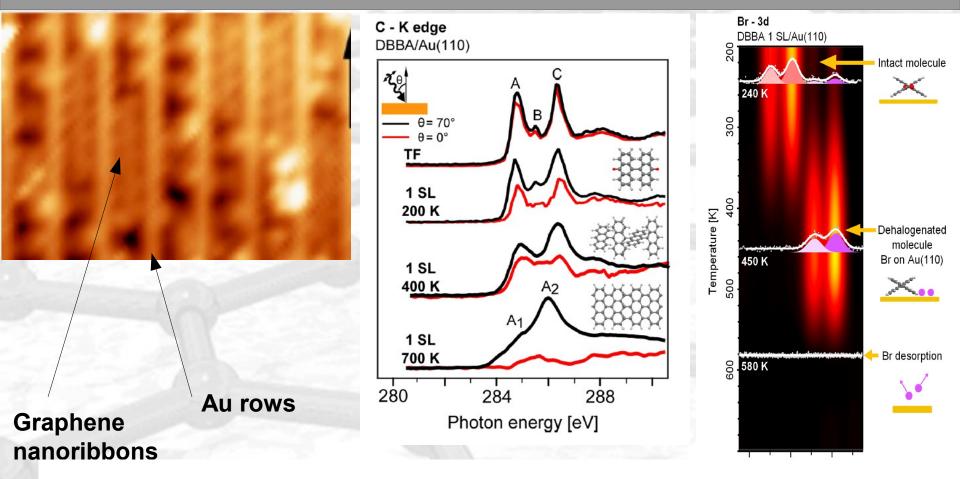
The 1x2-Au(110) surface can potentially serves as 1D template for the GNRs synthesis

Surface-Assisted Reactions toward Formation of Graphene Nanoribbons on Au(110) Surface

Lorenzo Massimi,**,[†] Oualid Ourdjini,[†] Leif Lafferentz,[‡] Matthias Koch,[‡] Leonhard Grill,^{§,‡} Emanuele Cavaliere,^{||} Luca Gavioli,^{||} Claudia Cardoso,[†] Deborah Prezzi,[†] Elisa Molinari,^{†,‡} Andrea Ferretti,*,[†] Carlo Mariani,[†] and Maria Grazia Betti[†]



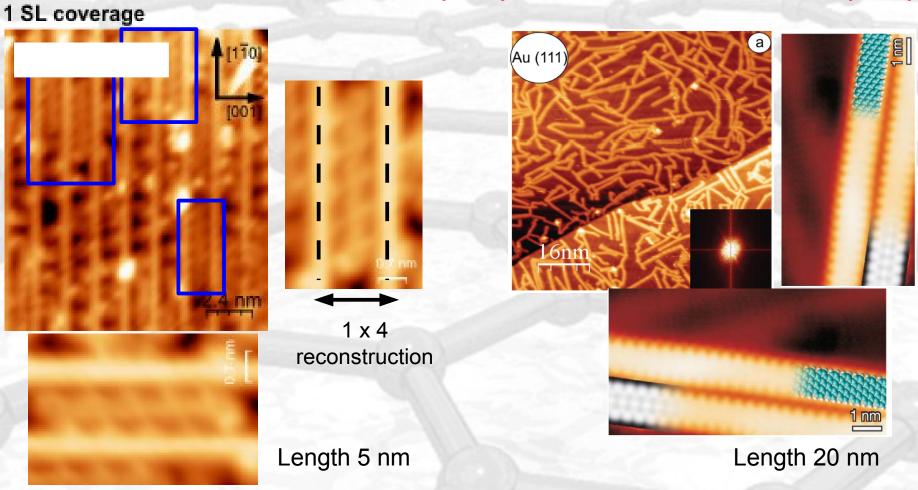
Ordered nanoribbons on Au(110) surface



- The reconstructed 1x2-Au(110) catalyzes the chemical reactions
- The surface corrugation prevents the molecular diffusion

Graphene nanoribbons

Nanoribbon on Au(111) vs Nanoribbon on Au(110)



Nanoribbons on Au(110) are smaller (5 nm) than on Au(111) (>20 nm)

Lower molecular mobility due to surface roughness hinders formation of GNRs

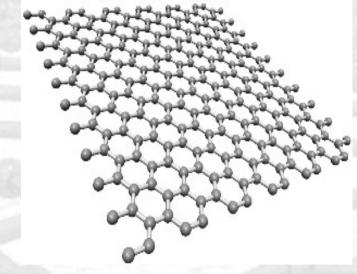
Graphene synthesis

1- we can grow, not only highly ordered graphene sheets, but also ordered graphene nanoribbons!

2- work in progress on the electronic structure....

3- preliminary result: gap opening at 0.7eV

Outline



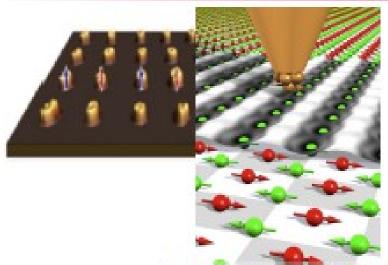
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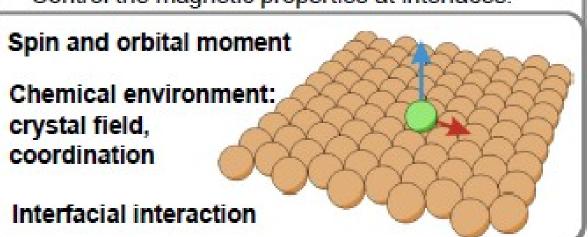
Surface-supported magnetic nanostructures

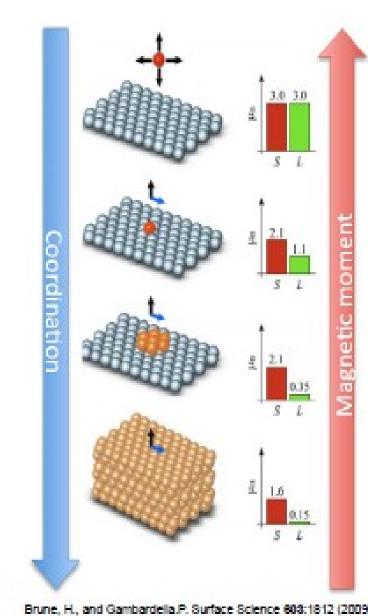


S. Henze, Science 288, 1805-1808 (2000).

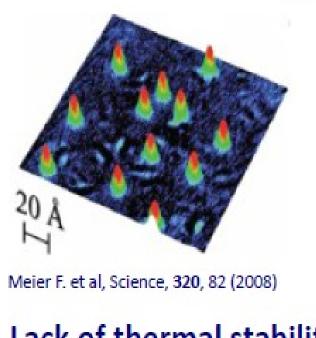
Manipulating single spins: spintronics, nanosized memory, quantum state storage...

Control the magnetic properties at interfaces:





Ordered array of magnetically anisotropic sites However...

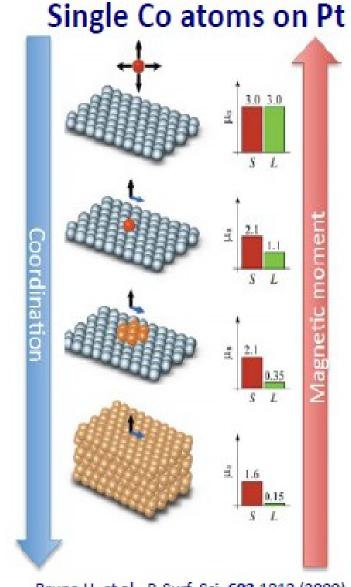


Lack of thermal stability

Undesired clustering

No long range order

Magnetic quenching



Brune H. et al., P. Surf. Sci, 603, 1812 (2009)

Ordering properties

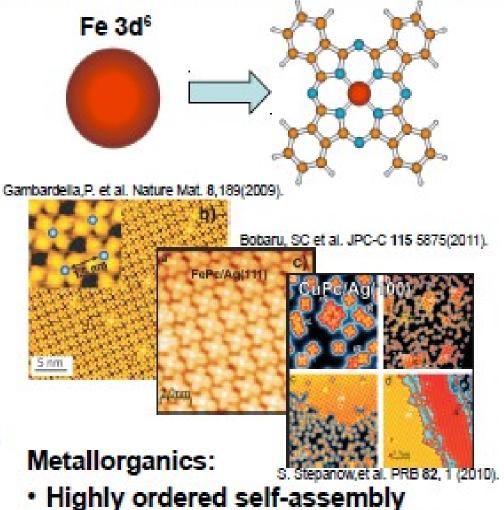
Co atoms on Pt(111)

[1] Meler, F. et al., Science 320, 82-6 (2008).

Single atoms:

- Difficult to order
- Strong interaction with substrate
- Cluster formation
- How to control the electronic properties?

Embedding in a organic matrix: Metallorganics



Chemical control of organic ligand

Organometallic Molecules:

Self-assembly

Spontaneous assembly of molecules into structured aggregates under equilibrium.

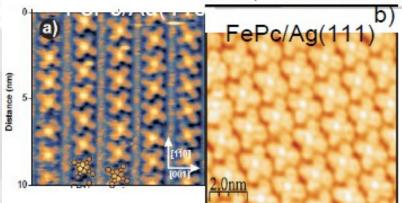
Whitesides GM et al., Science 254, 1312(1991)

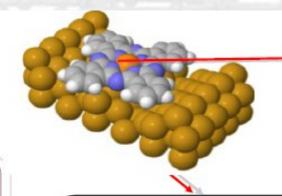


2D ordered structure: Spin Network

M.G. Betti et al., Langmuir

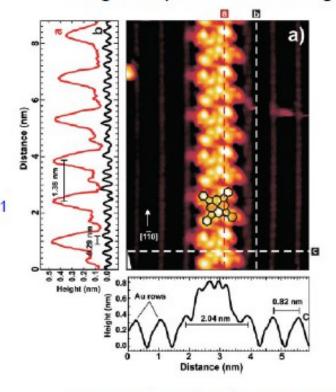
28 (37), 13232-13240 (2012) Bobaru, SC et al. JPC-C 115 5875(2)11





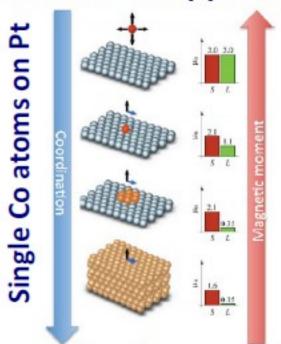
Central magnetic atom

Organic part: "anchoring effect"



Fortuna et al., J. Phys. Chem. C. 116, 6265 (2012)

Bare atoms approach



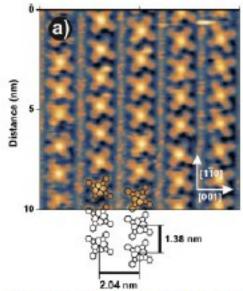
Brune H. et al., P. Surf. Sci, 603,1812 (2009)

- High magnetic anisotropy than isolated atom;
- High magnetic moment;

BUT:

- Lack of thermal stability
- Clustering Quenching

Molecules on metals



Betti et al., Langmuir, 28, 13232 (2012)

- High thermal stability
- No clustering

BUT:

Quenched magnetic moments

Potti et al. cubmitted to Dhuc Dou P.

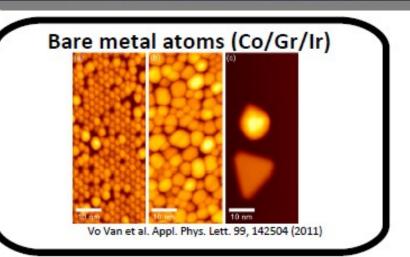
Molecules on Graphene

ordered?

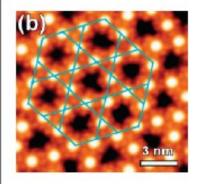
Metal substrate decoupling?

Quenching?

Why FePc?



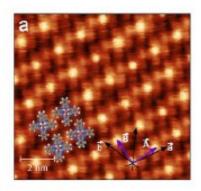
ordered lattices



FePc/Gr/Ru

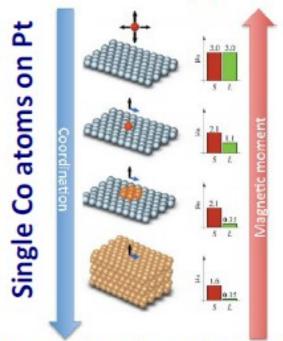
Mao et al., JACS. 131, 14136 (2009)

CoPc/Gr/Ir



Hamalainen et al., J. Phys. Chem. C, in press

Bare atoms approach



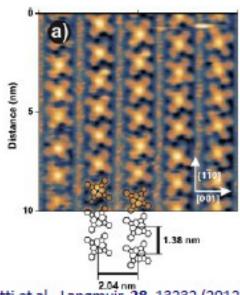
Brune H. et al., P. Surf. Sci, 603,1812 (2009)

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Molecules on metals



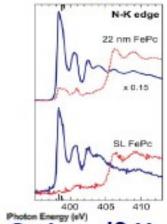
Betti et al., Langmuir, 28, 13232 (2012)

- High thermal stability
- No clustering

BUT:

Quenched magnetic moments

Molecules on Graphene

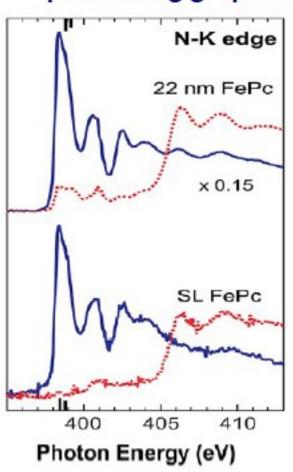


Photon Energy (eV)
Ordered? Yes!

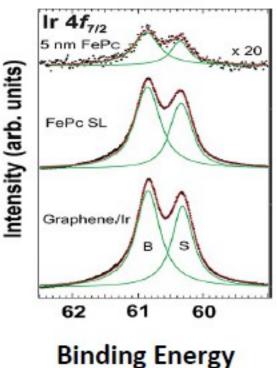
Decoupled? Yes!

Quenching?

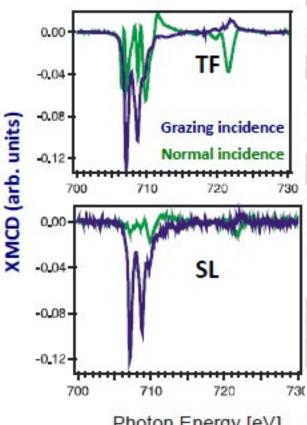
Molecules grow flat preserving graphene



Molecules decoupled from metal



Enhanced magnetic anisotropy



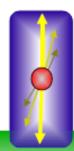
Photon Energy [eV]

The role of Graphene/Ir(111) and FePc

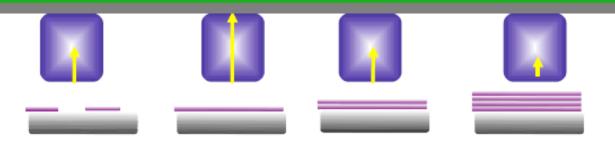
Non-quenching of the magnetic properties



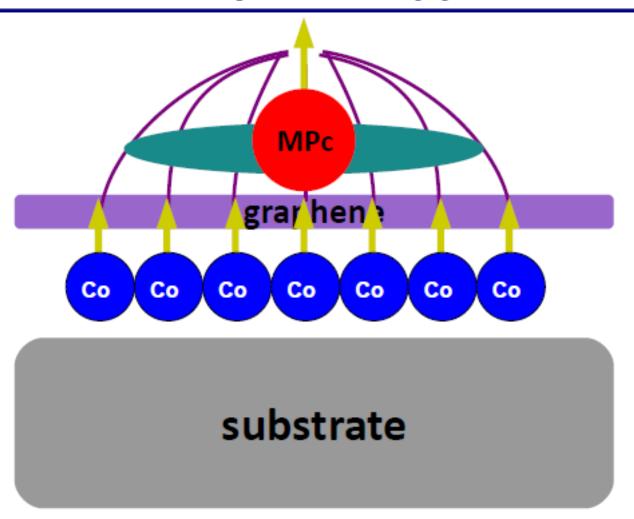
- Enhanced anisotropy -->
- → increased correlation



Intriguing behaviour as a function of FePc thickness



Co intralayer on supported Gr



Enhancing anisotropy exploiting the interaction

Graphene for energy

I'm doing my part

Lithium battery

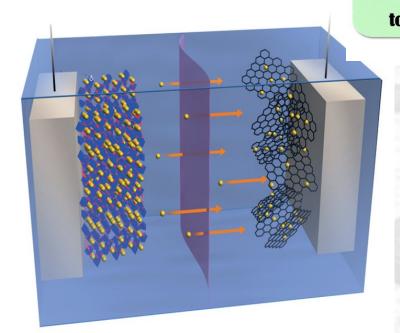


Figure 1 | A schematic representation of a hybrid battery-capacitor device, in which an intercalation material would be used as the cathode (left) and graphene as the anode material (right). Lithium ions (yellow) are inserted and de-inserted during charge and discharge cycles. Figure reproduced with permission from ref. 16, © 2011 Wiley.

Solar cell

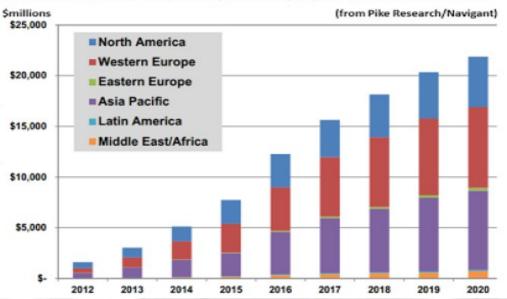


Graphene for lithium batteries

Li-ion batteries

Li-ion Batteries





Graphene flagship for Energy: objectives for 2020

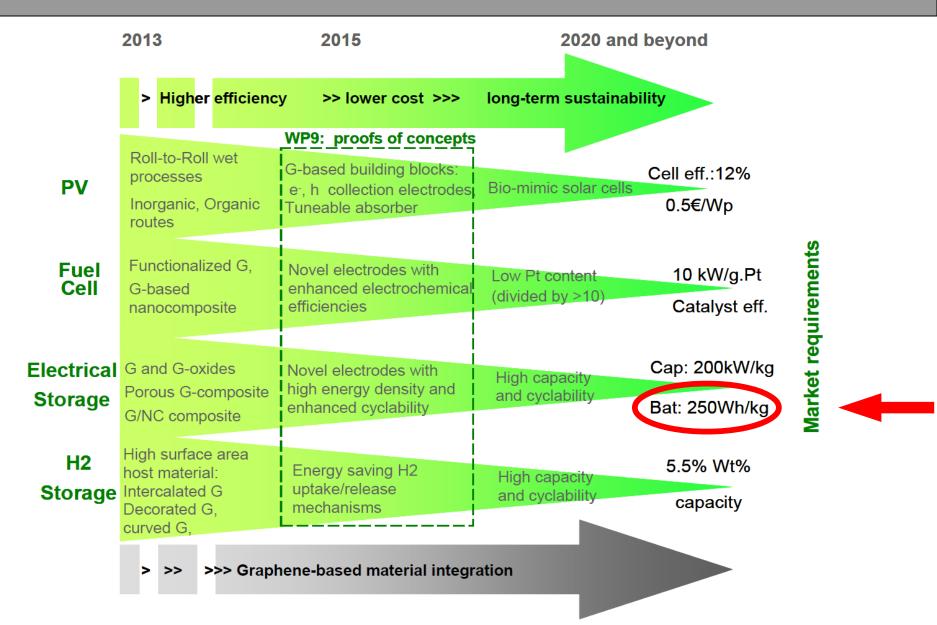
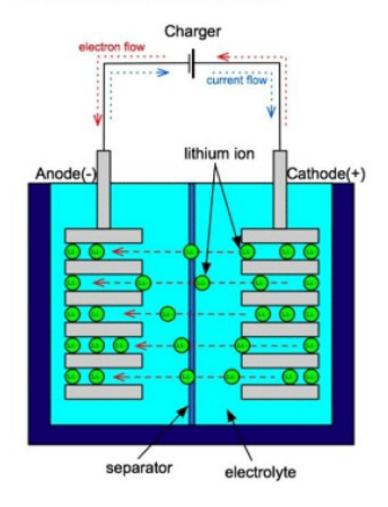
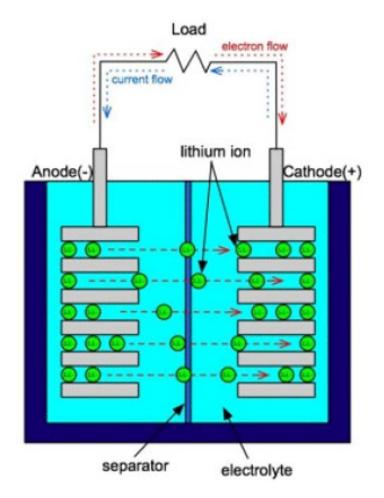


Figure 1-22: *Graphical representation of progress in WP9. In the figure, G stands for graphene.*

Li-ion batteries

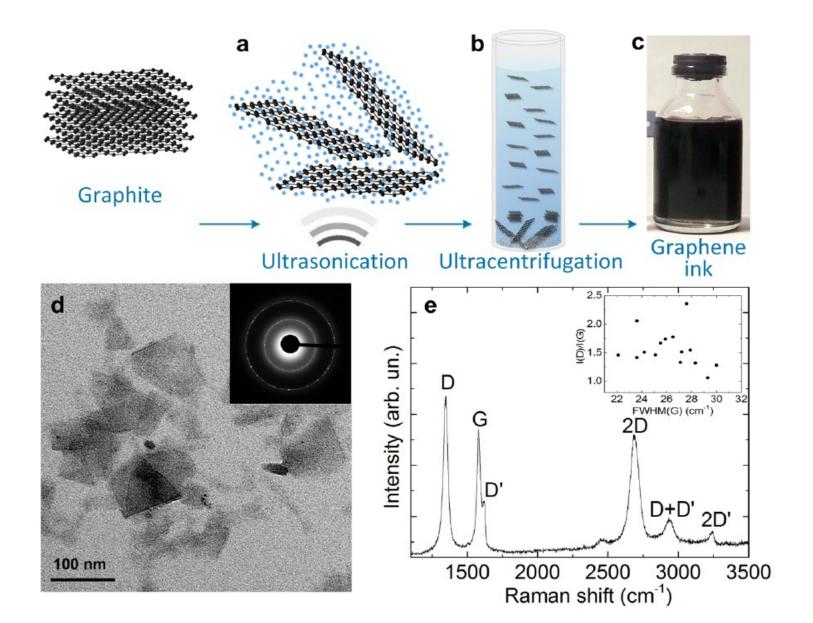




CHARGING

DISCHARGING

Graphene flakes and graphene ink



Li uptake: Graphene more effective than Graphite

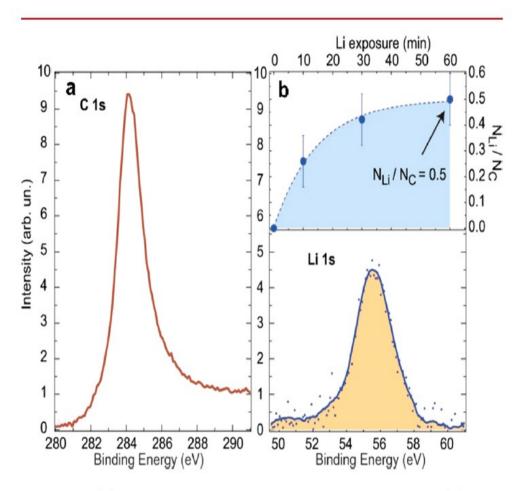
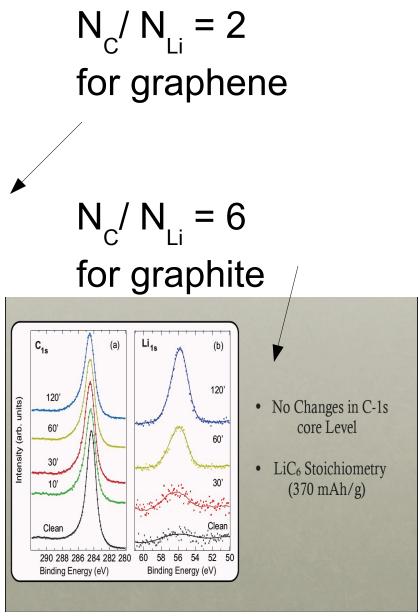
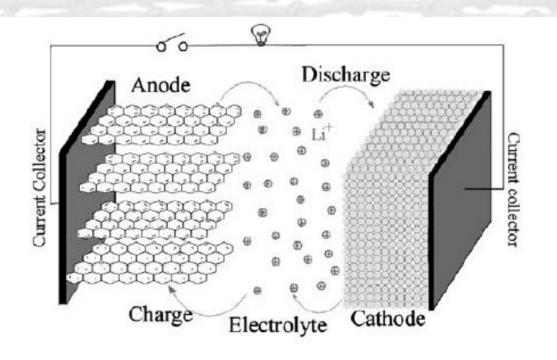
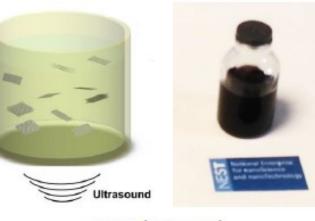


Figure 2. (a) XPS spectral density of the C 1s core-level. (b) XPS spectral density of the Li 1s core-level (lower panel) and estimated number of Li atoms per C atom (upper panel), obtained through the cross-section weighted intensity ratio of the core-levels.



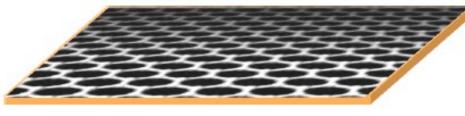


Solution processing

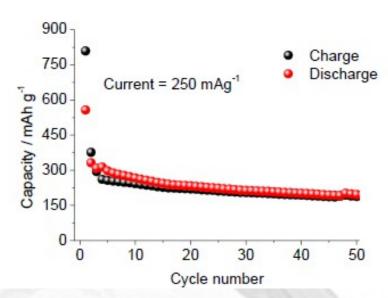


Graphene Ink

Functional electrodes



Deposition of graphene ink on Cu



Graphene flagship for Energy: objectives for 2020

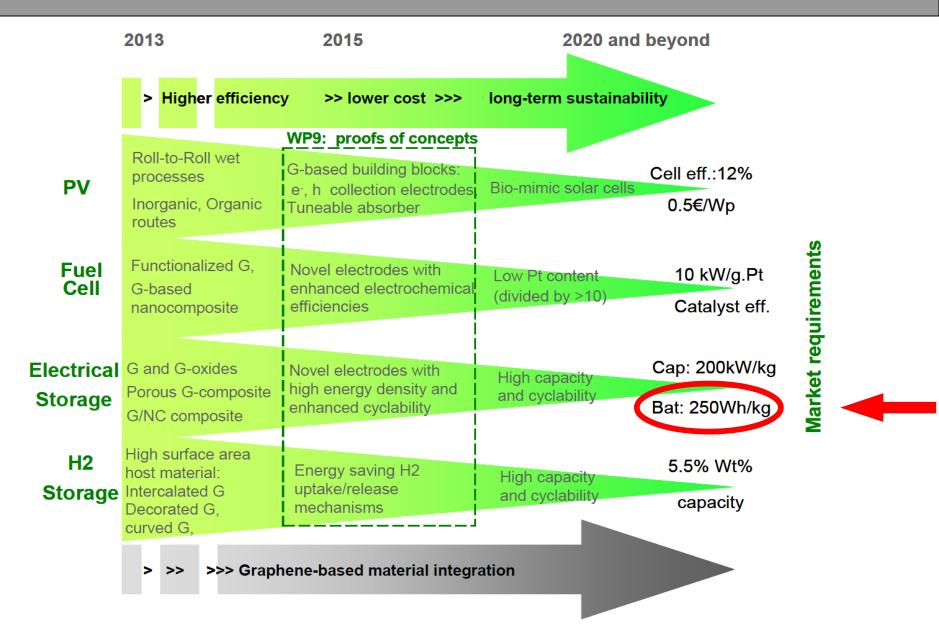
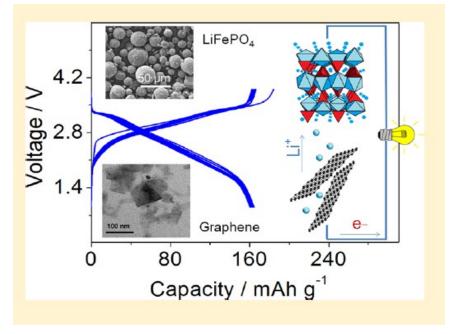


Figure 1-22: *Graphical representation of progress in WP9. In the figure, G stands for graphene.*



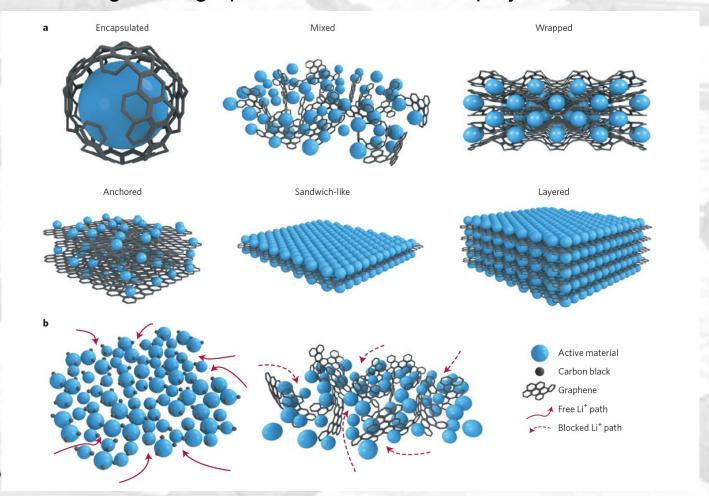
An Advanced Lithium-Ion Battery Based on a Graphene Anode and a Lithium Iron Phosphate Cathode

Jusef Hassoun,**,†,¶ Francesco Bonaccorso,*,‡,§,||,¶ Marco Agostini,† Marco Angelucci, $^{\perp}$ Maria Grazia Betti, $^{\perp}$ Roberto Cingolani, ‡ Mauro Gemmi, $^{\sharp}$ Carlo Mariani, $^{\perp}$ Stefania Panero, † Vittorio Pellegrini, $^{\ddagger,||}$ and Bruno Scrosati*, $^{\ddagger,\nabla}$



Why Li uptake is so effective in graphene?

Edge and defects cannot justify the factor 3, Packing of the graphene flakes seems to play a crucial role!



New ideas: porous graphene

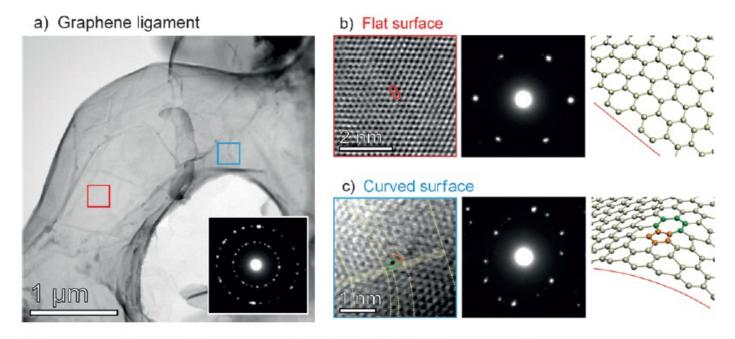


Figure 2. a) Typical low-magnification BF-STEM image of nanoporous graphene. The selected area electron diffraction pattern (inset) shows multiply orientated graphene sheets in the nanoporous configuration. b) HRTEM image and the electron diffraction pattern taken from the flat region of the nanoporous graphene. The atomic structure is consistent with the 2D model. c) The BF-STEM image and the electron diffraction patterns taken from a region with a large curvature gradient. The pentagon—heptagon pair lattices, together with large lattice bending, can be observed. The yellow dashed lines show the lattice directions.

Experimental techniques

Electronic structure: electron spectroscopies

- Photoemission (in-situ LOTUS Lab. Dip. Fisica Università "La Sapienza"
- Polarization dependent X-Ray absorption (Synchrotron radiation: beamlines ID08 @ ESRF ALOISA @ ELETTRA)
- X-ray Photoemission (Synchrotron radiation: beamlines CIPO and ALOISA @ ELETTRA)

Magnetic measurements

 X-Ray Magnetic Circular Dichroism (Synchrotron radiation + magnetic field: beamline ID08 @ ESRF)

Structural investigation: microscopy and diffraction

- Scanning Tunneling Microscopy (STM) in collaboration with Prof. Silvio Modesti TASC Trieste (Synchrotron radiation + magnetic field: beamline ID08 @ ESRF)
- Grazing Incidence X-ray Diffraction (Synchrotron radiation: beamline ID03 @ ESRF)
- · Low Energy Electron Diffraction (LEED) (in situ)





This work is an effort of

LOTUS GROUP

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NANORIBBONS Lorenzo Massimi. Oualid Ourdjini, Carlo Mariani LITHIUM BATTERYJacopo Chiarinelli, Marco Angelucci (now INFN), Lorenzo Massimi, Carlo Mariani

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A. Baraldi, S. Lizzit, R. Larciprete (SuperESCA beamline)

Andrea Ferretti (CNR-MO)
Claudia Cardoso
Deborah Prezzi
Elisa Molinari
Daniele Varsano
Stefano Fabris (SISSA-Ts)

ITT V. Pellegrini F. Bonaccorso (graphene ink)

STMicroscopy Silvio Modesti Università Trieste Luca Gavioli Università Brescis Leonhard Grill Unversitat Wien

Theory