Fabrication du graphène par exfoliation du graphite

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Contexte - généralités

- que désigne le terme “graphène” ?

- voies de synthèse du graphène

Exfoliation du graphite (voies chimiques)

- Oxyde de graphène (oxyde de graphite)

- exfoliation assistée par sonication

- exfoliation en voie réductrice

Ton-scale graphene from industry ?

Graphene : a single layer of hexagonally arranged carbon atoms

painting by Bleue Roy, http://www.bleue-roy.com/Animals/animals.html

The ultimate membrane:

- ☑ thinnest
- ☑ strongest
- ☑ flexible yet tough
- ☑ electrically conductive

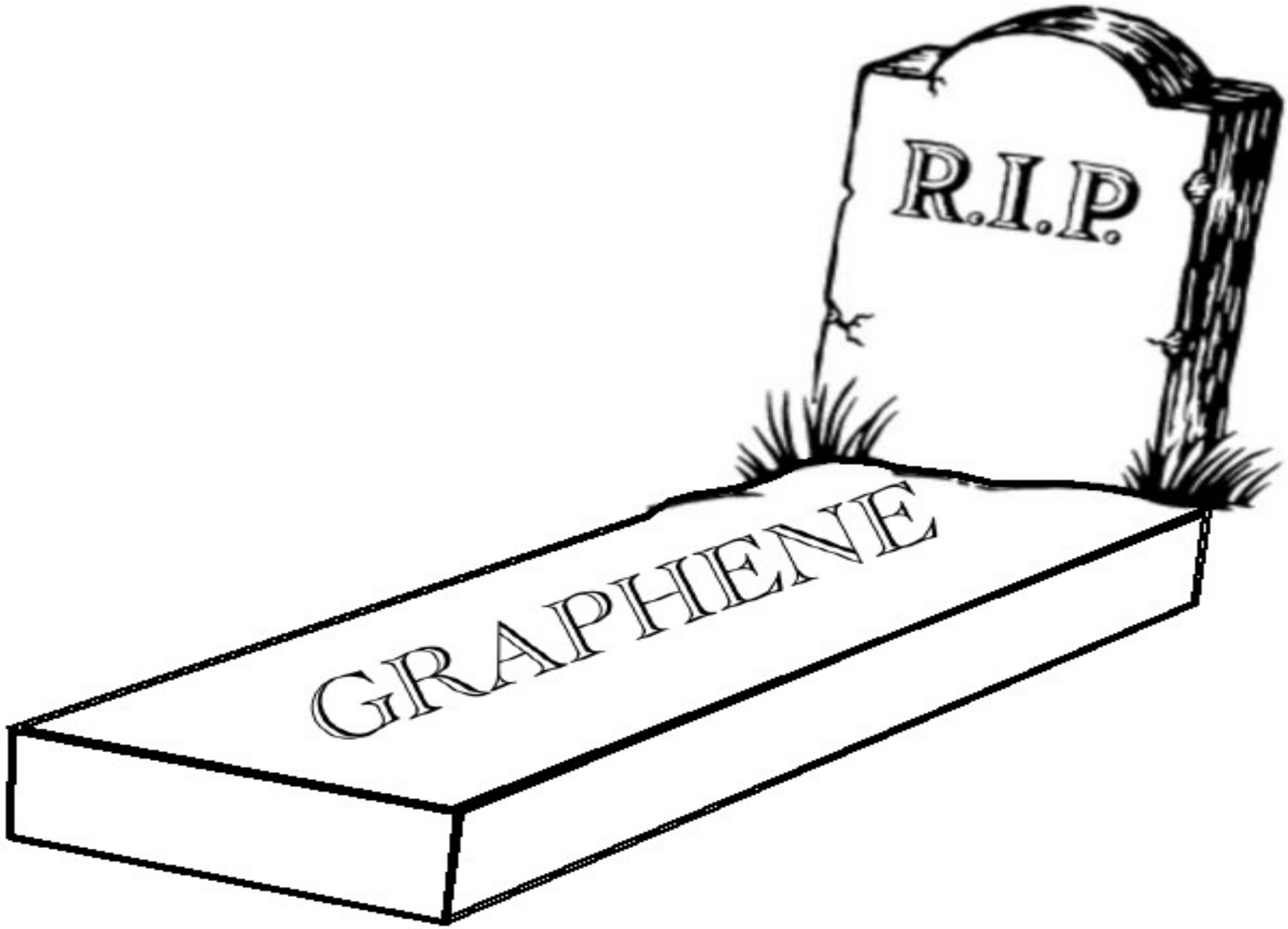
Mass less electrons: photon-like physics

- ☑ ballistic current (l < 1 micron)
- ☑ high mobility (up to 200 000 $cm^2/V.s$)
- ☑ no electronic gap

Nobel prizes 2010

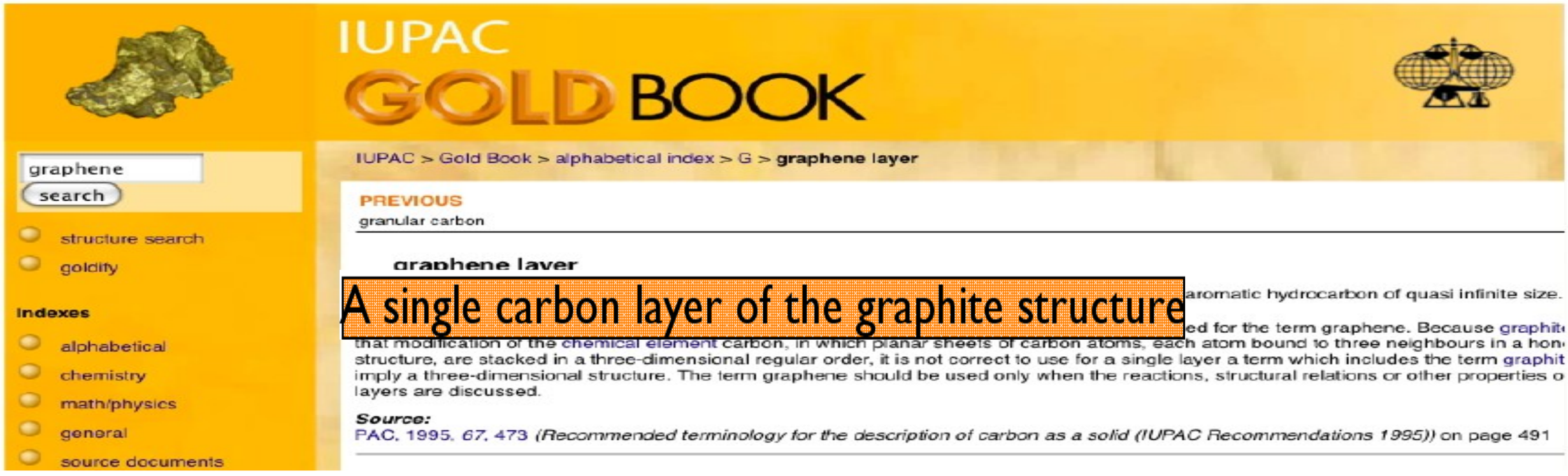
Novoselov Geim Diamond

Sémantique : graphène, nanographène, nanorubans de graphène



Sémantique : graphène, nanographène, nanorubans de graphène

http://goldbook.iupac.org/



"Graphene is the name given to a flat monolayer of carbon atoms tightly packed into a two-dimensional (2D) honeycomb lattice"

Geim & Novoselov, Nature Materials 2007

When does 2D becomes 3D ?

... "single-, double- and few- (3 to <10) layer graphene to be distinguished as three different types of 2D crystals ('graphenes')."

Geim & Novoselov, Nature Materials, 2007

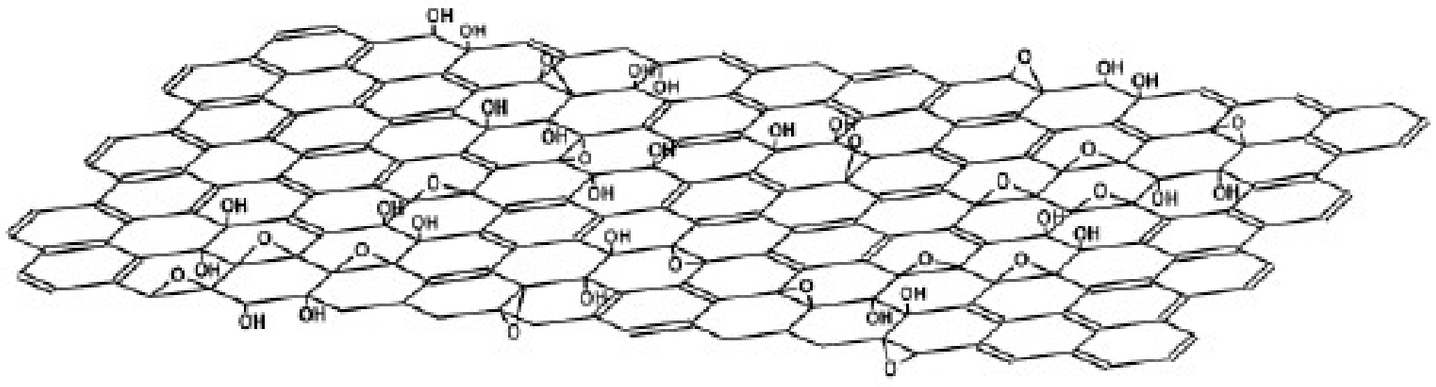
Sémantique : graphène, nanographène, nanorubans de graphène

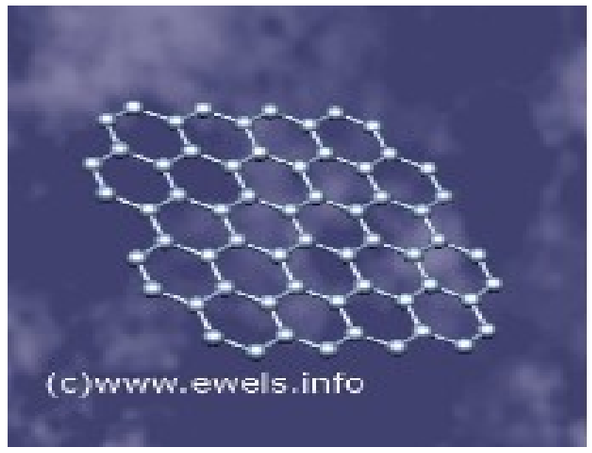
Graphene = few (<10) graphitic layers

Few Layers Graphene

Sémantique : graphène, nanographène, nanorubans de graphène

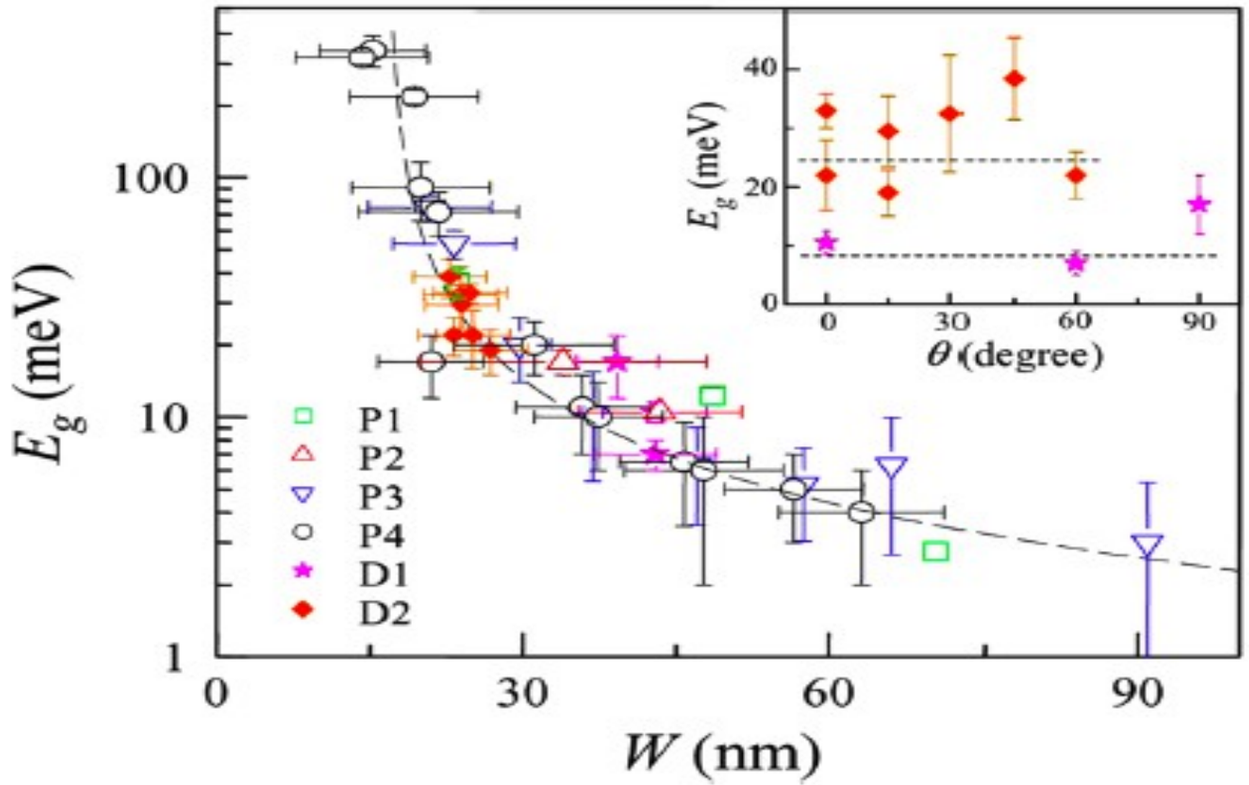
Graphene = Oxyde de graphène réduit



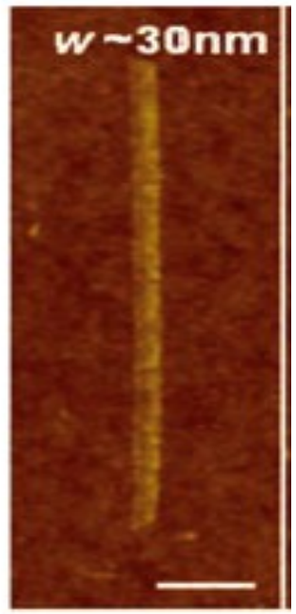


Sémantique : graphène, nanographène, nanorubans de graphène

Graphene nanoribbons: graphene is already “nano” in thickness :
“nano” should apply to width



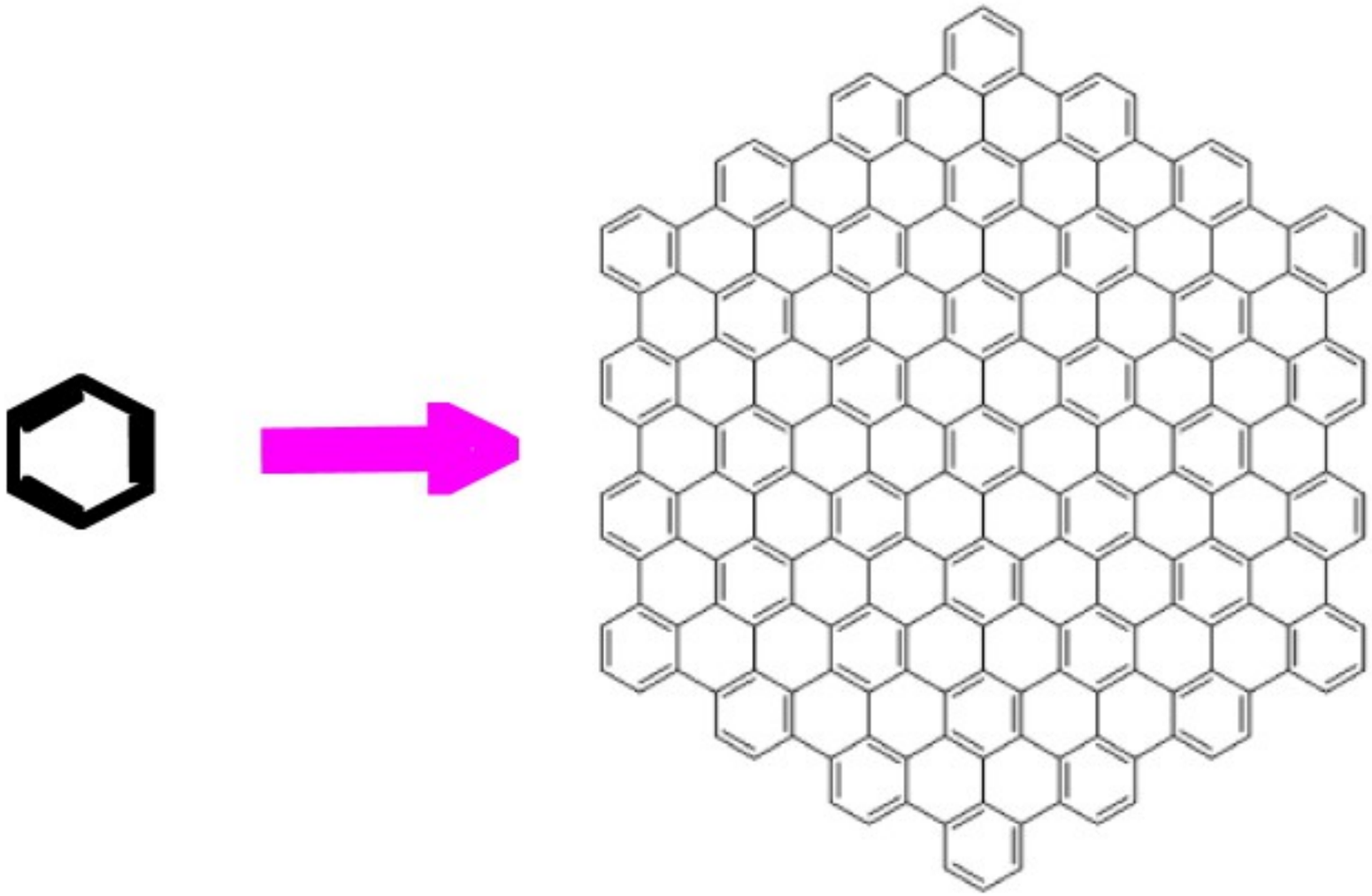
Kim et al., PRL, 2007



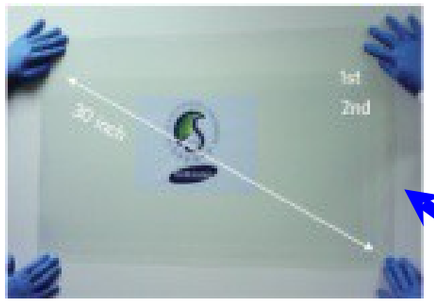
H. Dai et al., Science 2008

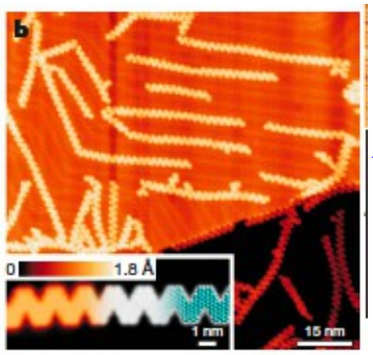
Sémantique : graphène, nanographène, nanorubans de graphène

Where PolyAromatic Hydrocarbons (PAHs) and Graphene meet...

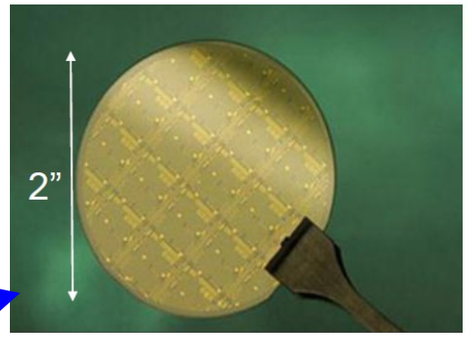


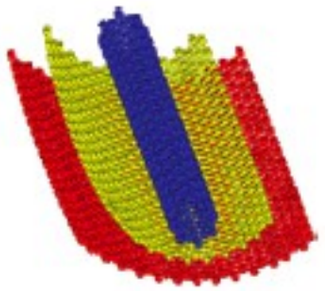
Graphene production methods

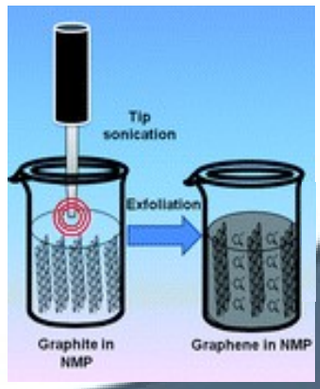




	☺	☹
Mechanical exfoliation	• Quality	• Low yield • High costs
Epitaxial growth on SiC	• Quality, •Large area	• Substrat •high cost
Chemical Vapor Deposition	• Large area	• High costs • Substrat
CNT unzipping	• ribbons	•quality, cost
Total synthesis	•monodisperse size	•quantities, cost
Graphite Oxide Reduction	• Large scale	• Quality reduced
Dispersion of Graphite	• Large scale	• partial exfoliation



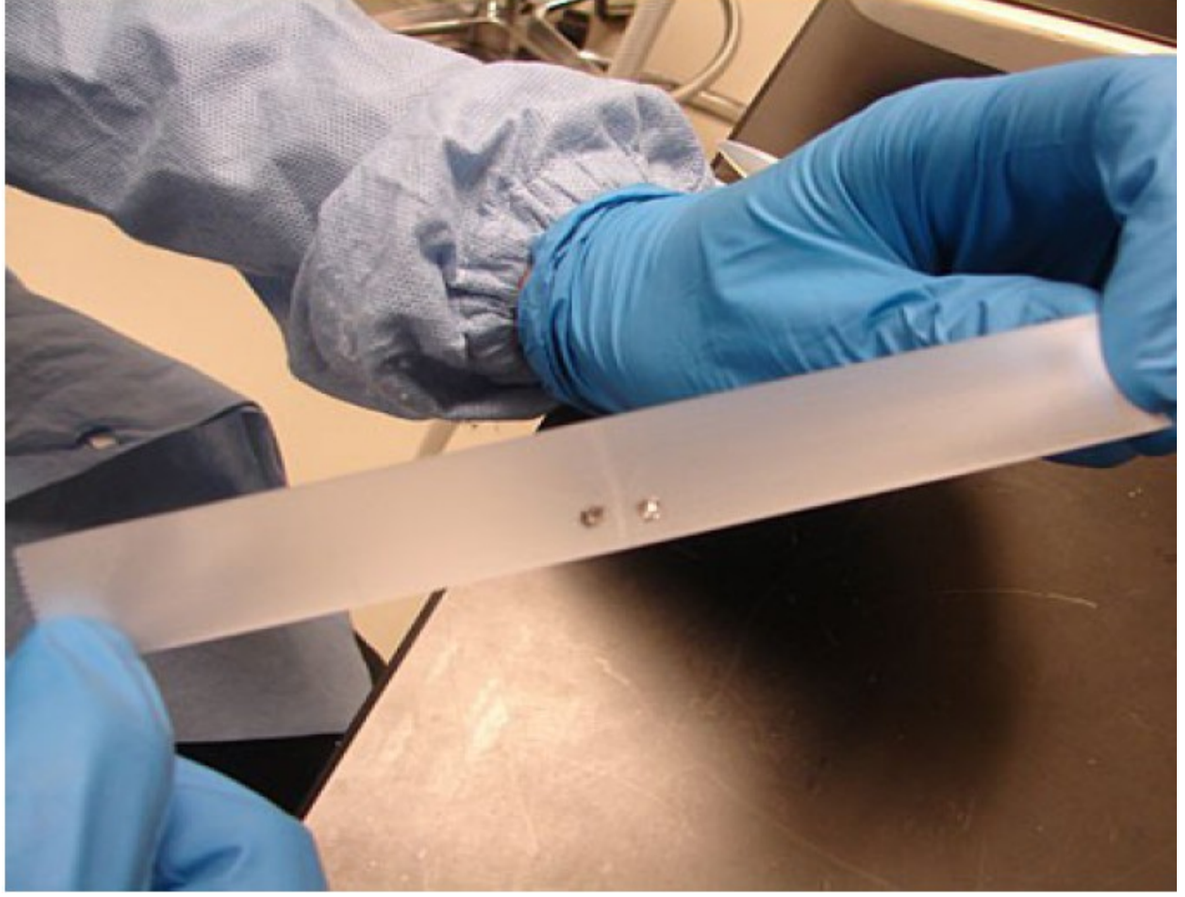


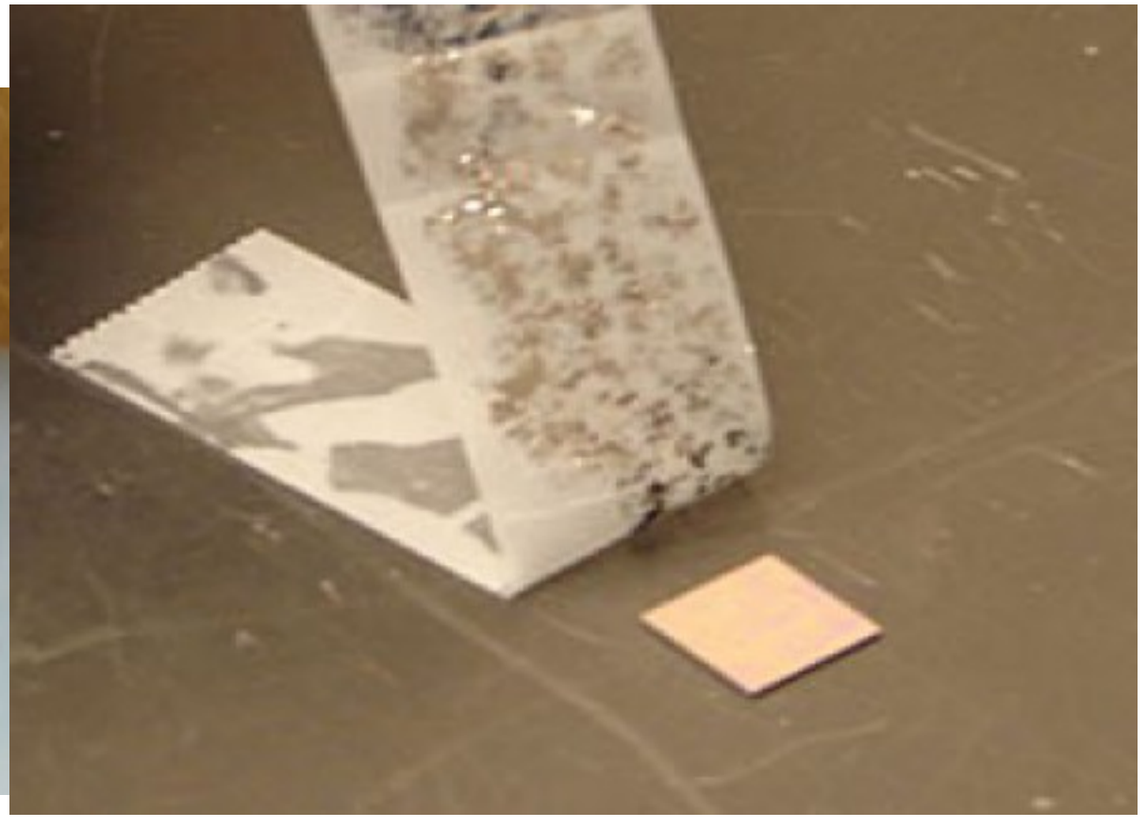


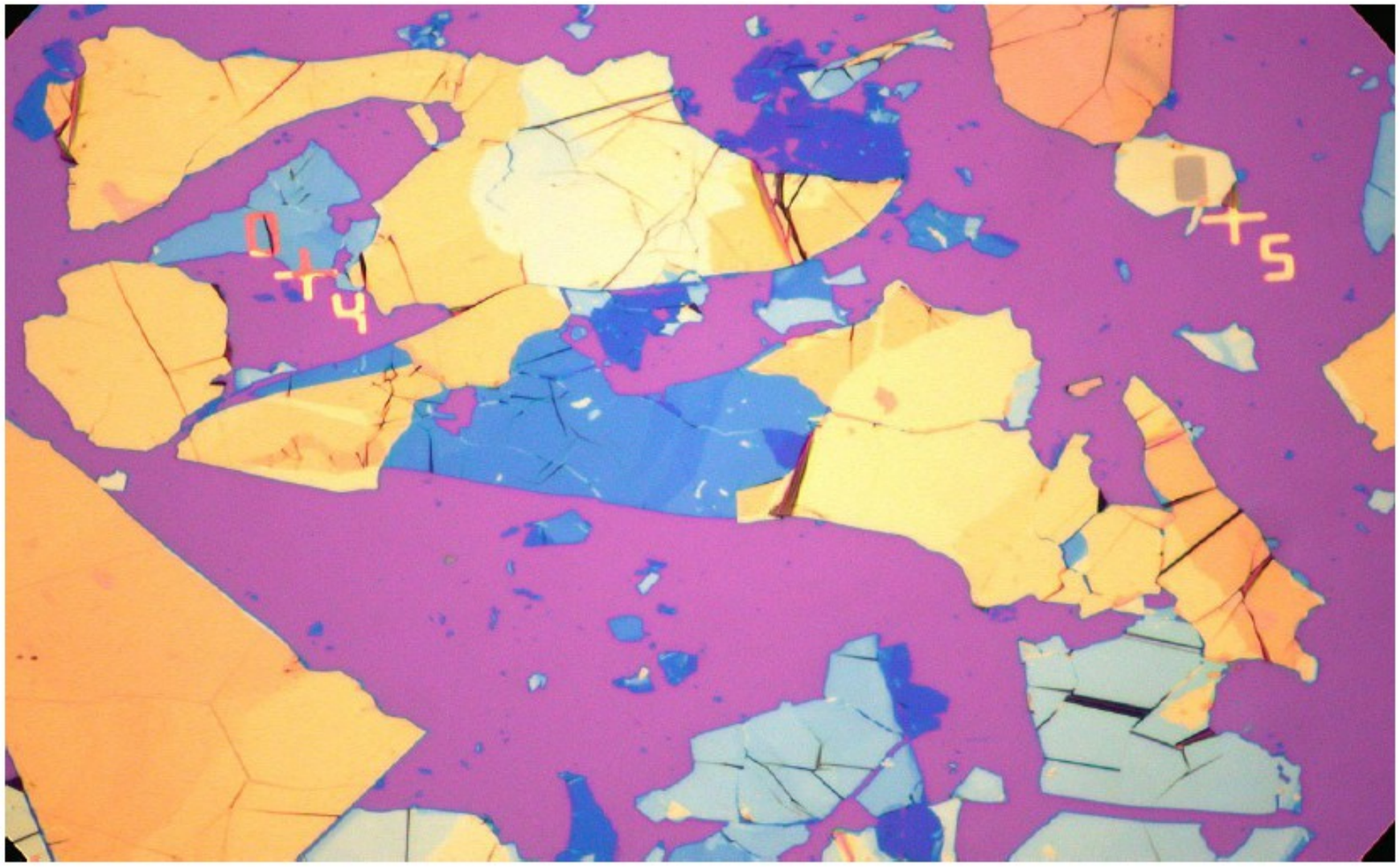
→ Solution of Graphite intercalation Compounds (GICs) in organic solvents

slide inspired from J.N. Fuchs

+

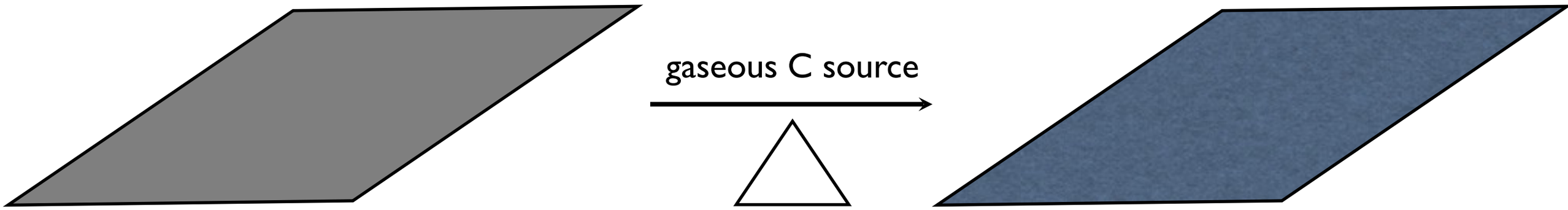






slide inspired from J.N. Fuchs

graphene by CVD

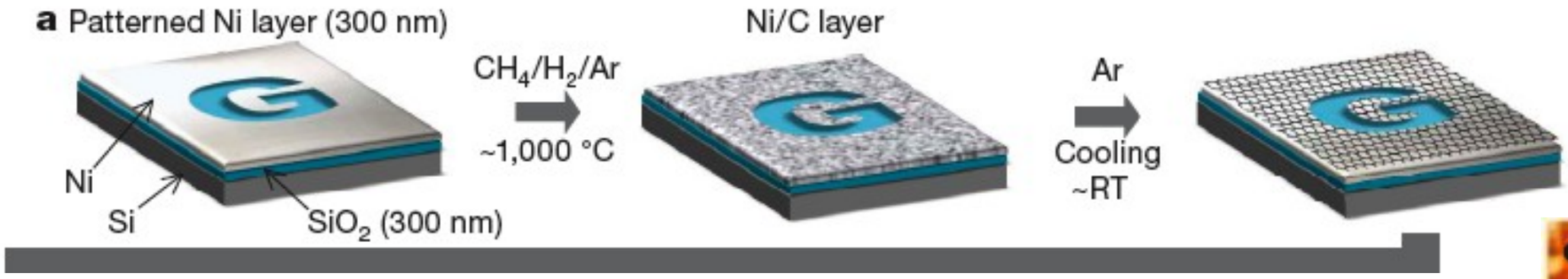


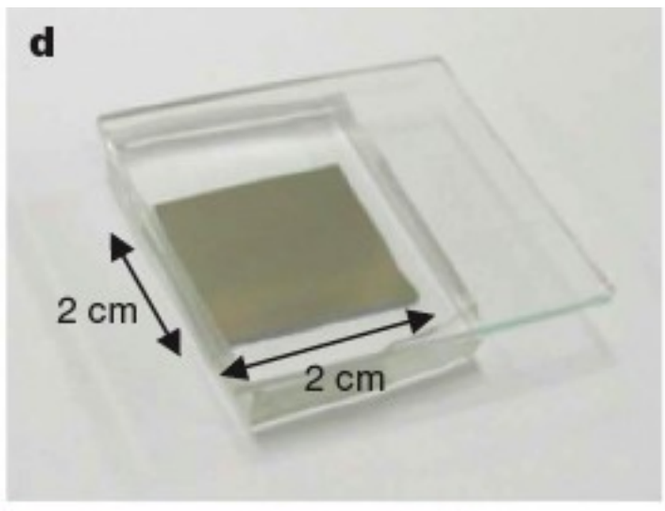
etching of the substrate
or stamping

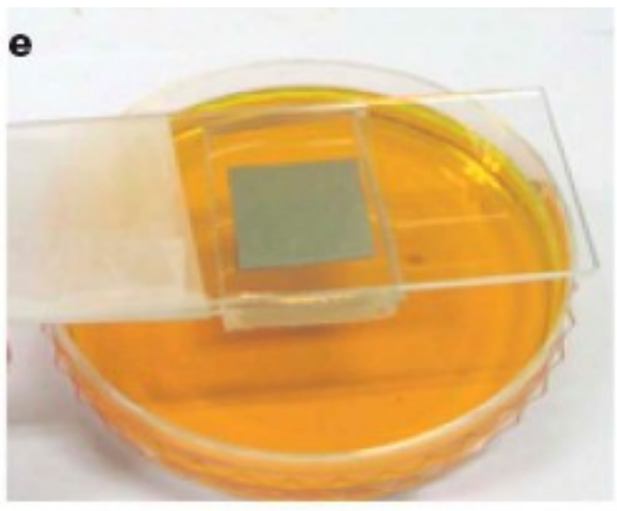
Large-scale pattern growth of graphene films for stretchable transparent electrodes

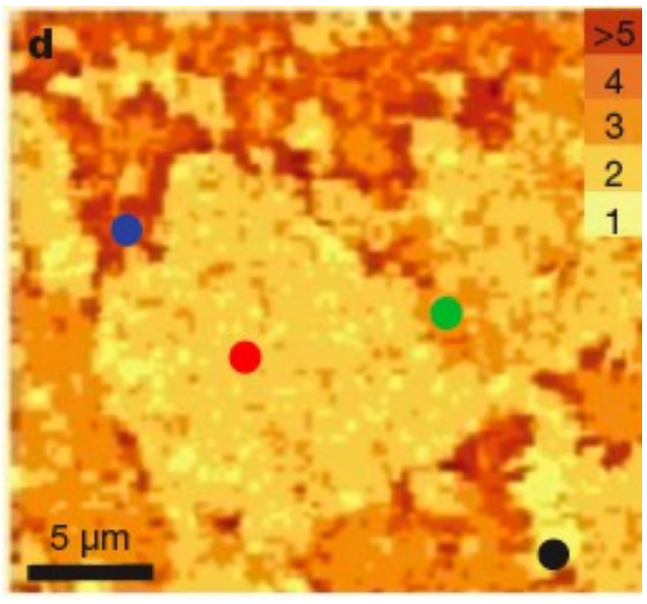
Keun Soo Kim[1,3,4], Yue Zhao[7], Houk Jang[2], Sang Yoon Lee[5], Jong Min Kim[5], Kwang S. Kim[6], Jong-Hyun Ahn[2,3], Philip Kim[3,7], Jae-Young Choi[5] & Byung Hee Hong[1,3,4]

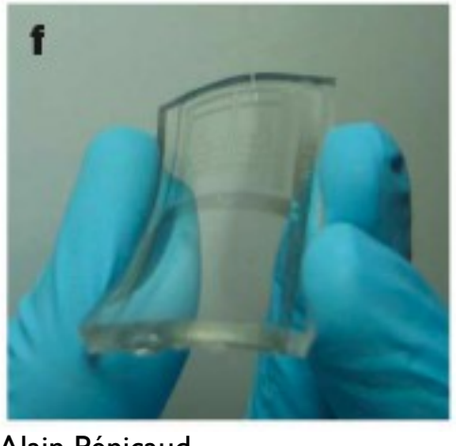
Nature, 14 Janvier 2009

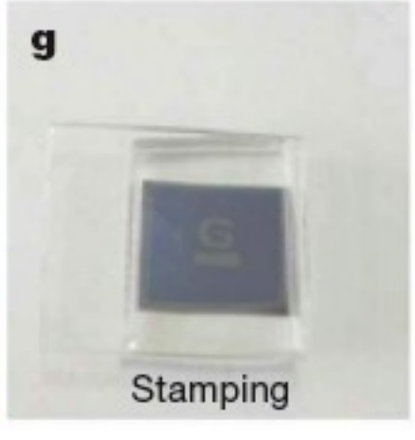


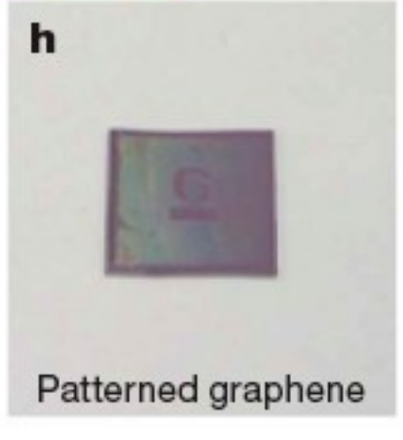


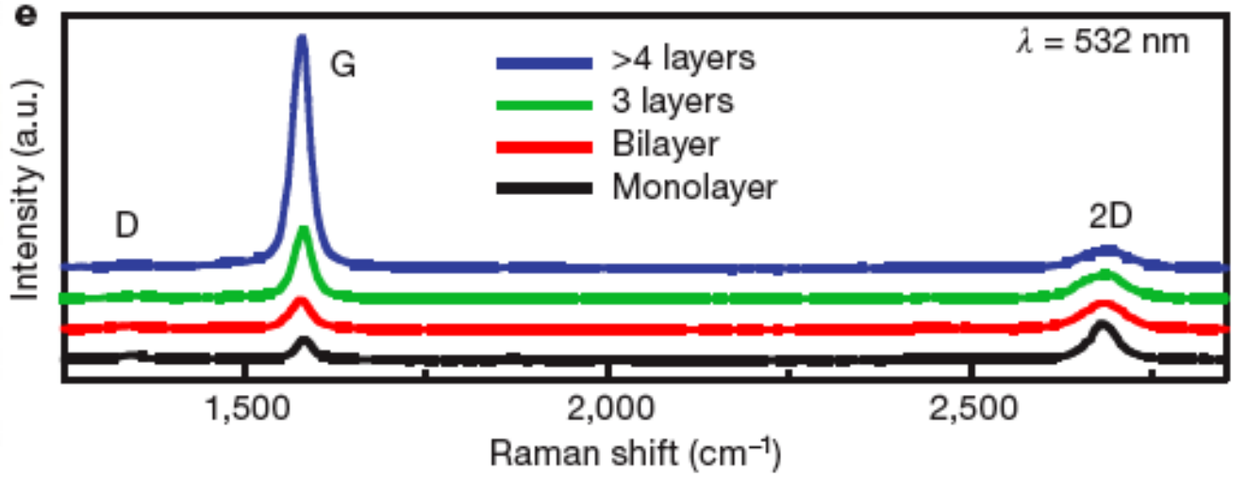


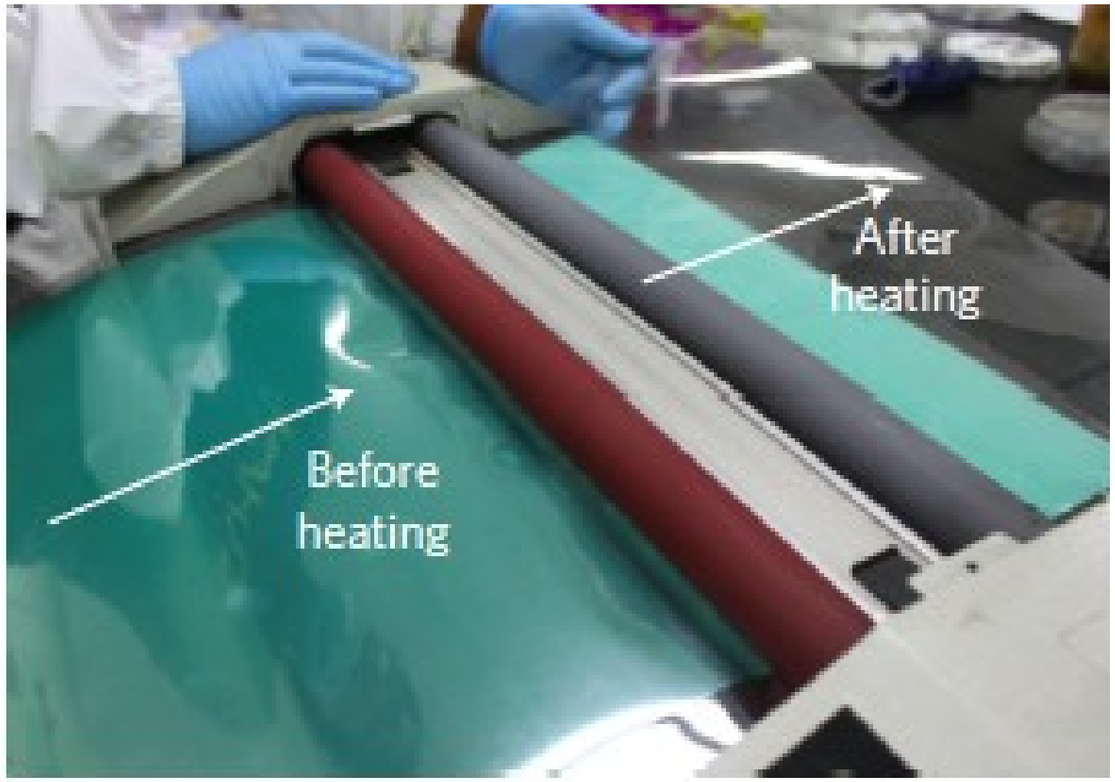












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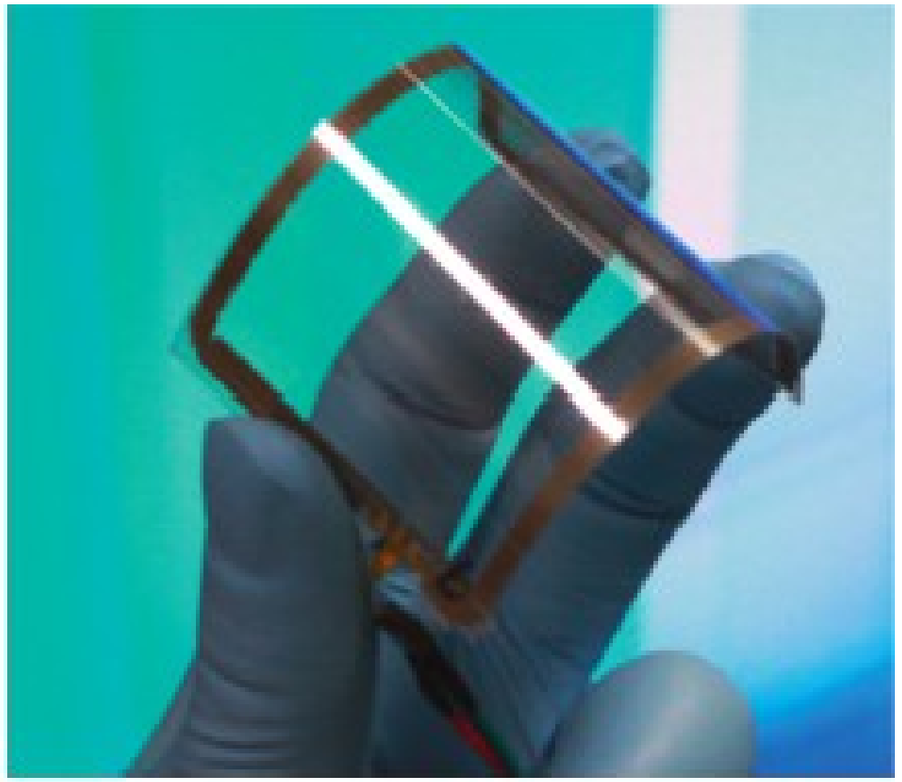

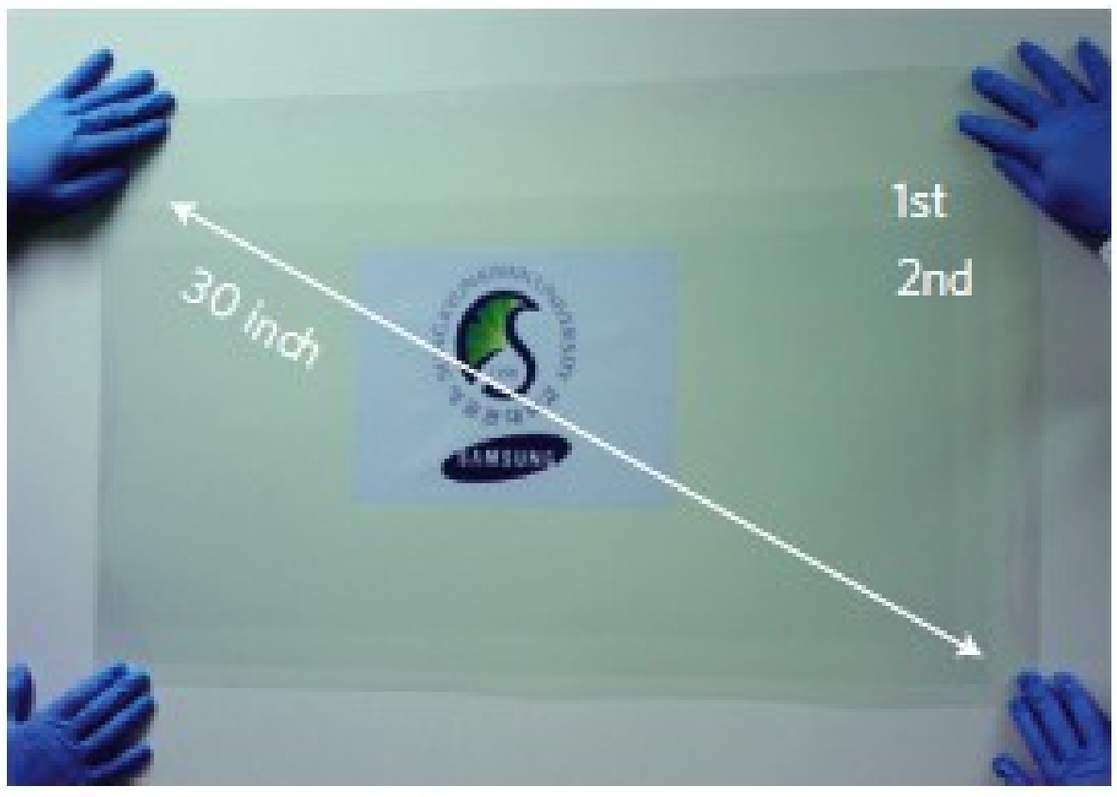

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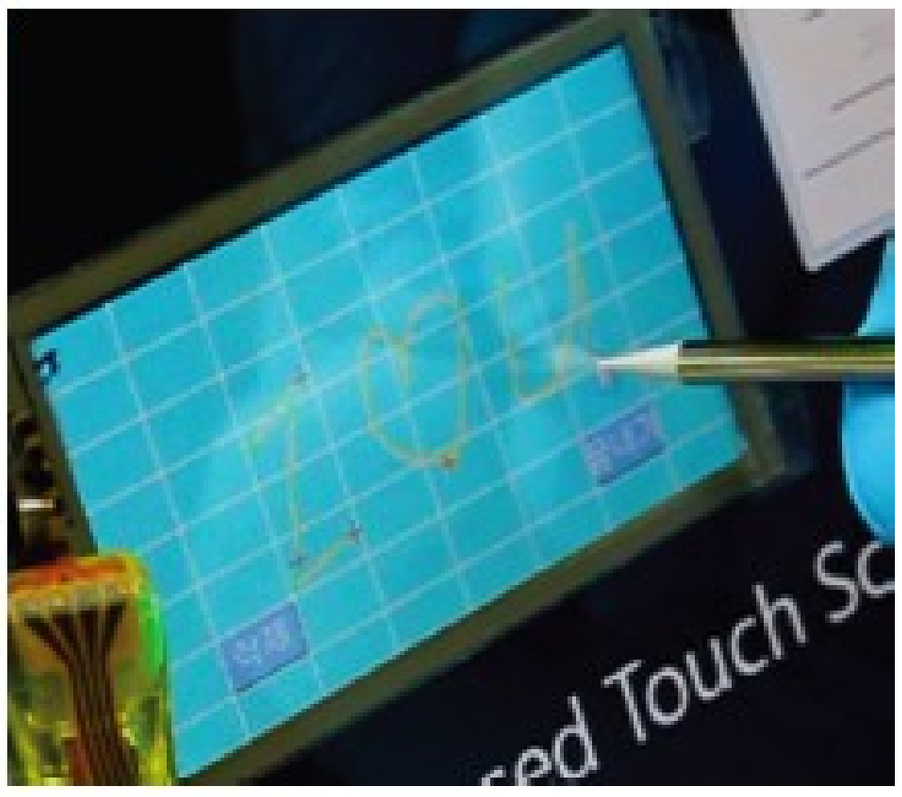
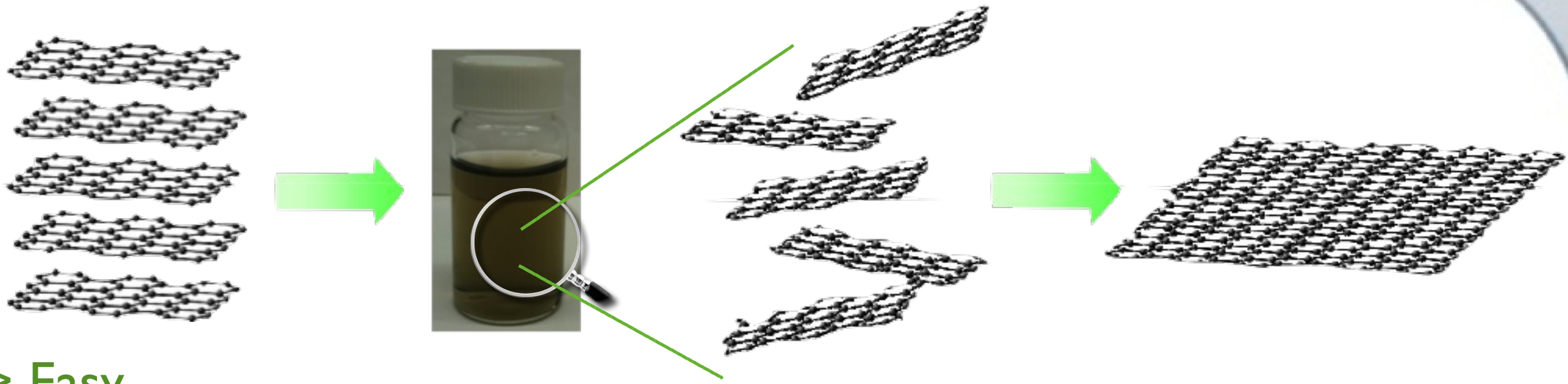
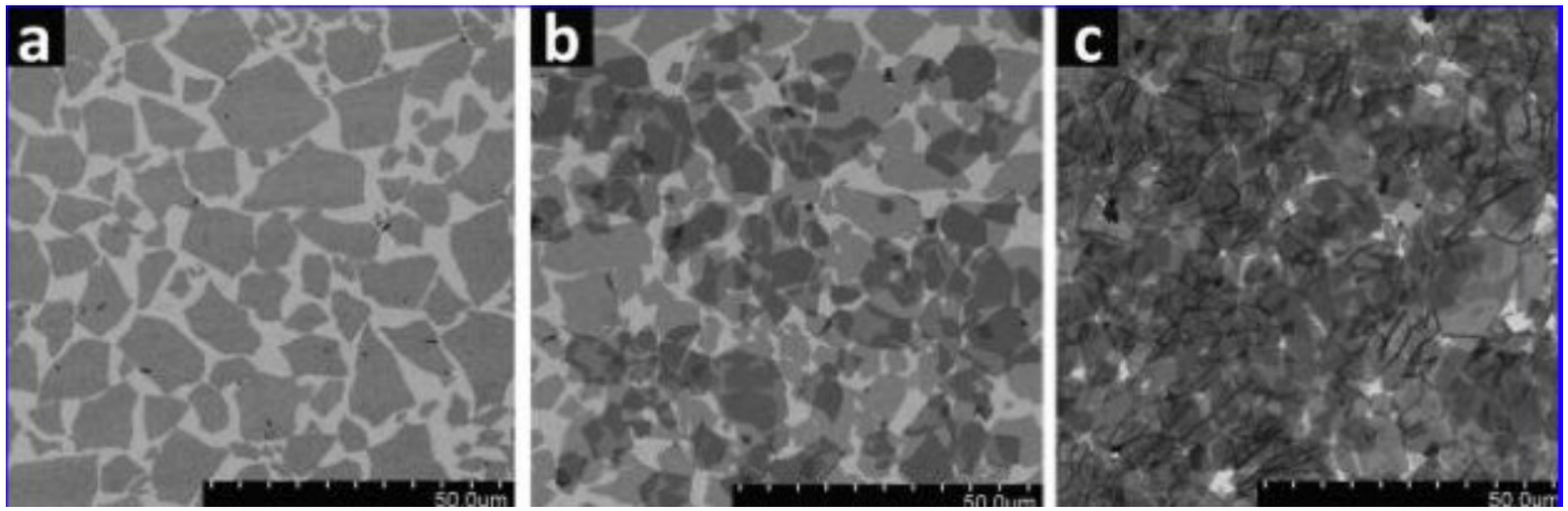


Byung Hee Hong et al., Nature Nanotechnology, 2010

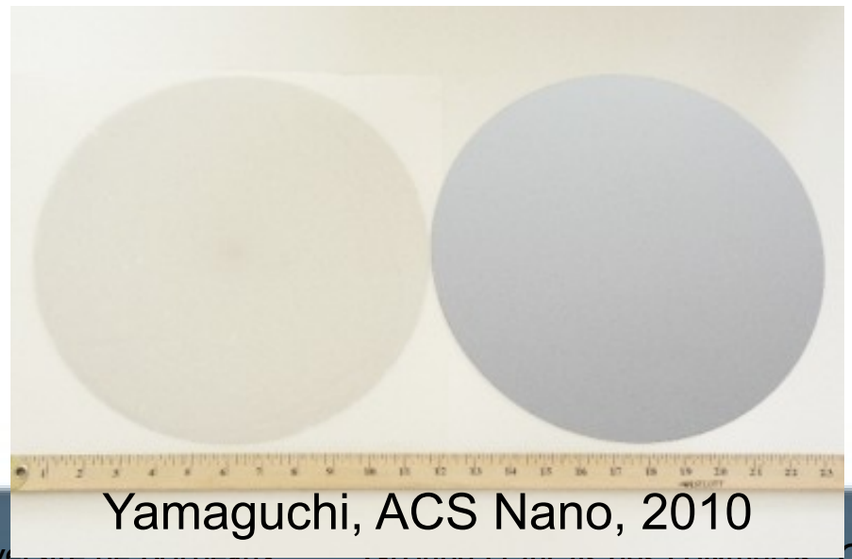
Why solution process?



- > Easy
- > Cheap
- > Large quantity
- > Scalable
- > Chemical modifications



Cote, JACS, 2008



Yamaguchi, ACS Nano, 2010

Which graphite ?

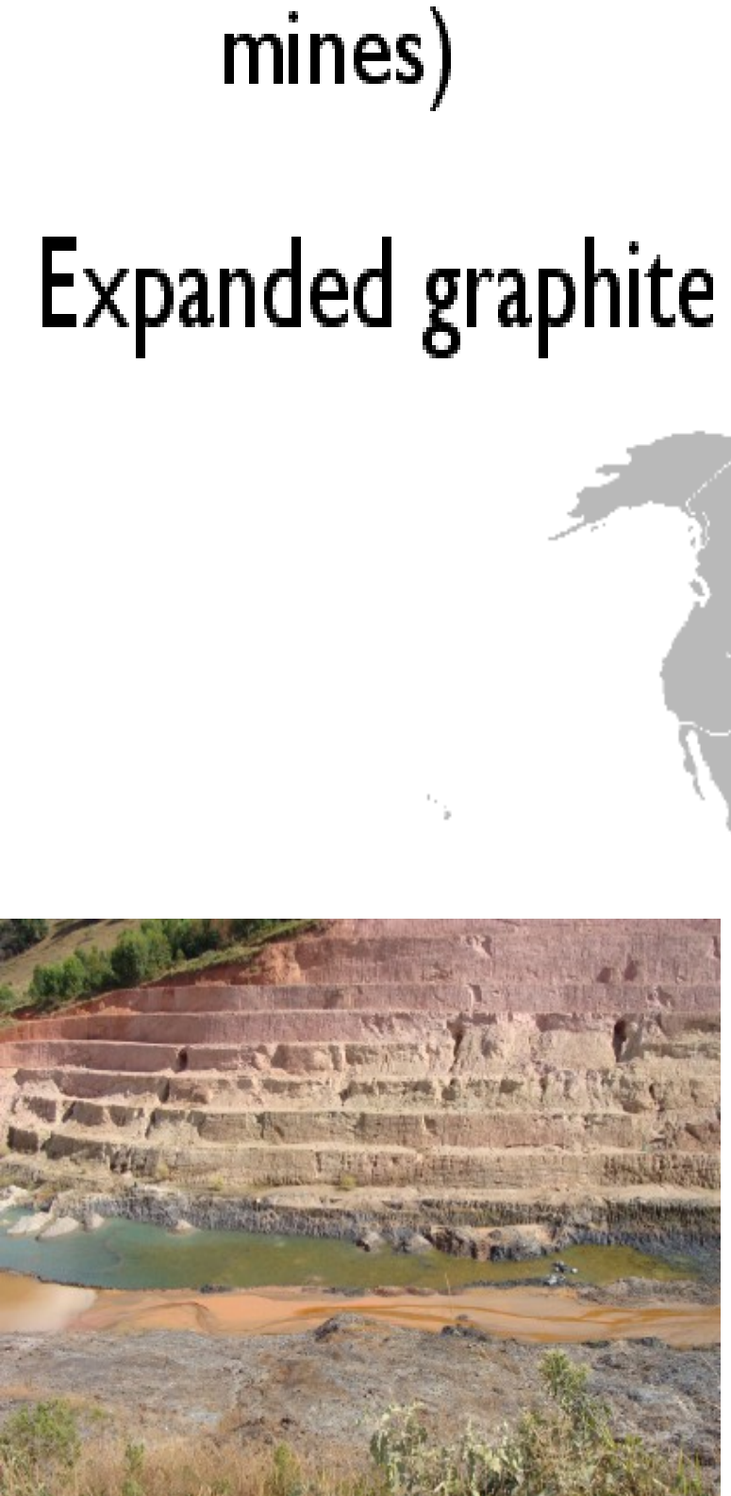
Natural graphite (extracted from mines)

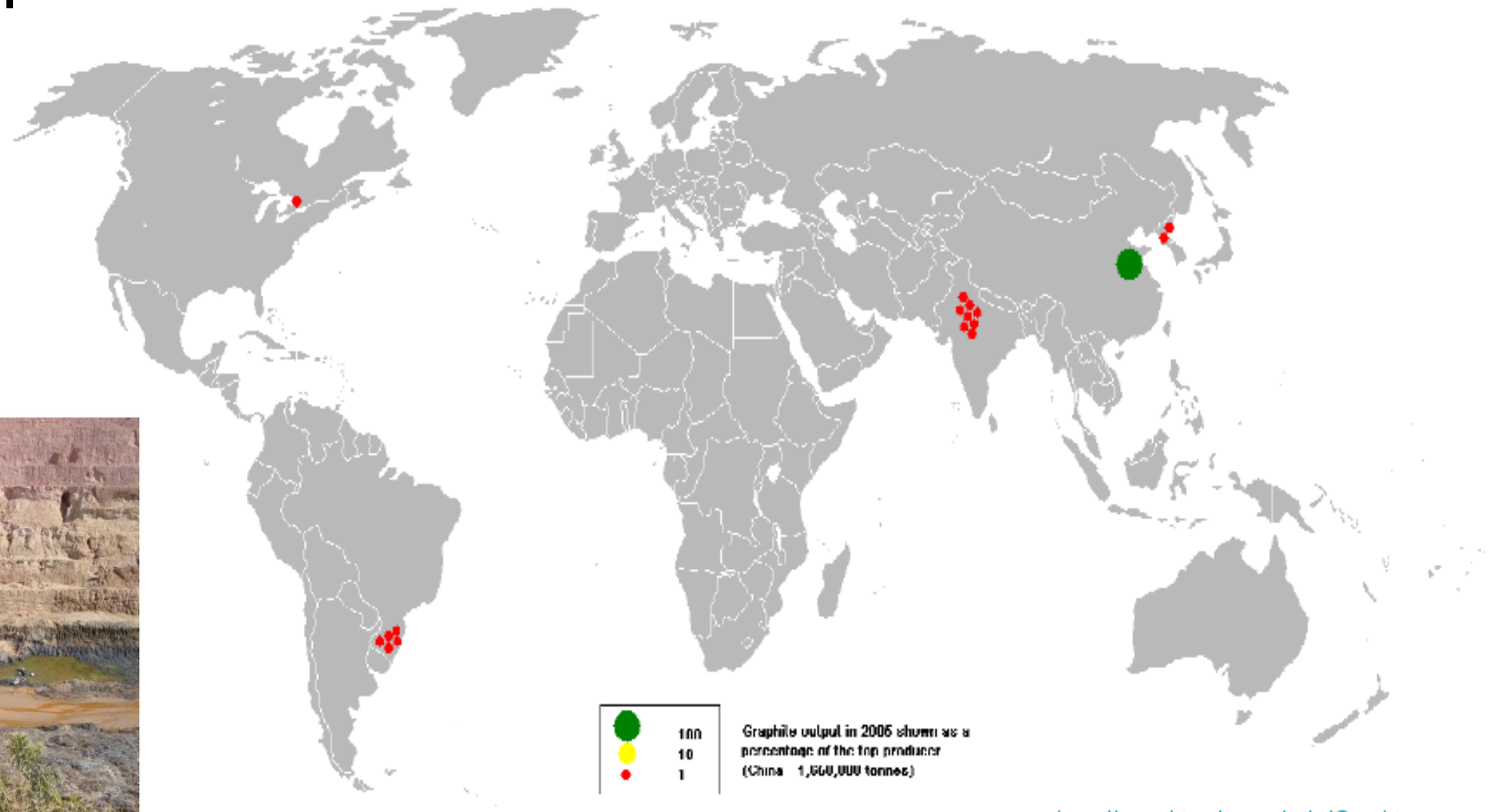
Expanded graphite

Kish graphite (recycled of the steel industry)

Highly Oriented Pyrolytic Graphite (HOPG)

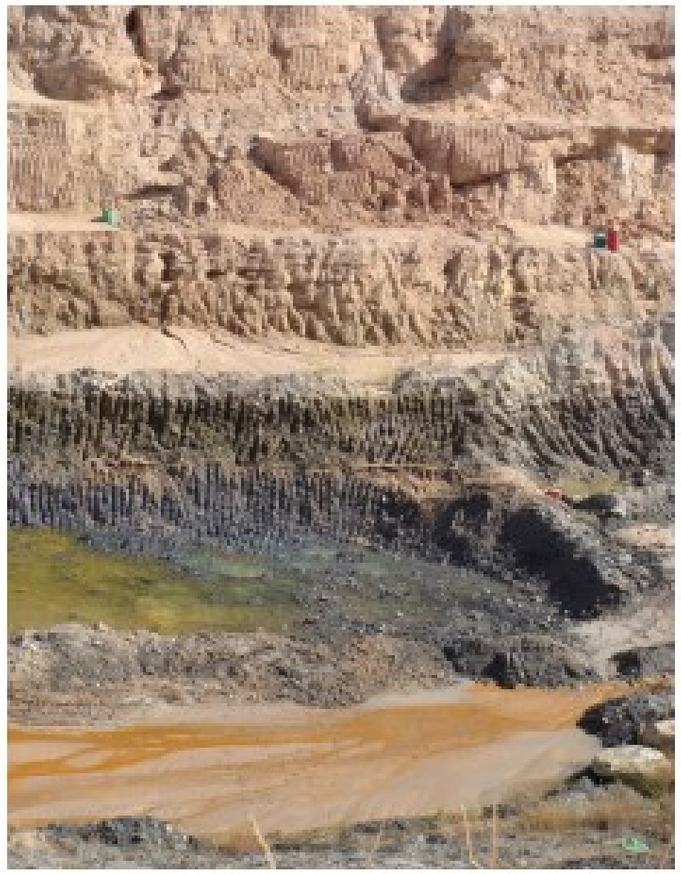
Natural graphite





http://en.wikipedia.org/wiki/Graphite

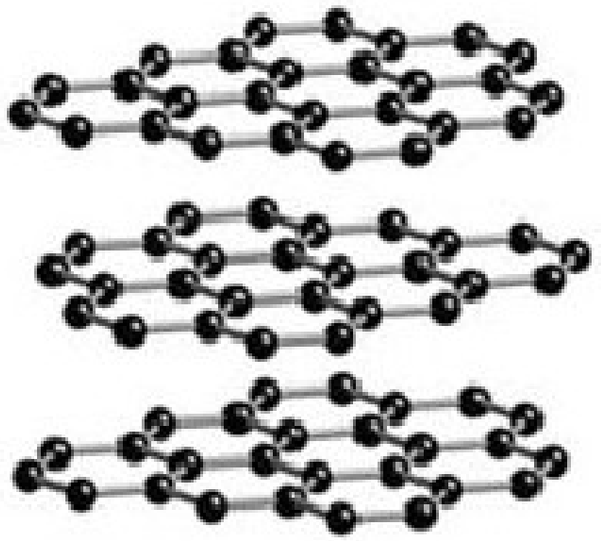
Natural graphite

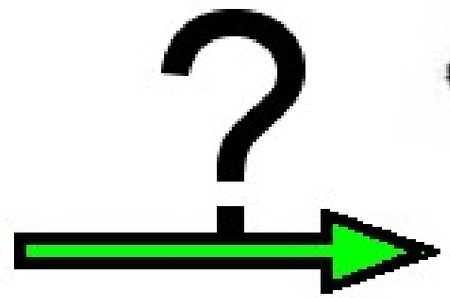


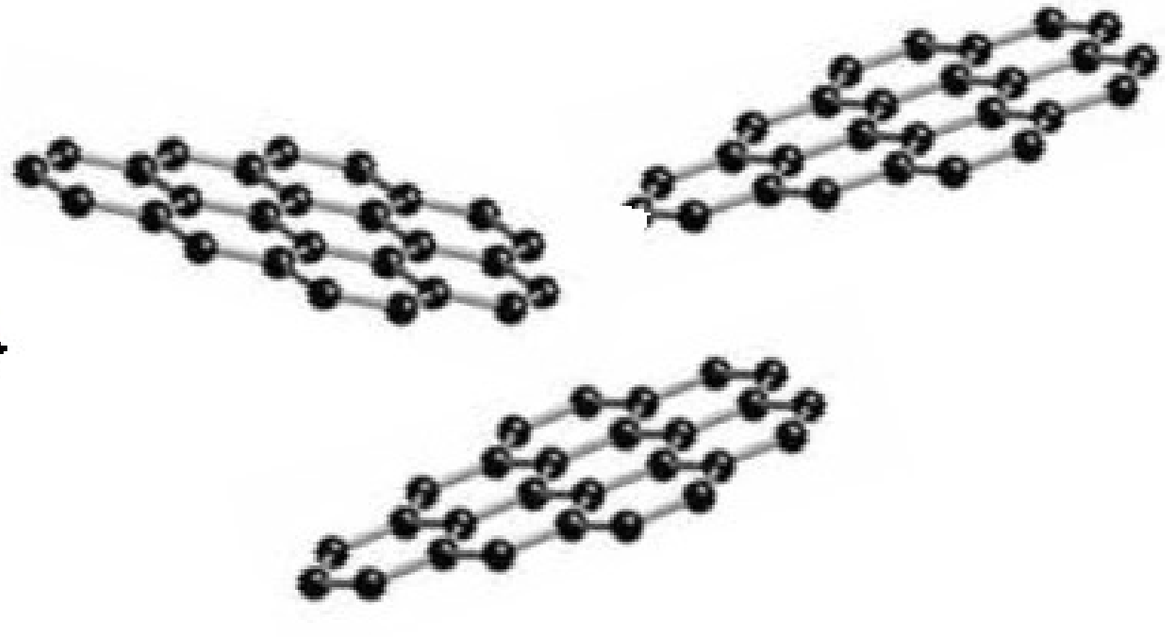
Graphite mine in Minas Gerais, Nacional de Grafite, Brazil,(photo by A. Pénicaud)

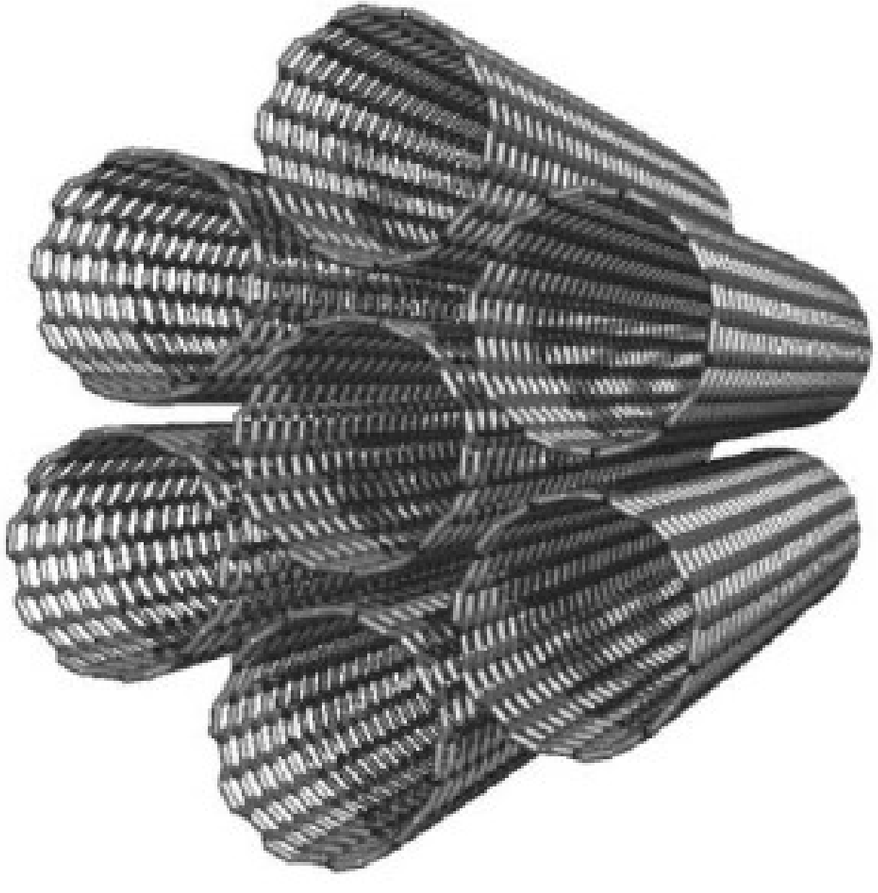
Photo N. Rosas, nacional de Grafite

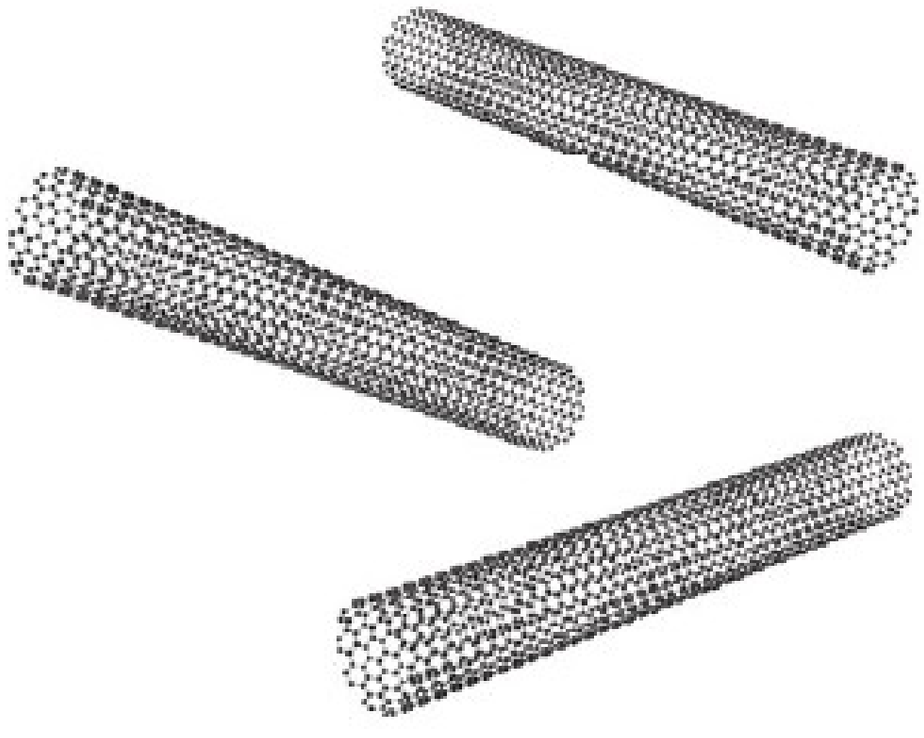
Bags of graphite, Nacional de Grafite, Brazil(photo by A. Pénicaud)







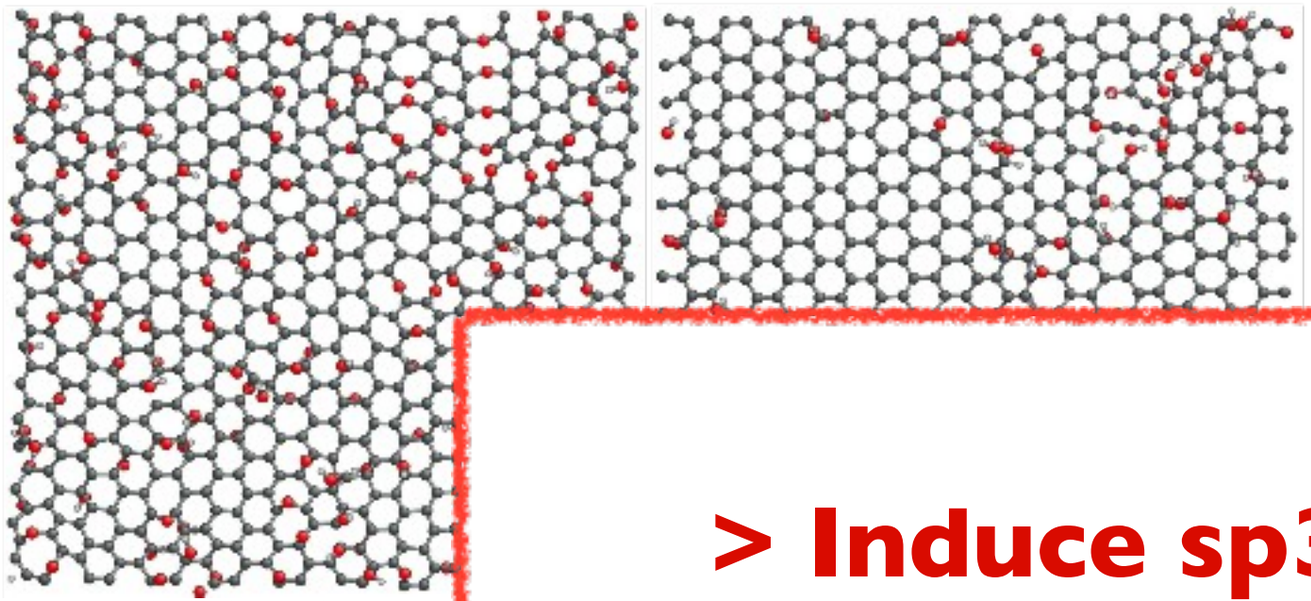




Solution process

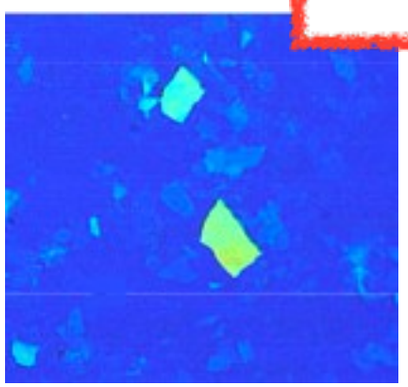
Chemical treatment:

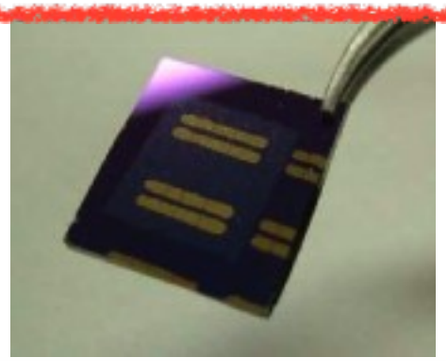
Graphene oxide
(known since 1859!)



GO (25% oxyg

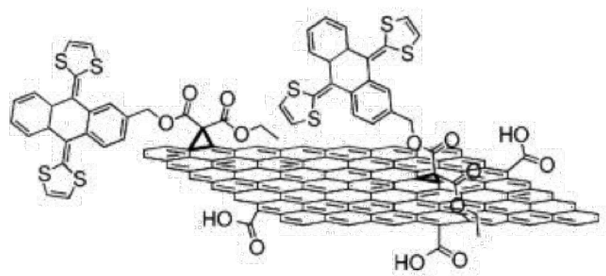
> Induce sp3 defects...

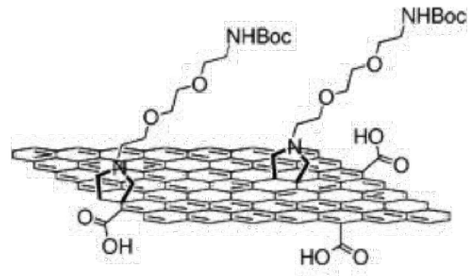




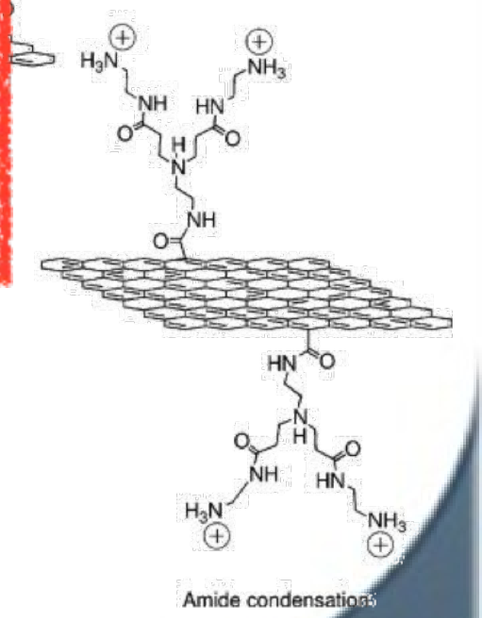
Bagri, Nature Chem, 2010

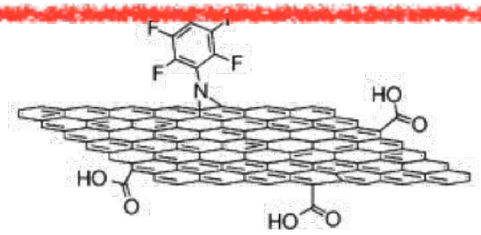
Fonctionalization of dispersed graphene
(based on reactions developped for CNTs)





1,3-dipolar cycloaddition





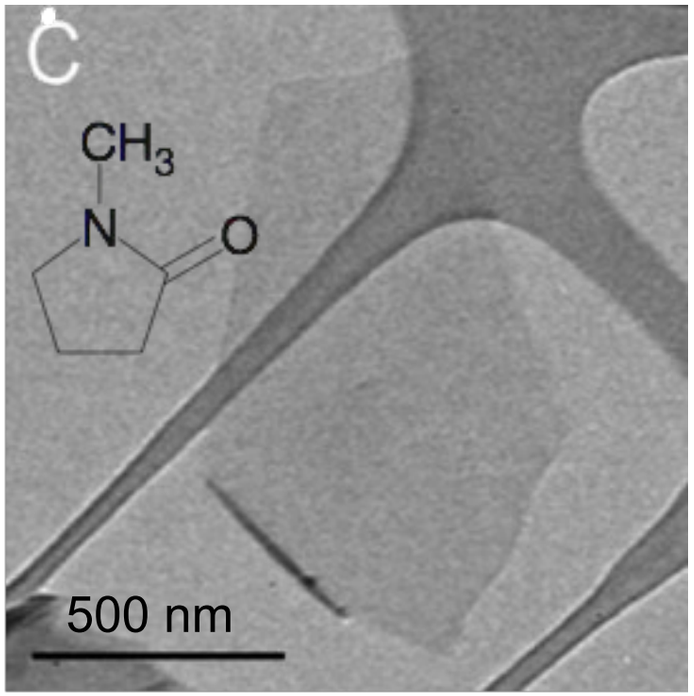
Quintana, Account Chem Resch, 2012

Georgiakilas, Chem Rev, 2012

Solution process

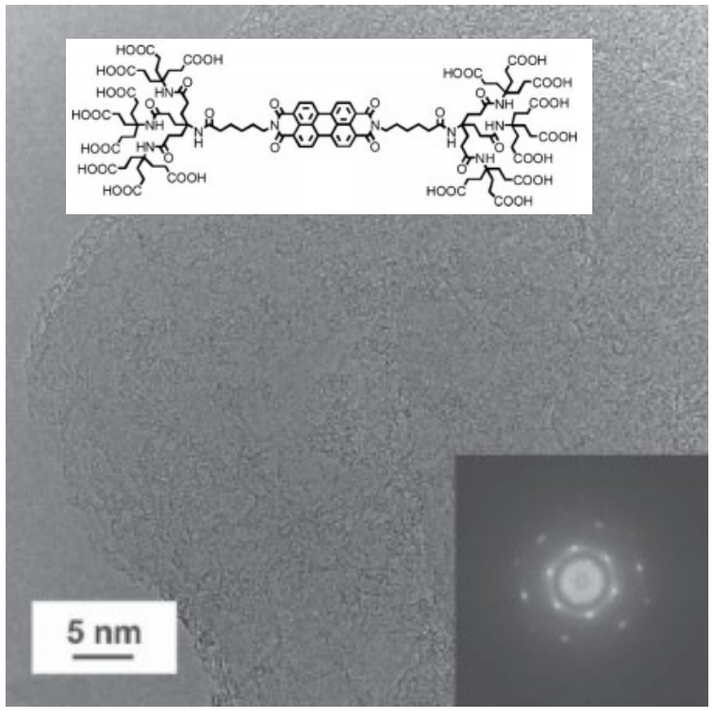
Dispersion:

Organic solvent

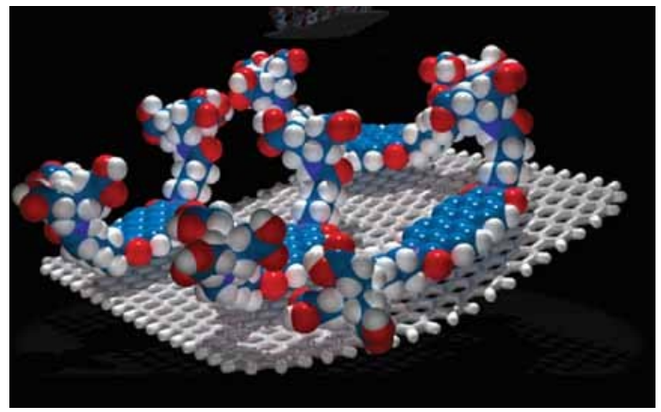


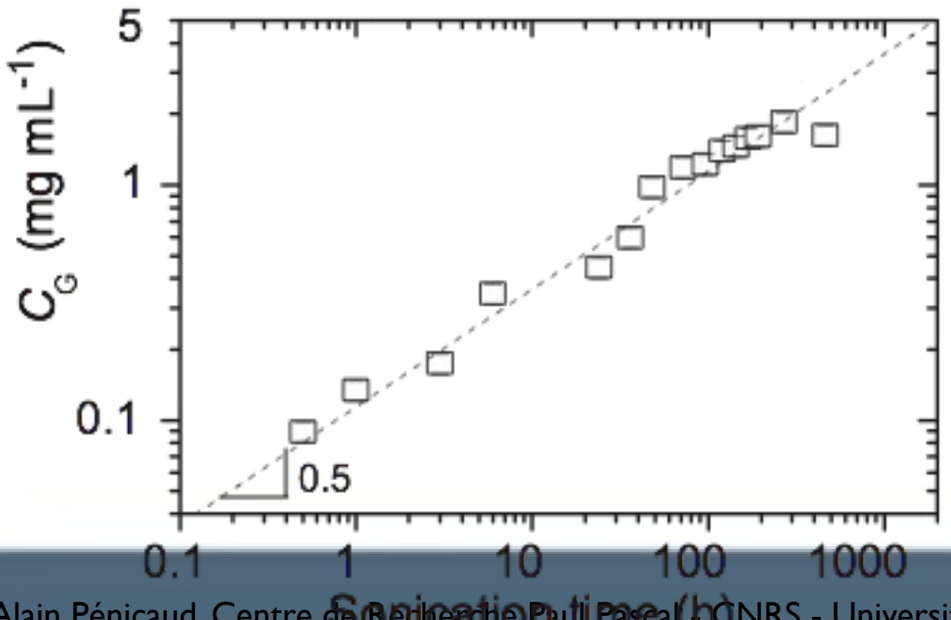
Khan, Small, 2010

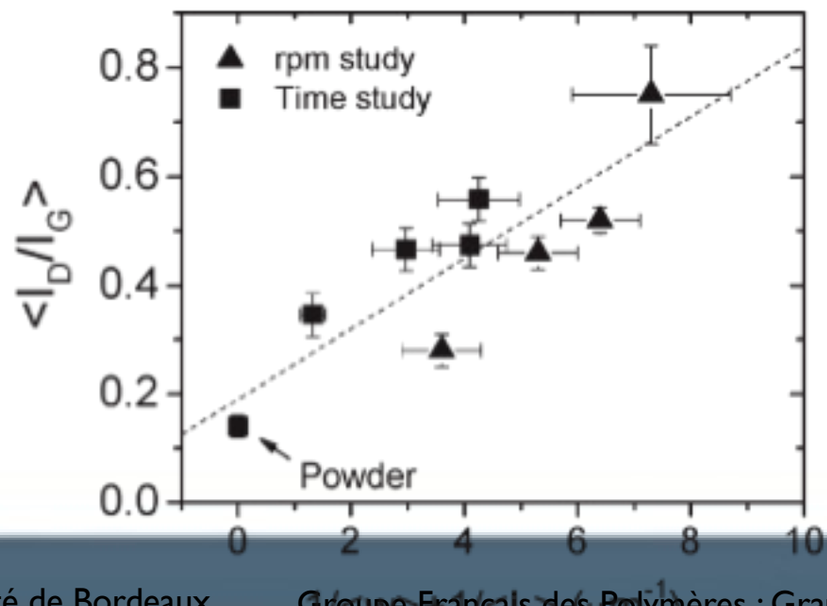
Surfactant



Englert, Adv. Mater., 2009

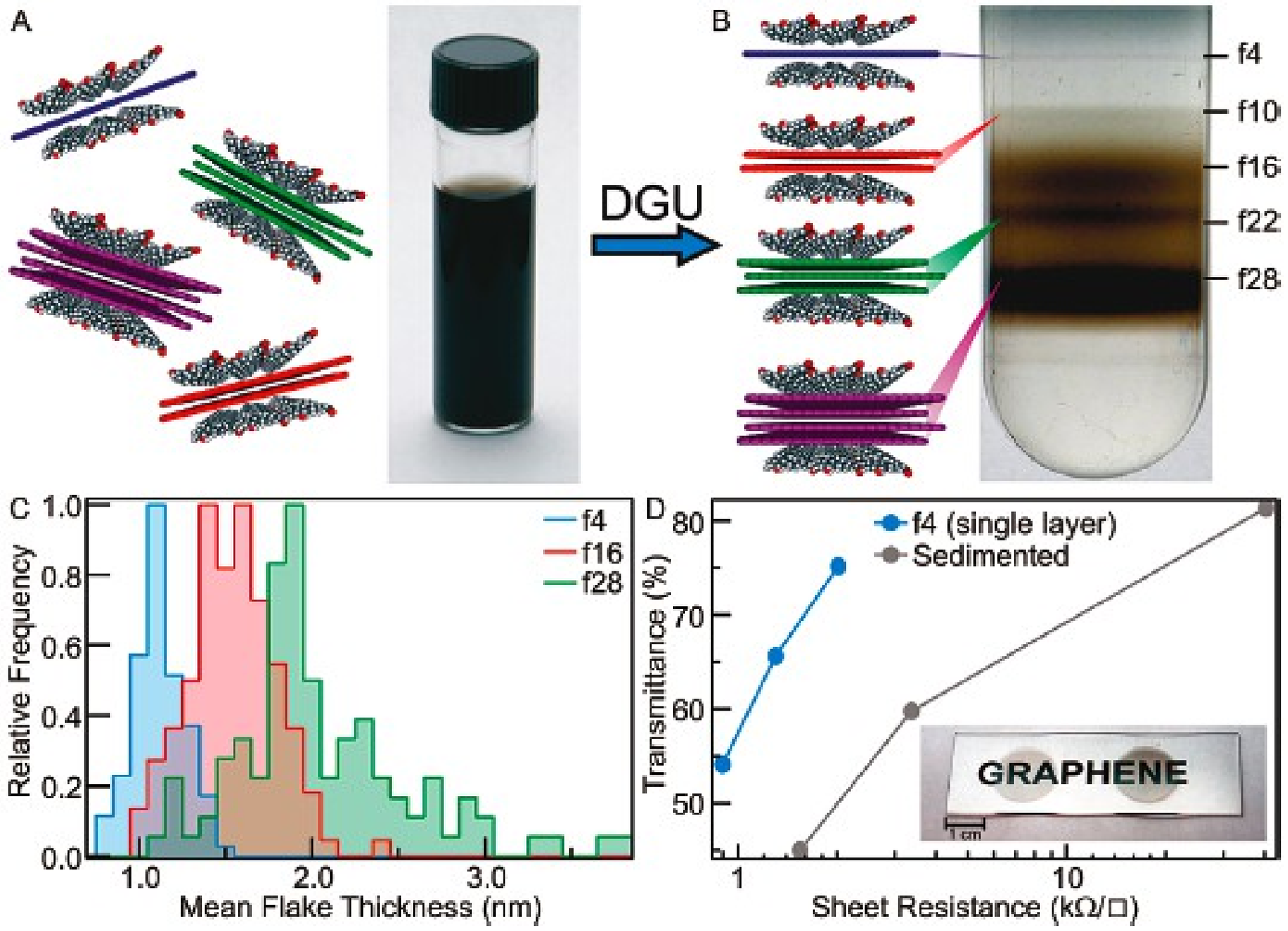






> Strong sonication
>Defects
>Decrease size

Graphene from Graphite



Green and Hersam, J. Phys. Chem. Lett. 2010
Green and Hersam, Nanolett, 2009

Reductive dissolution

Little bit of background....

Reductive dissolution

In the case of carbon nanotubes:

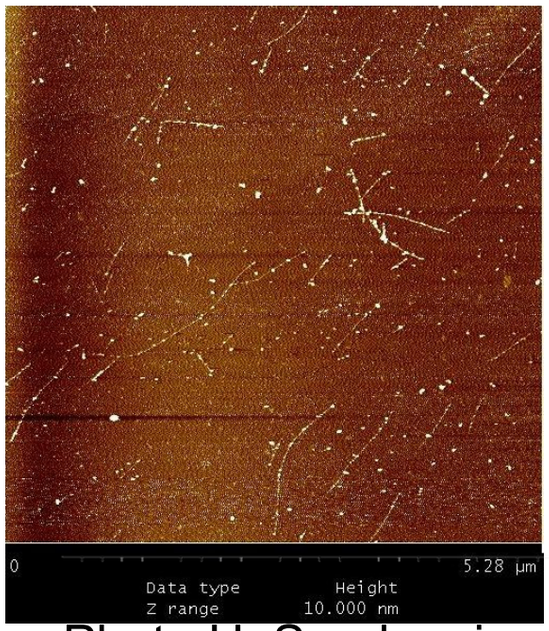
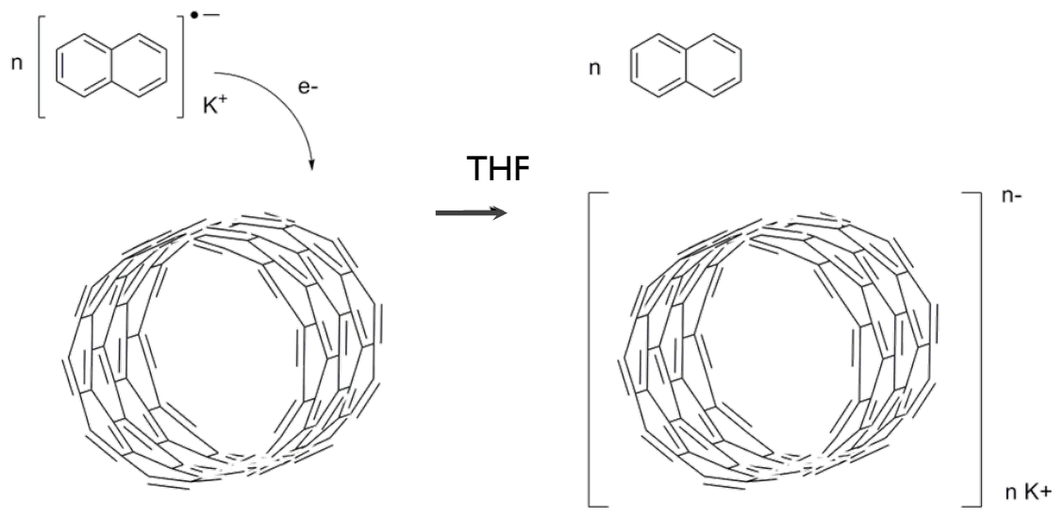
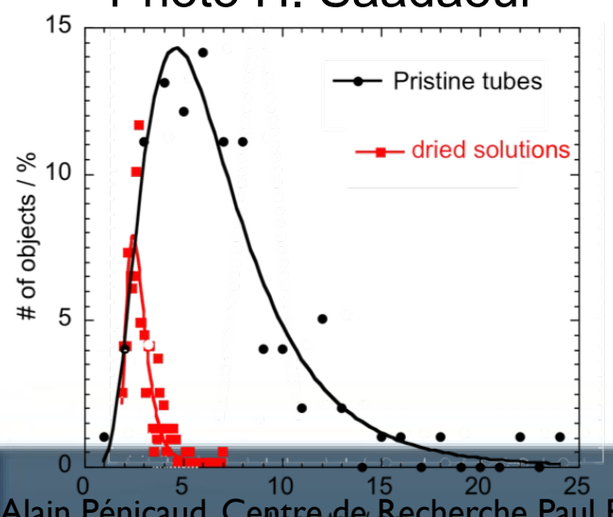
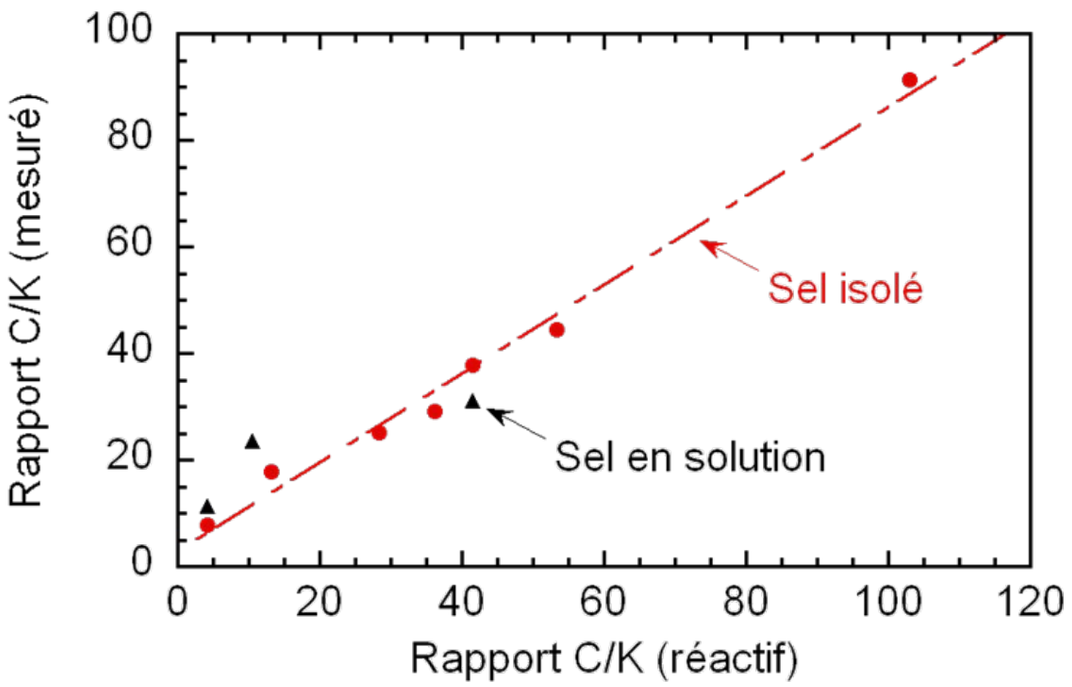
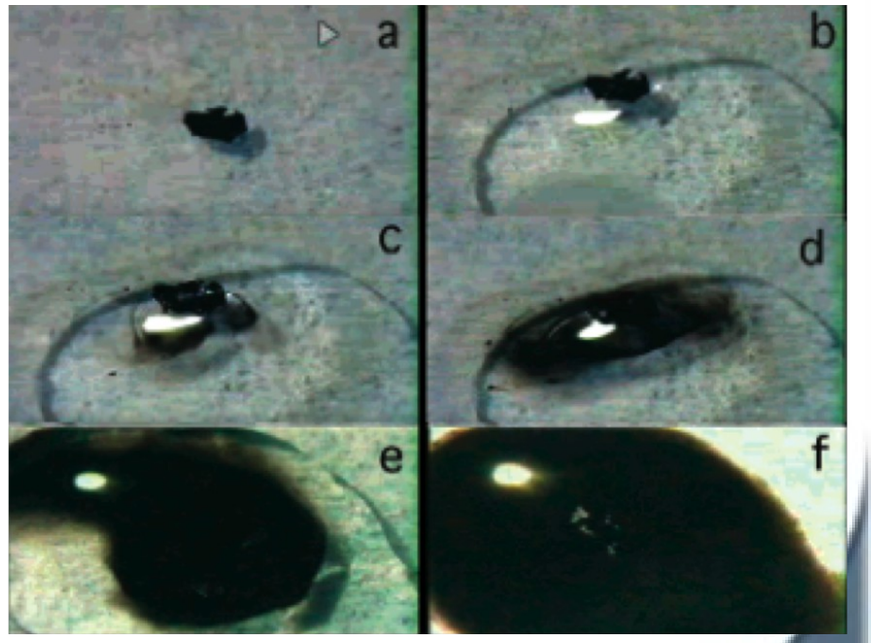


Photo H. Saadaoui





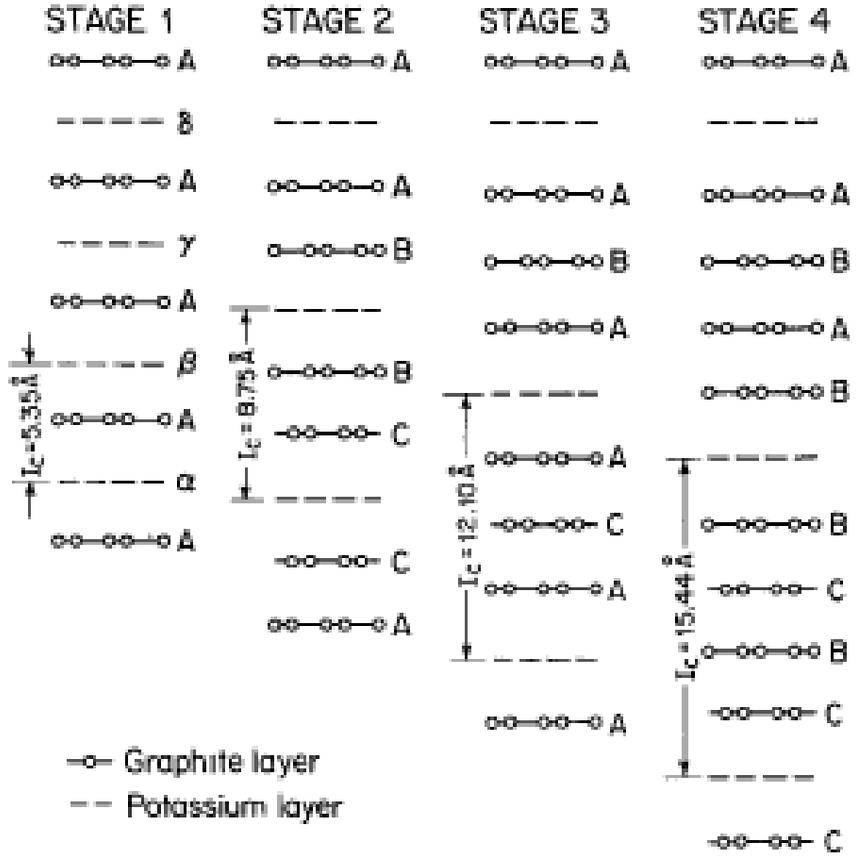


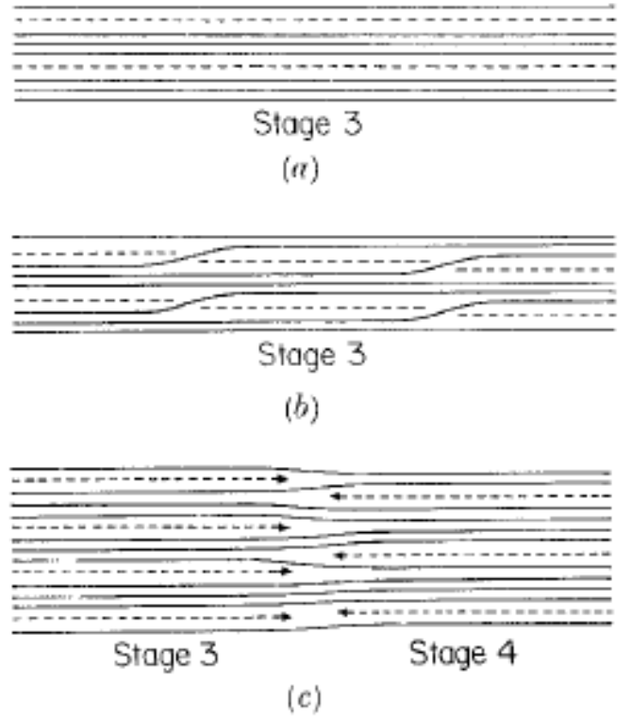


Pénicaud, JACS, 2004

Voiry, J. Mat. Chem., 2010

Graphene from Graphite Intercalation Compounds



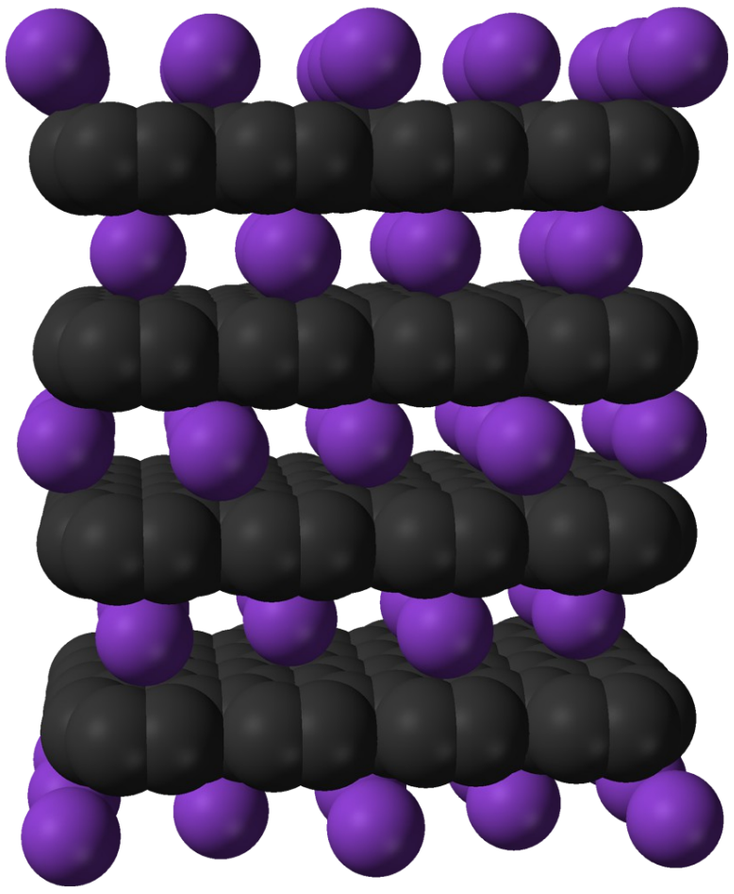


Daumas & Hérold

Graphite Intercalation Compounds

M. Dumas©Marabout

KC_8

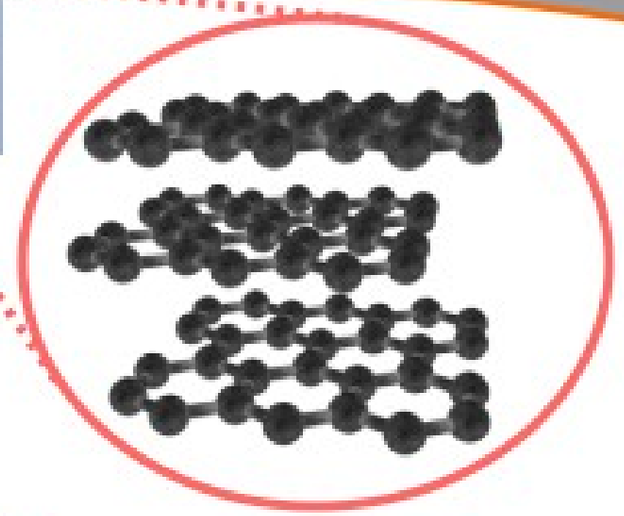


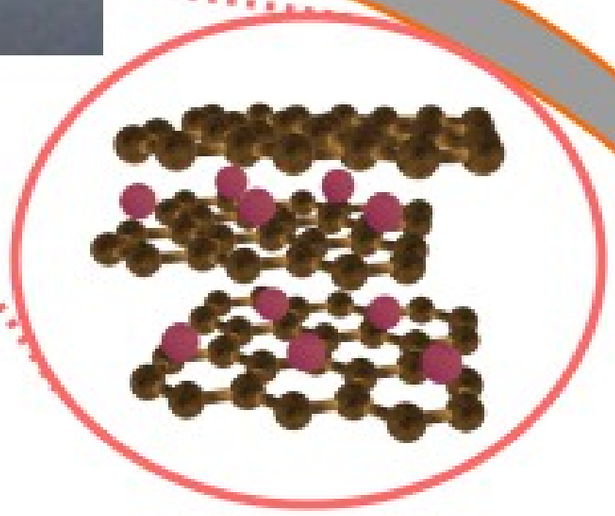
(Image from Wikimedia Commons)
(data from P. Lagrange et al.,
Annales de chimie, 1978)

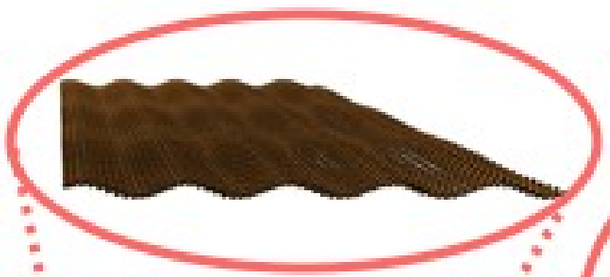
graphite

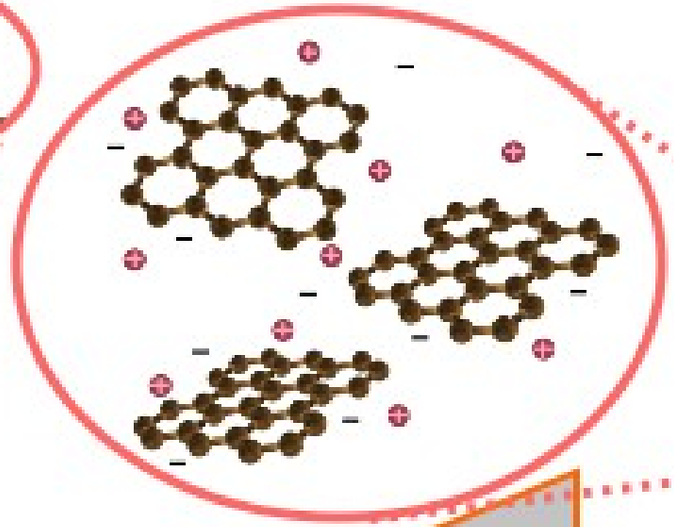
KC_8

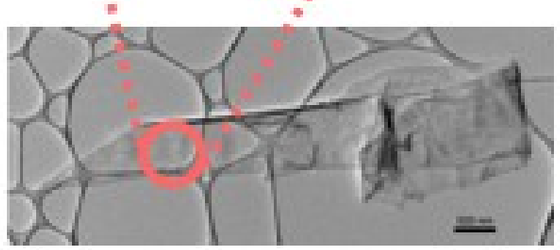
Fredenhagen & Cadenbach, *Z. Anorg. Allg. Chem.* **1926**











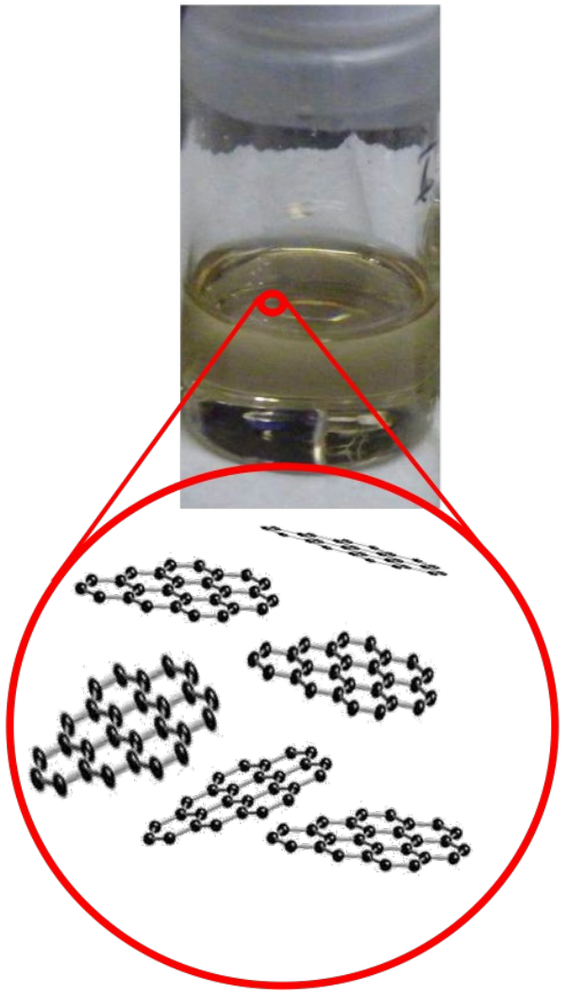
graphene

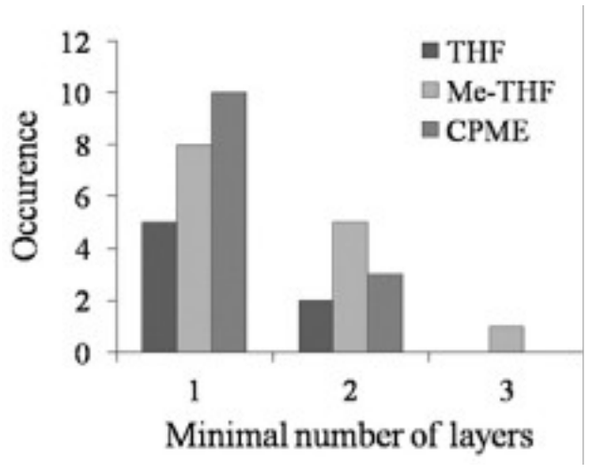
graphenide solution

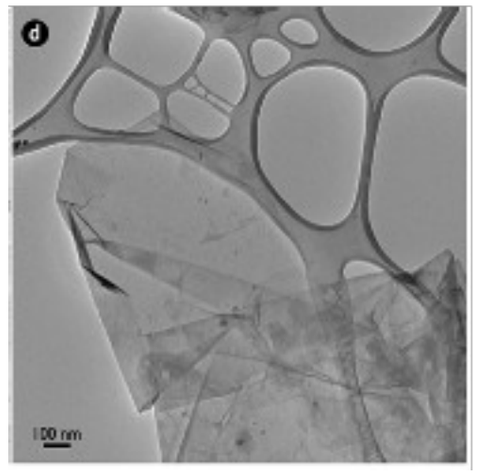
(Up to 0.7 mg/ml)

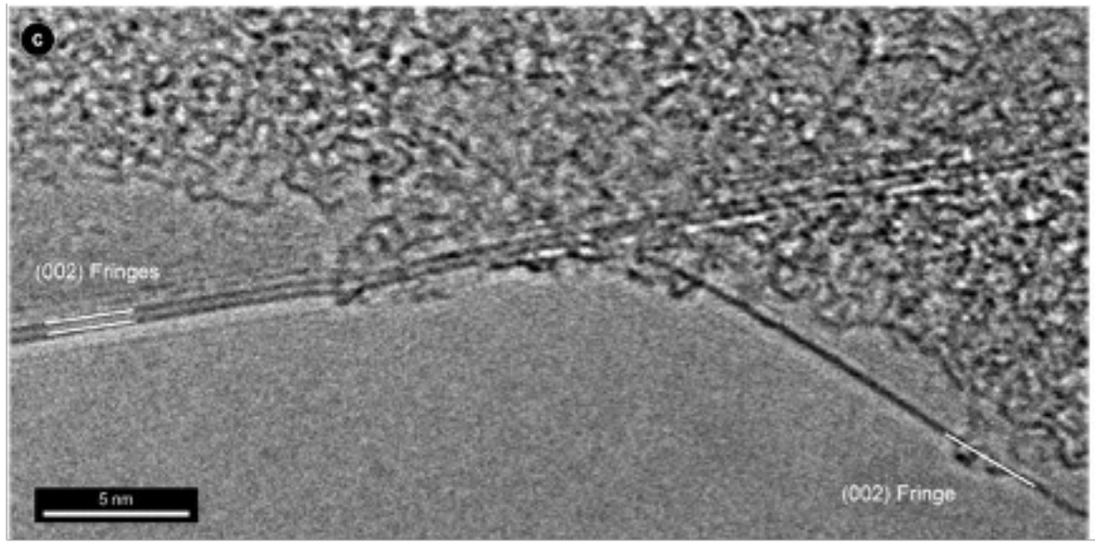
Vallés et al., Patent, 2007, Vallés et al., J. Am. Chem. Soc., 2008, Catheline et al. Chem. Commun, 2011
Catheline et al., Soft Matter, 2012, Pénicaud & Drummond, Accounts of Chemical Research, 2012

Exfoliation of graphene



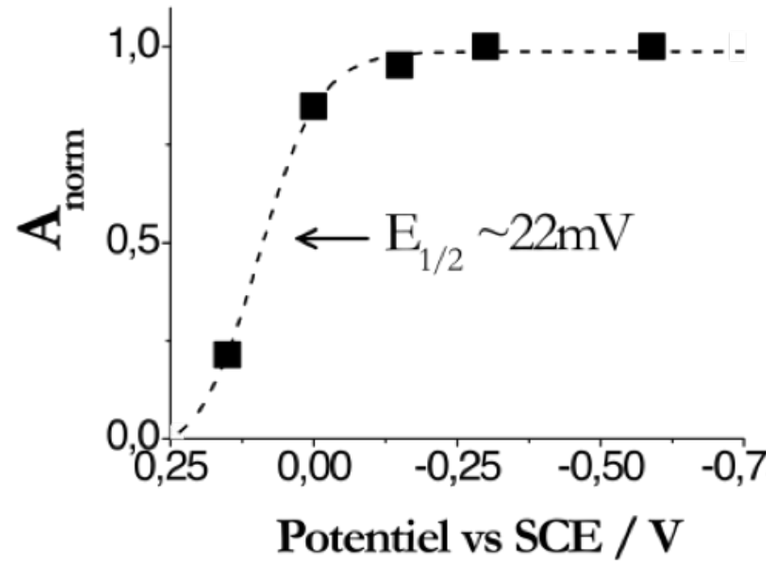


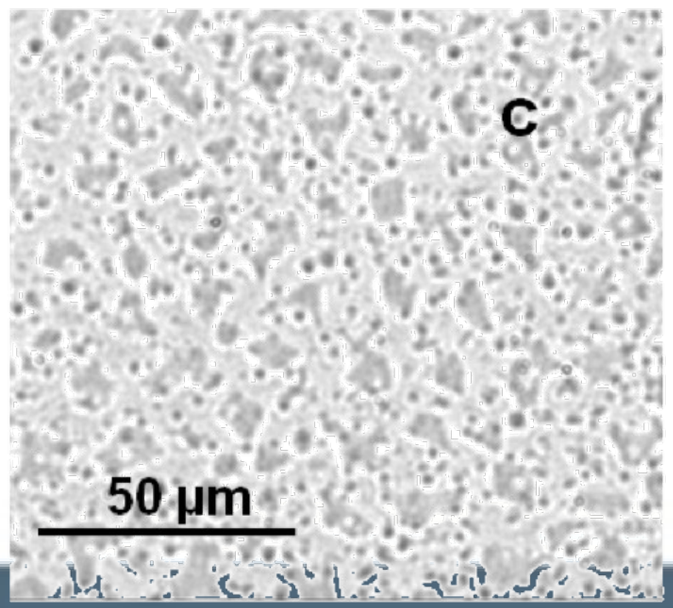


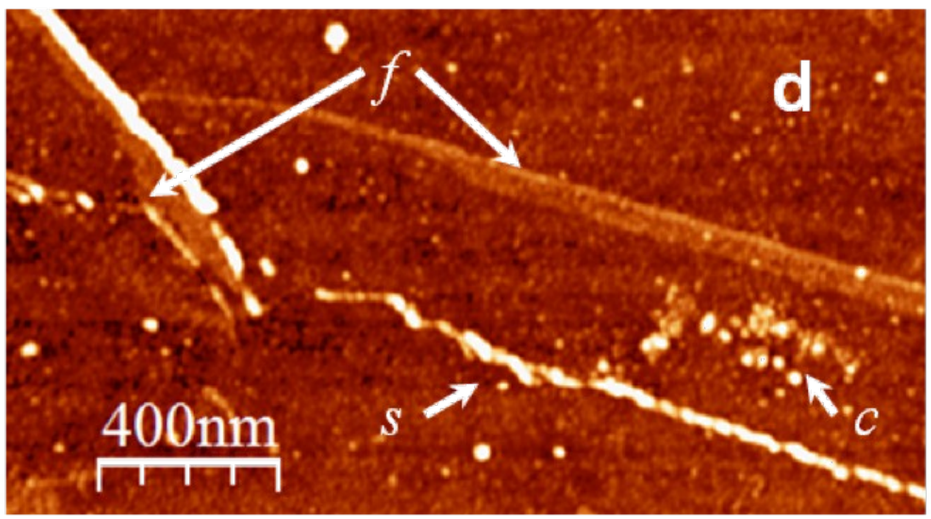


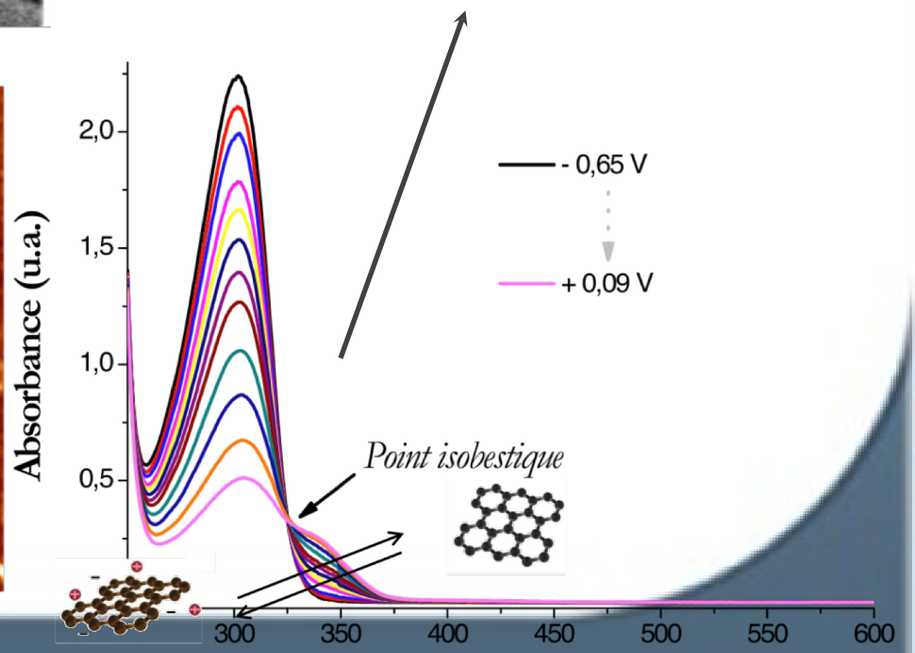
Catheline, Chem. Commun, 2011

Catheline, Soft Matter, 2012









Nature Nanotechnology, Octobre 2009

Selling graphene by the ton

Michael Segal

Small start-up companies are making large volumes of graphene, the world's thinnest material, for applications such as composites and electrodes.

Graphene is, by any measure, a story of extremes. Consisting of a few sheets of carbon atoms, it is the strongest material ever measured[1], it has a thermal conductivity more than double that of diamond[2] and has a charge mobility that is among the highest of any semiconductor[3]. But just as remarkable has been the speed at which this material has moved from the research laboratory to the marketplace.

The exceptional electrical properties of graphene were discovered only five years ago in experiments that involved manually peeling samples weighing picograms from bulk graphite[4]. Today the total production output of various flavours of graphene exceeds 15 tons per year, produced in more than 40,000 square feet of facilities, and this is set to increase to more than 200 tons per year within the next year or two. "We actually have a company asking the question right now, 'When will I get 5 tons?'" says Bor Jang, the chief executive officer of Angstron Materials, which is based in Dayton, Ohio. "We can't produce enough."

"The graphene is already there — all you have to do is peel it off."
Bor Jang

A shipment of Vor-x — a functionalized graphene ready to be sent to a development partner.

The use of acids can lead to oxidation of the graphite, and Vorbeck has licensed an approach developed at Princeton University[5,6] to convert graphite oxide into manufactured will not end up in advanced devices such as transistors. Instead, most applications fall into two broad and not always exclusive categories: composites and electrodes. Composites consist of graphene dispersed into a host matrix, and take on some of the properties of graphene as a result. These may include strength, stiffness, and electrical or thermal conductivity. For example, some containers used to store and transport volatile fuels are made from polymer or rubber composites. Incorporating graphene would increase their stiffness by an order of magnitude, and allow them to conduct electrical currents, reducing the probability of electrical discharges and increasing safety.

Similarly, packaging made from a graphene composite could shield electronics from radio frequency signals, conduct current to external devices or even store information. Vorbeck is focusing on printable conductive inks (a distinct class of composites), for applications in printed electronics such as radio-frequency identification tags, low-resolution displays and backlights, sensors, flexible connectors and packaging. Graphene makes these inks both highly conductive and easy to process.

Graphene-based electrodes take advantage of the material's electrical conductivity, transparency and surface area. One attractive target is the replacement of indium tin oxide.

What is graphene?

Although the International Union of Pure and Applied Chemistry (IUPAC) defines graphene as a single layer of carbon atoms researchers routinely talk of bilayer, trilayer bilayer, trilayer and multilayer graphene the definition further still, to include any any highly exfoliated graphite product uses predominantly single-layer graphene

ChemonTubes 2012

The “Nanotube and Graphene” team of CRPP

Amélie Catheline, **Damien Voiry**, Sandra Enriquez, **Yu Wang**, Fabienne Dragin, Elisa Del Canto, Kai Huang, **Carlos Drummond, Cécile Zakri** (CRPP)
Eric Anglaret (Montpellier), **Pascal Puech, Marc Monthioux** (Toulouse)
Luca Ortolani, Vittorio Morandi (CNR Bologna)
F. Paolucci, M. Iurlo, M. Marcaccio, S. Rapino, G. Valenti (Bologna)

ChemOnTubes 2014

March 30th - April 3rd, 2014

Riva del Garda, Italy

International Meeting on the Chemistry of Graphene and Carbon Nanotubes

Scope

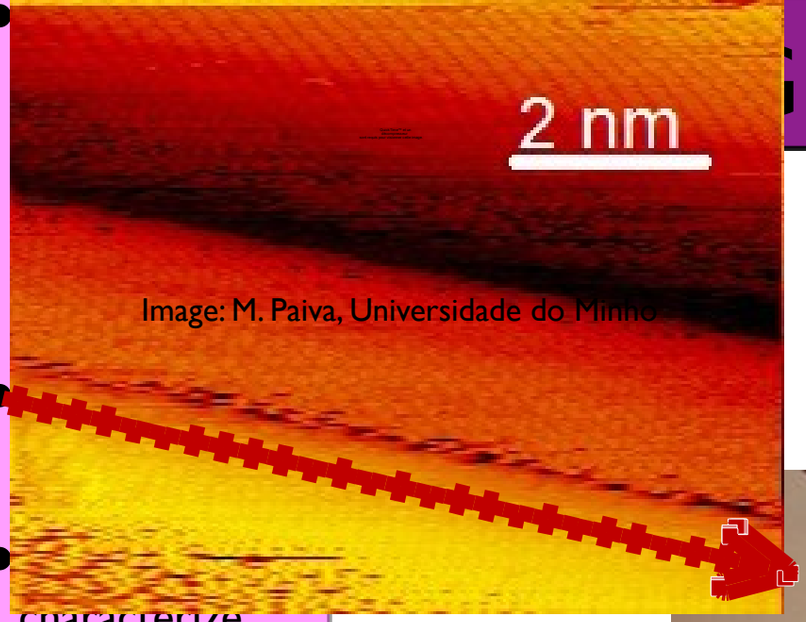
All sessions will be devoted to both graphene and carbon nanotubes

- Functionalization, dispersion, sorting
- Electrochemistry, devices
- Composites, foams, coatings
- Energy storage, conversion, harvesting
- Nanomedicine, biomaterials
- Functional materials
- Catalysis, filtration, membranes
- Organic electronics

Abstract submission deadline: December 12th, 2013
Registration deadline: January 31, 2014

Contact : ChemOnTubes@crpp-bordeaux.cnrs.fr

Graphene from carbon nanotubes



characterize them?

- Graphene from Graphite
- Graphene from GICs
- Graphene from carbon nanotubes
- Graphene from molecular precursors
- Ton-scale graphene

Industry has extended not only the definition of graphene, but also its history, questioning the claim that it is a new material. "The original synthetic work for graphene goes back into **the late 1800s** says Hahn. "It is hard to look at graphene and say it is a new material." This early work focused on intercalated or lamellar compounds of graphite, and by 1970 single layer graphene on nickel substrates, called monolayer graphite, had been isolated[9,10].

Graphene from carbon nanotubes

- Semantics: graphene, graphene nanoribbons, nanographene,
- Why chemical routes? What for?
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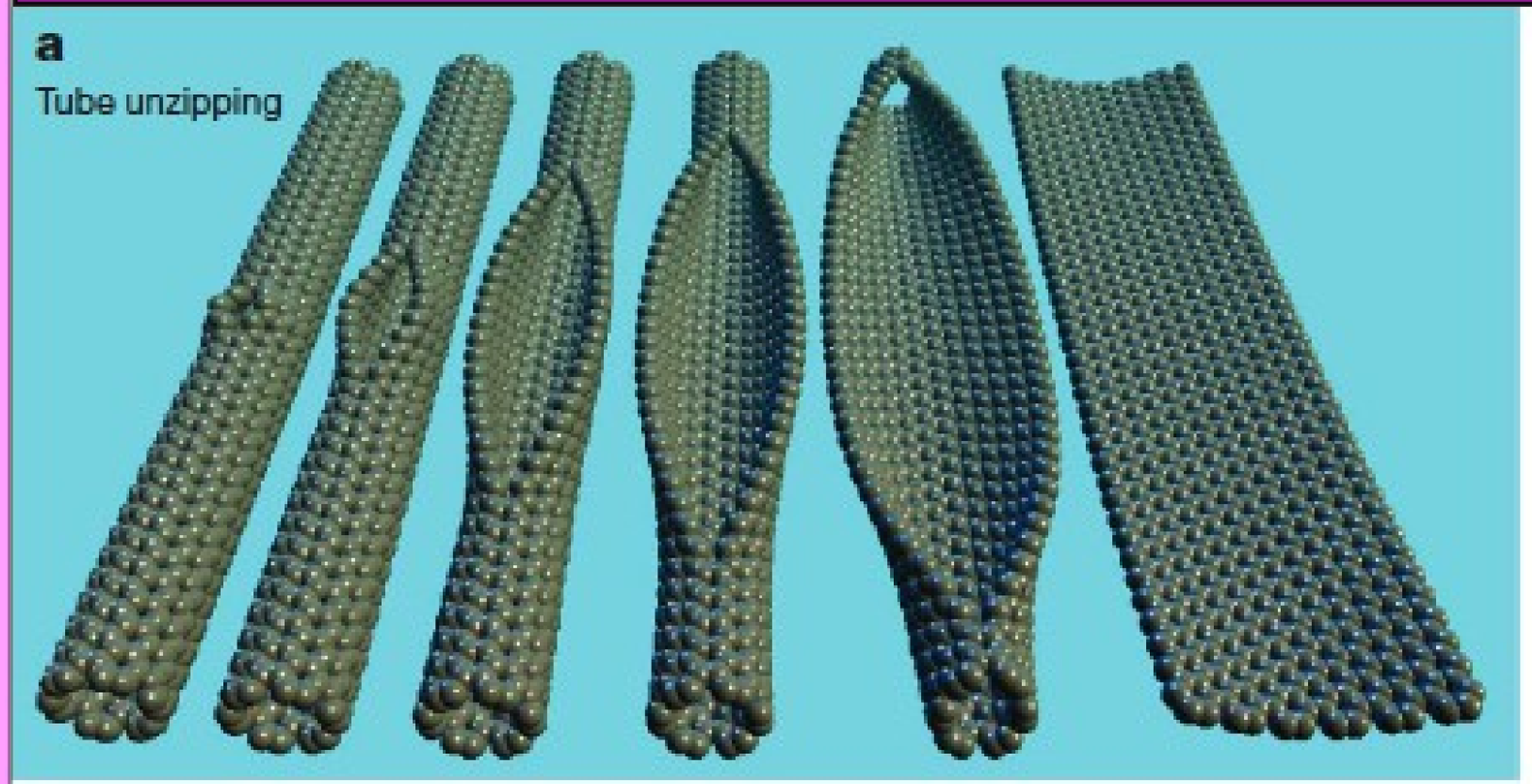

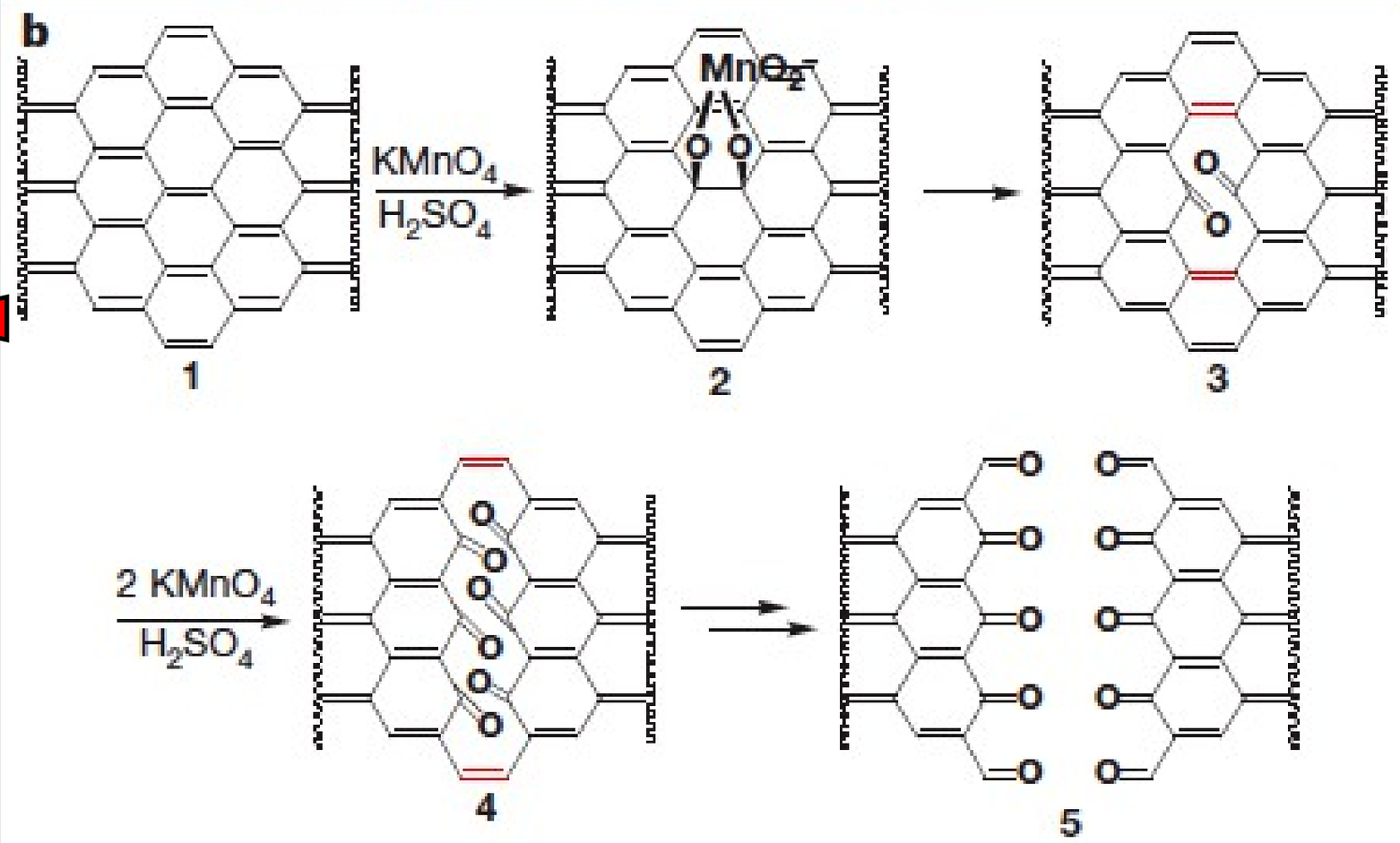

SEM image

Tour et al. nature 2009

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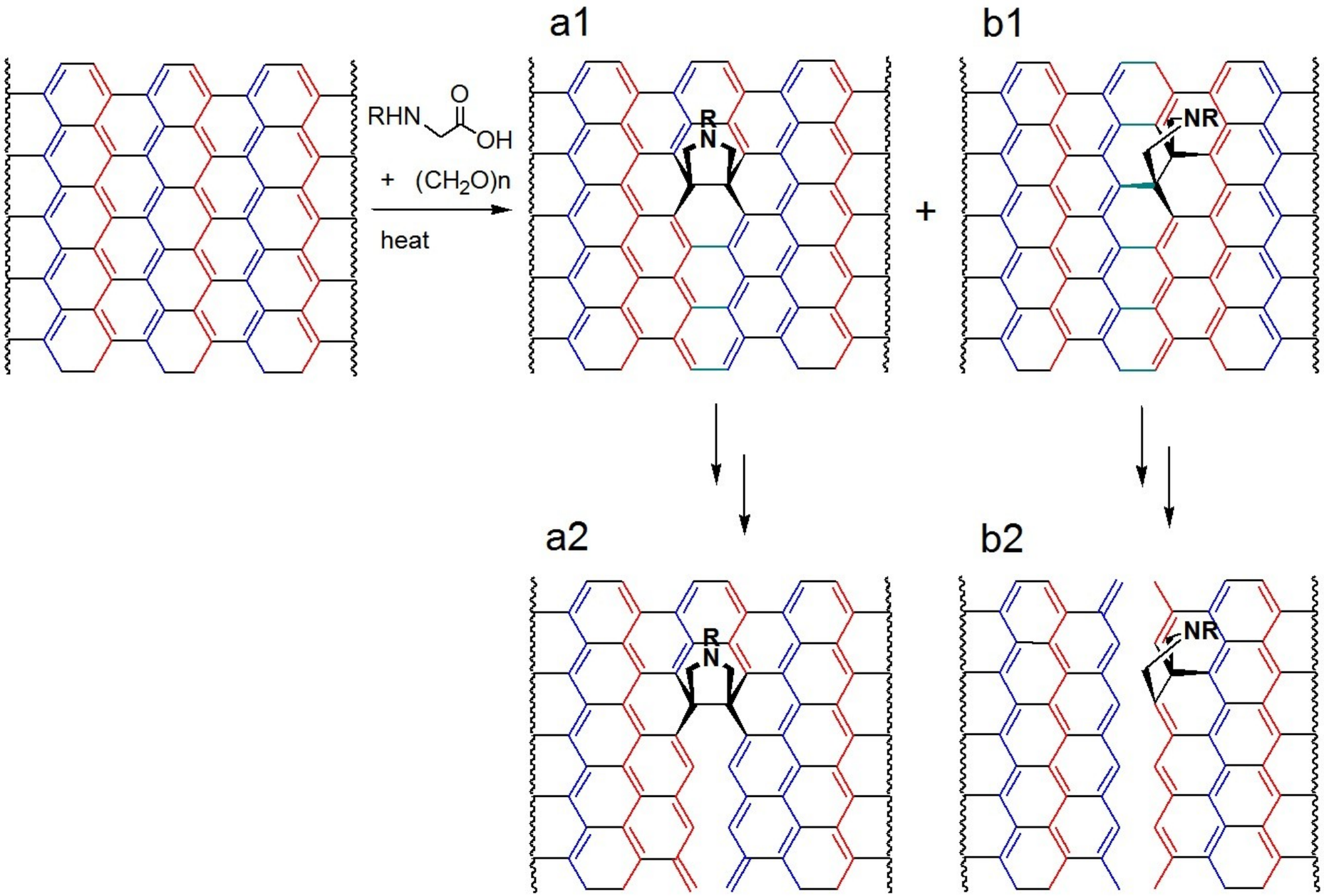
Graphene from carbon nanotubes

Unzipping of functionalized CNT to form graphene



Slide from Maria Paiva, Universidade do Minho, Portugal

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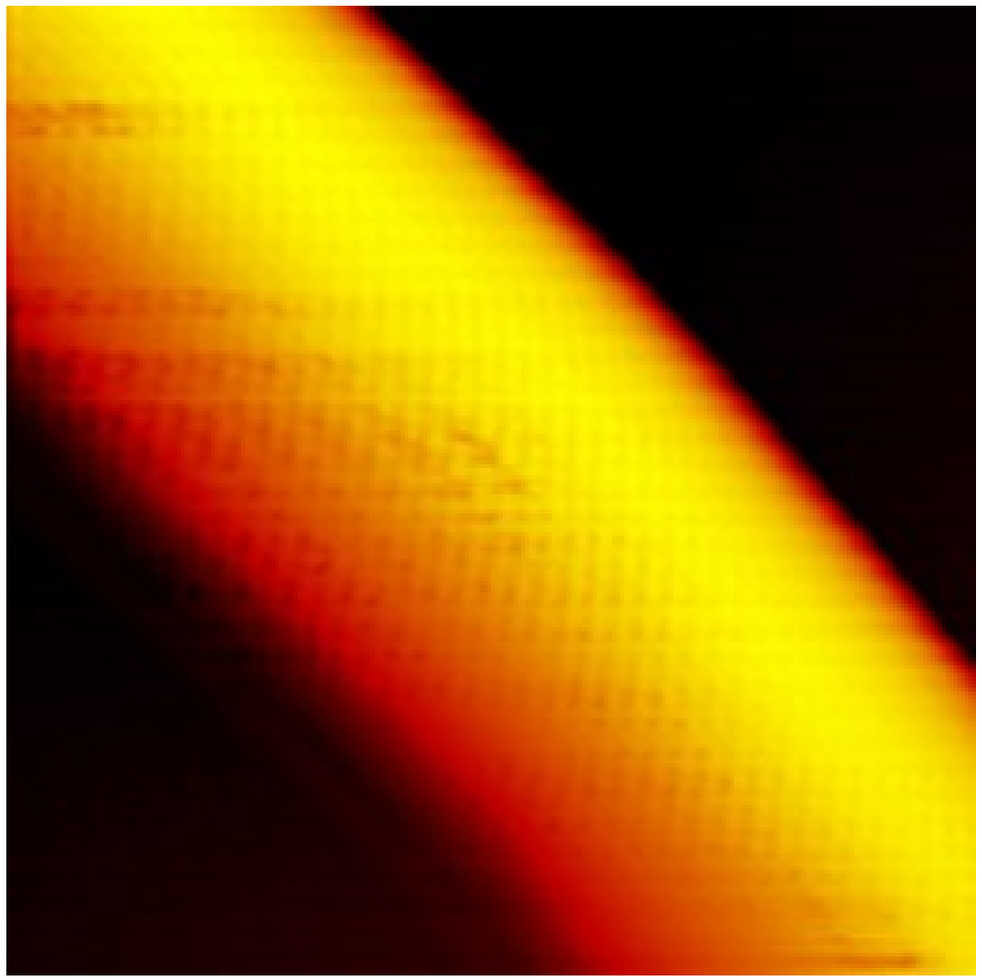
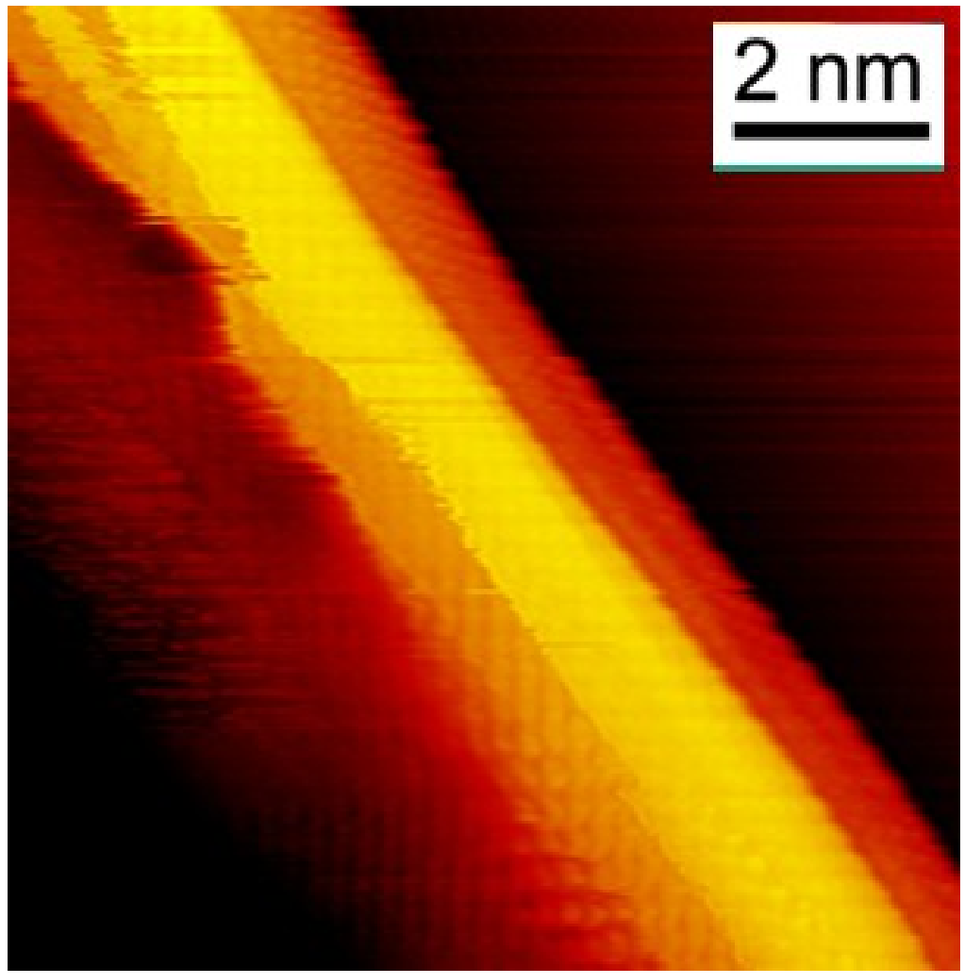
Graphene from carbon nanotubes

The 1,3-dipolar cycloaddition to CNT: nanotube unzipping



Non-functionalized nanotube



Unzipping of the outer nanotube layer

M. C. Paiva, W. Xu, M. F. Proença, R. M. Novais, E. Lægsgaard, F. Besenbacher, *Nano Letters*, 2010, 10, 1764-1768

Slide from Maria Paiva, Universidade do Minho, Portugal

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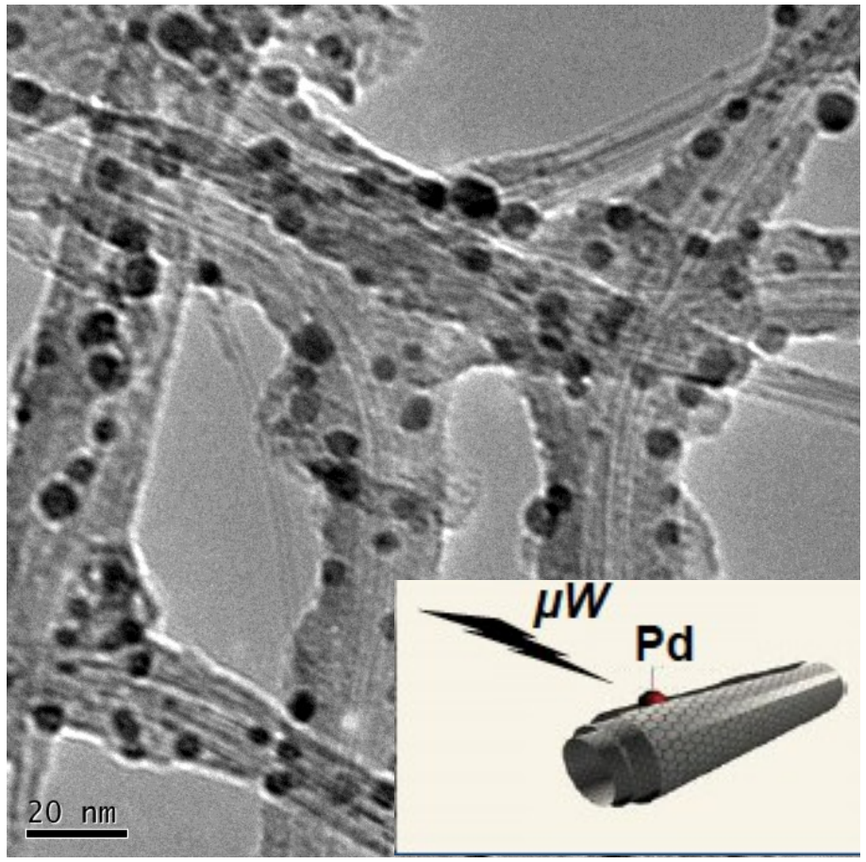

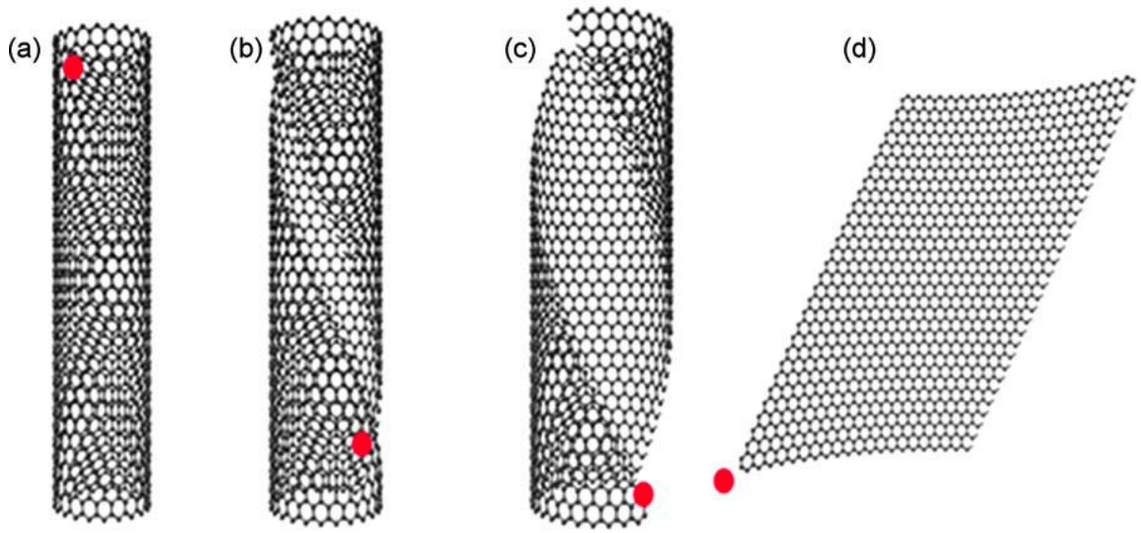

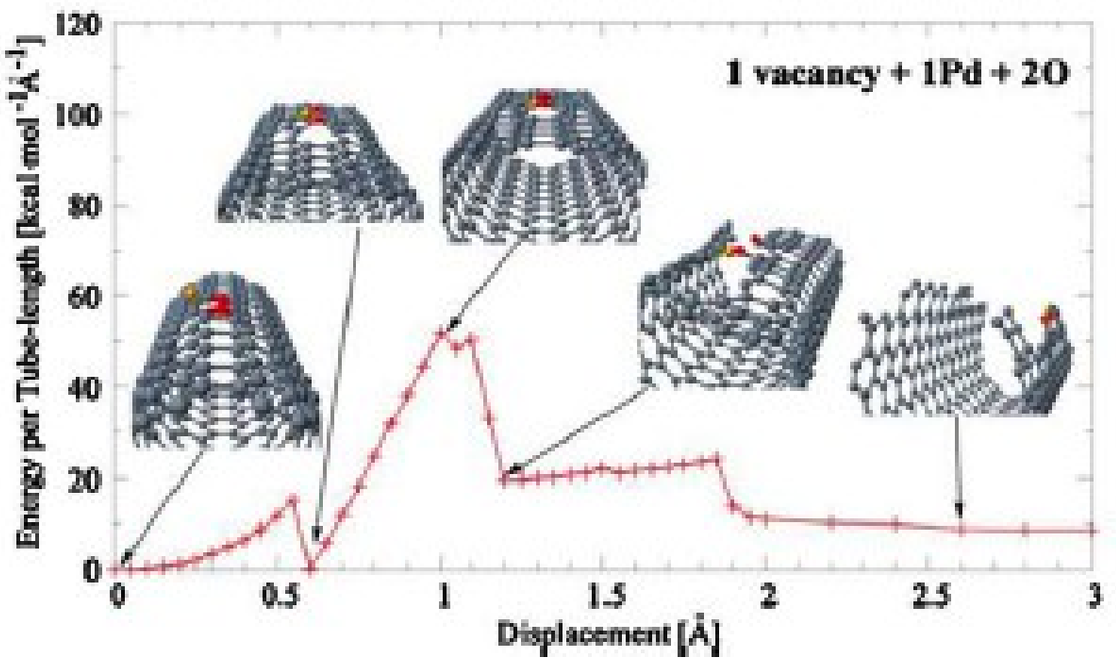

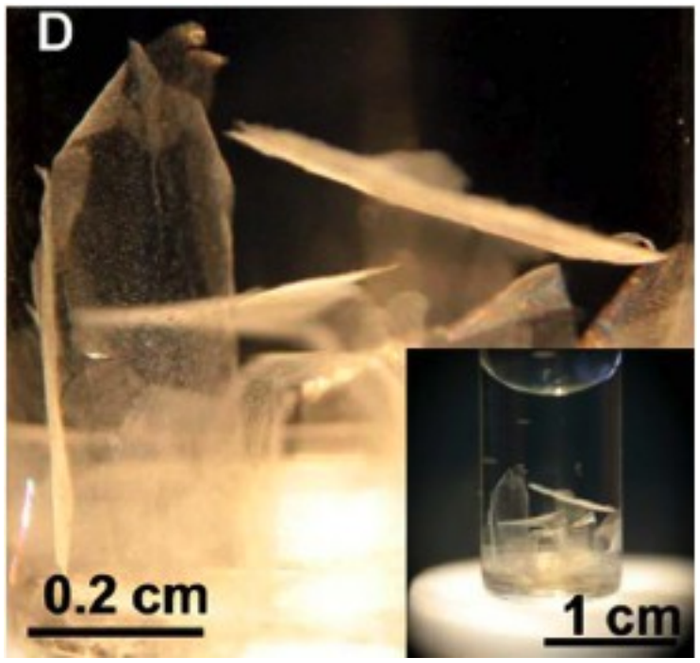

Janowska, Bégin et al. Appl. Catalysis A 2009

Graphene from carbon nanotubes

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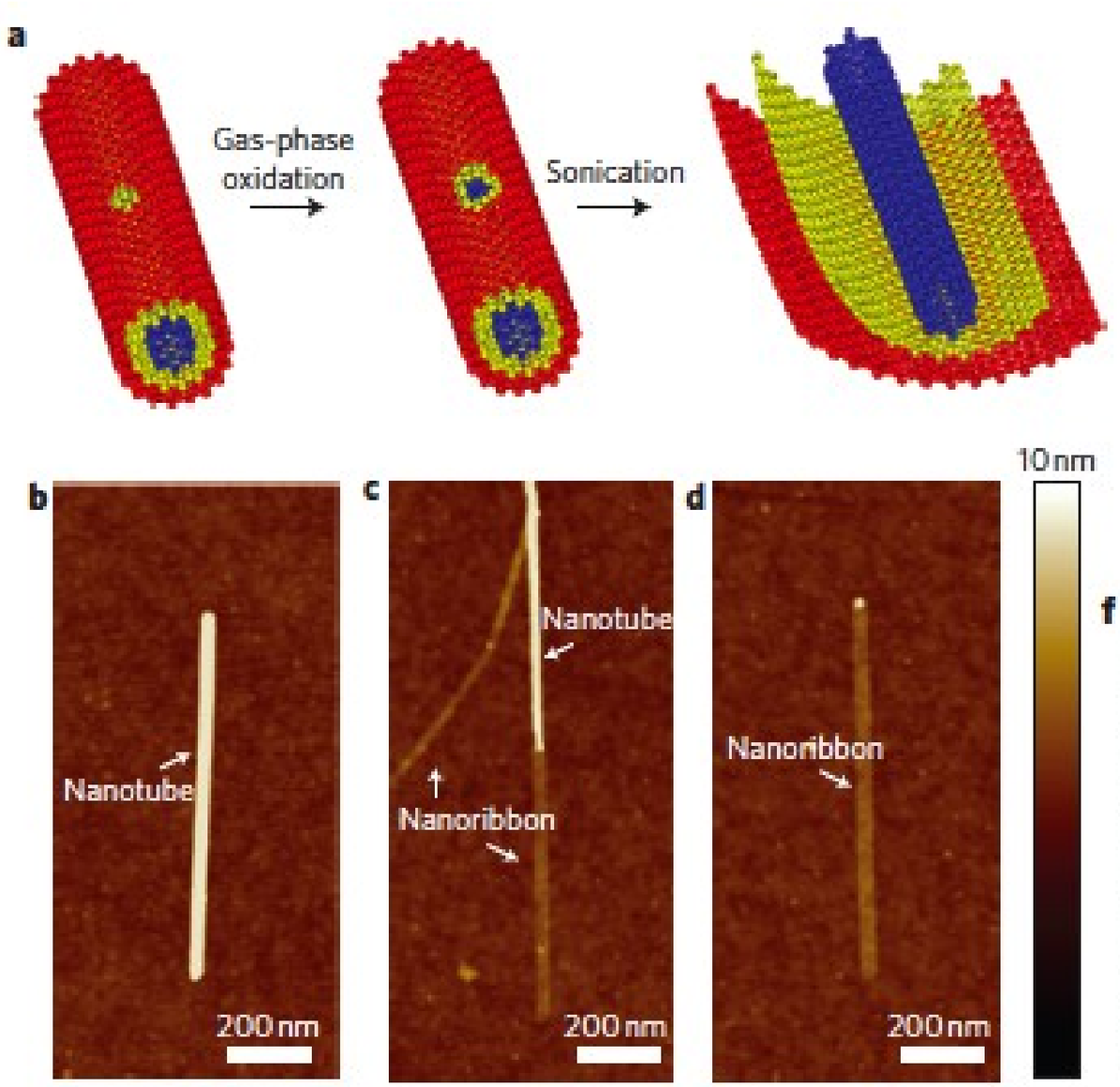

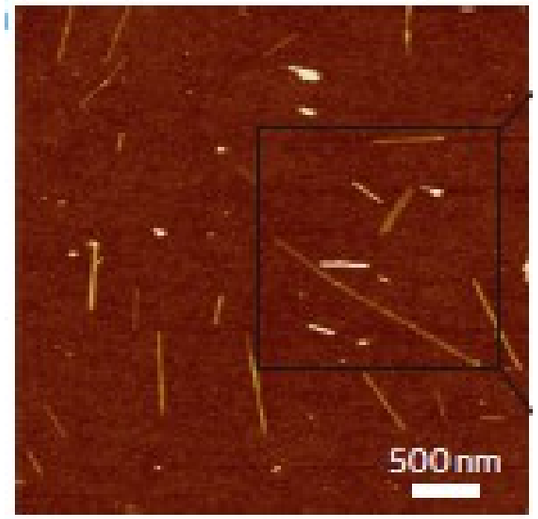

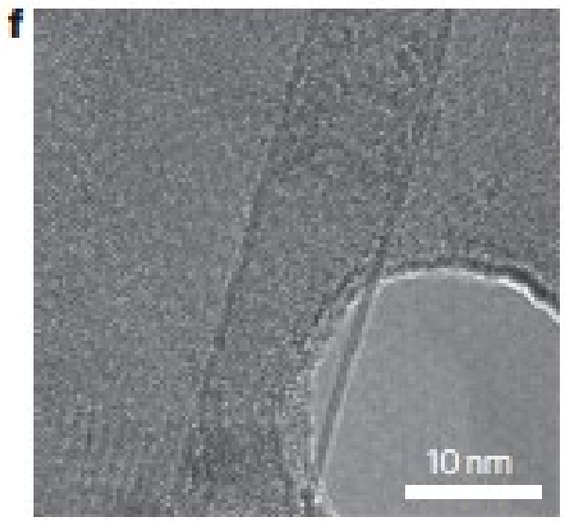

Hongjie Dai et al., Nature Nanotechnol. 2010

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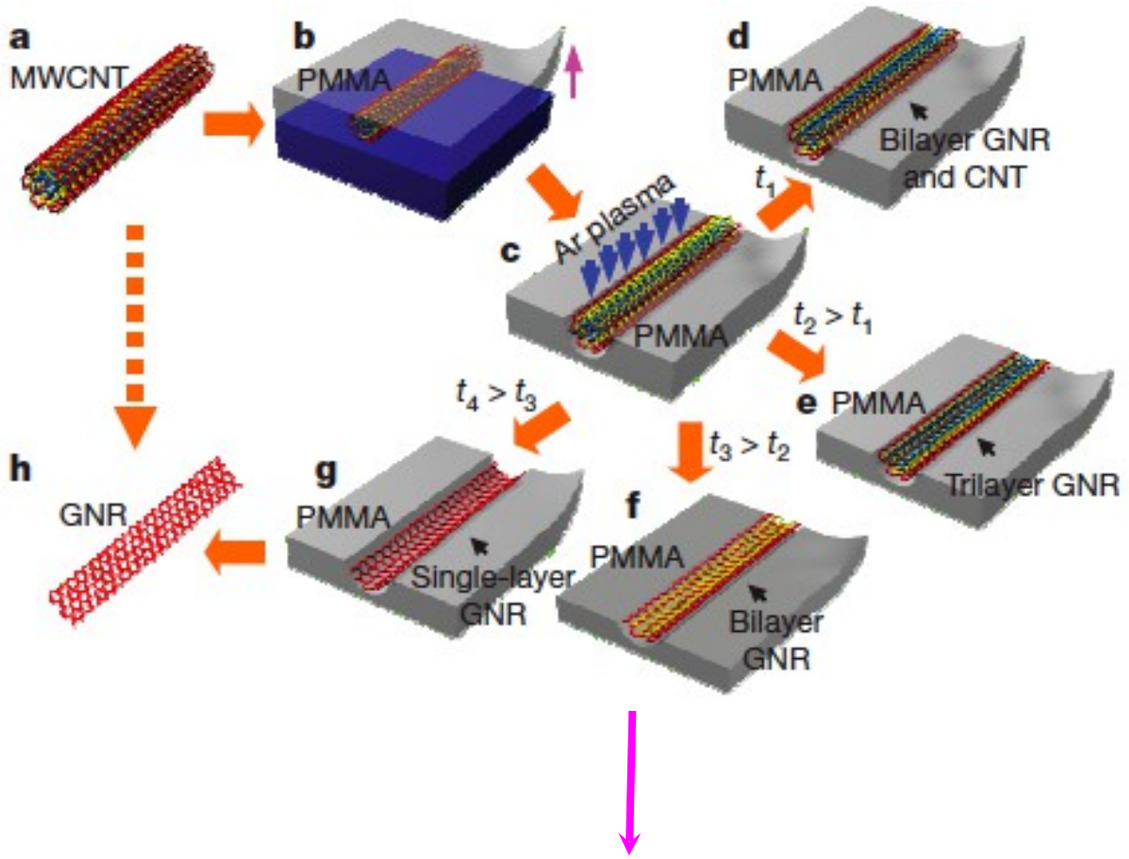
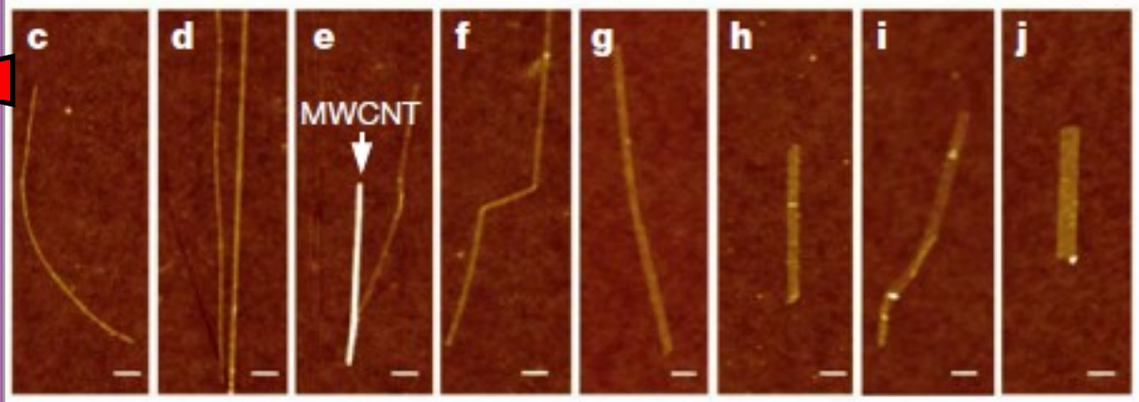
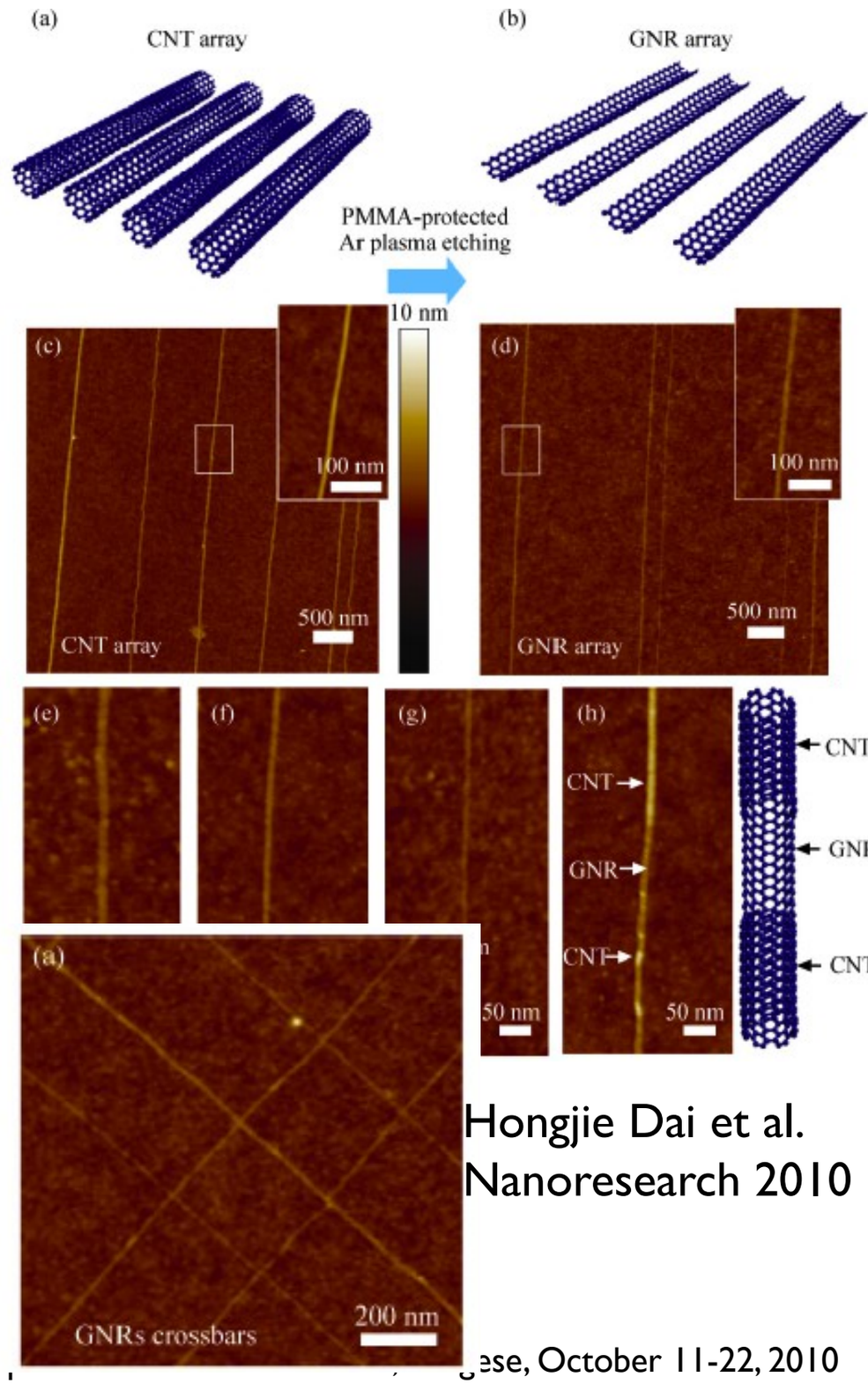
Graphene from carbon nanotubes

nanotube unzipping by Ar plasma etching





Hongjie Dai et al. Nature 2009



Hongjie Dai et al. Nanoresearch 2010

Graphene from molecular precursors

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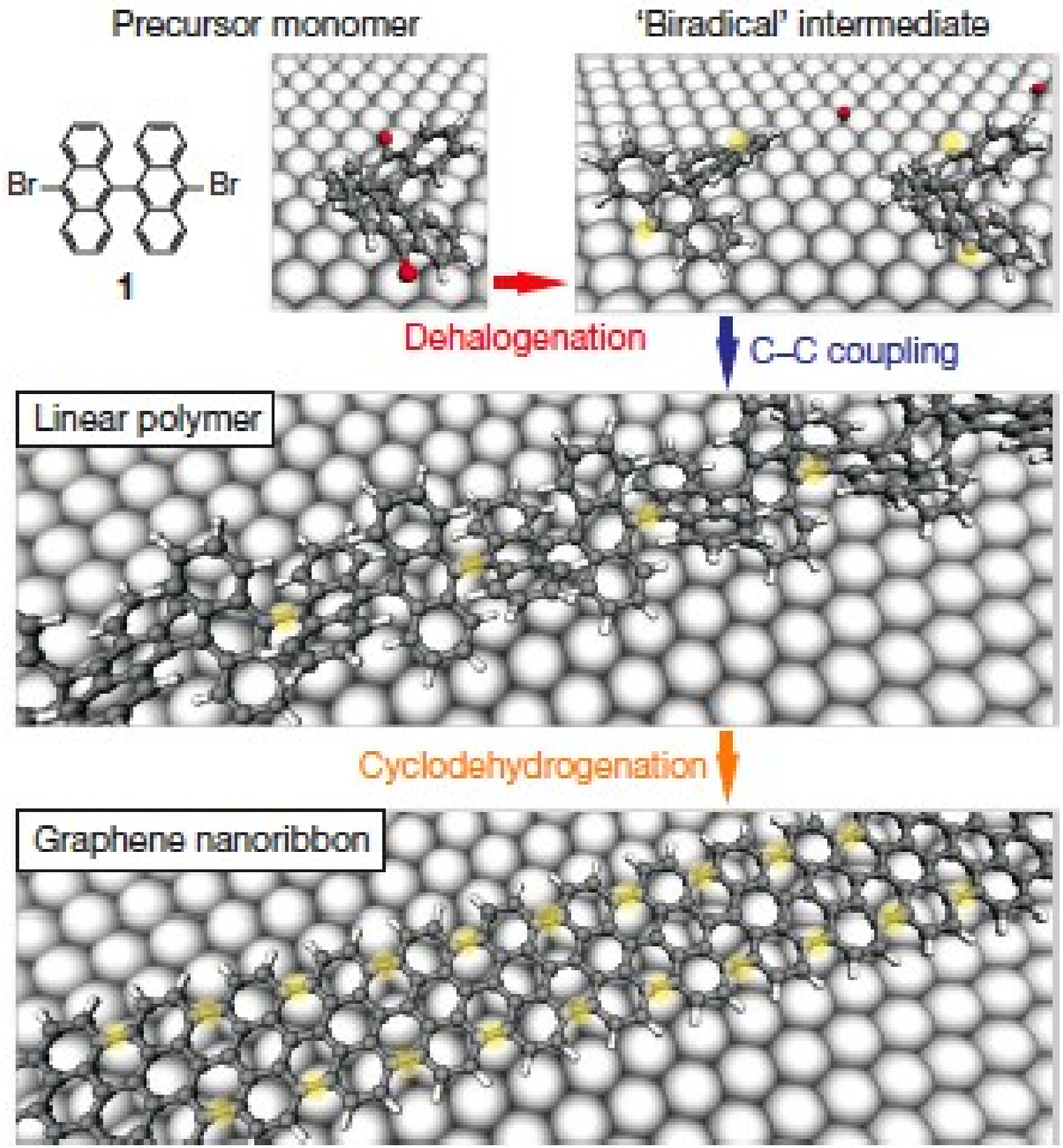

Fasel, Müllen et al., Nature 2010

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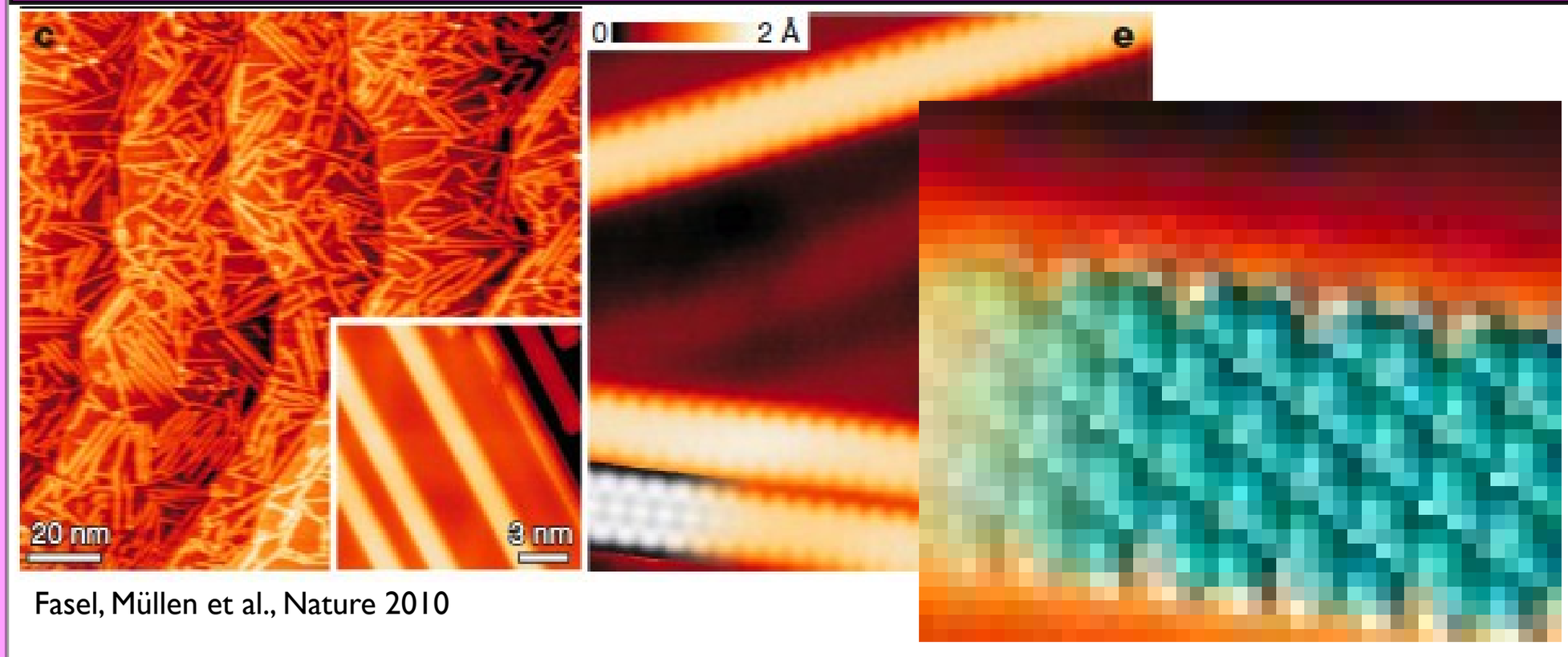
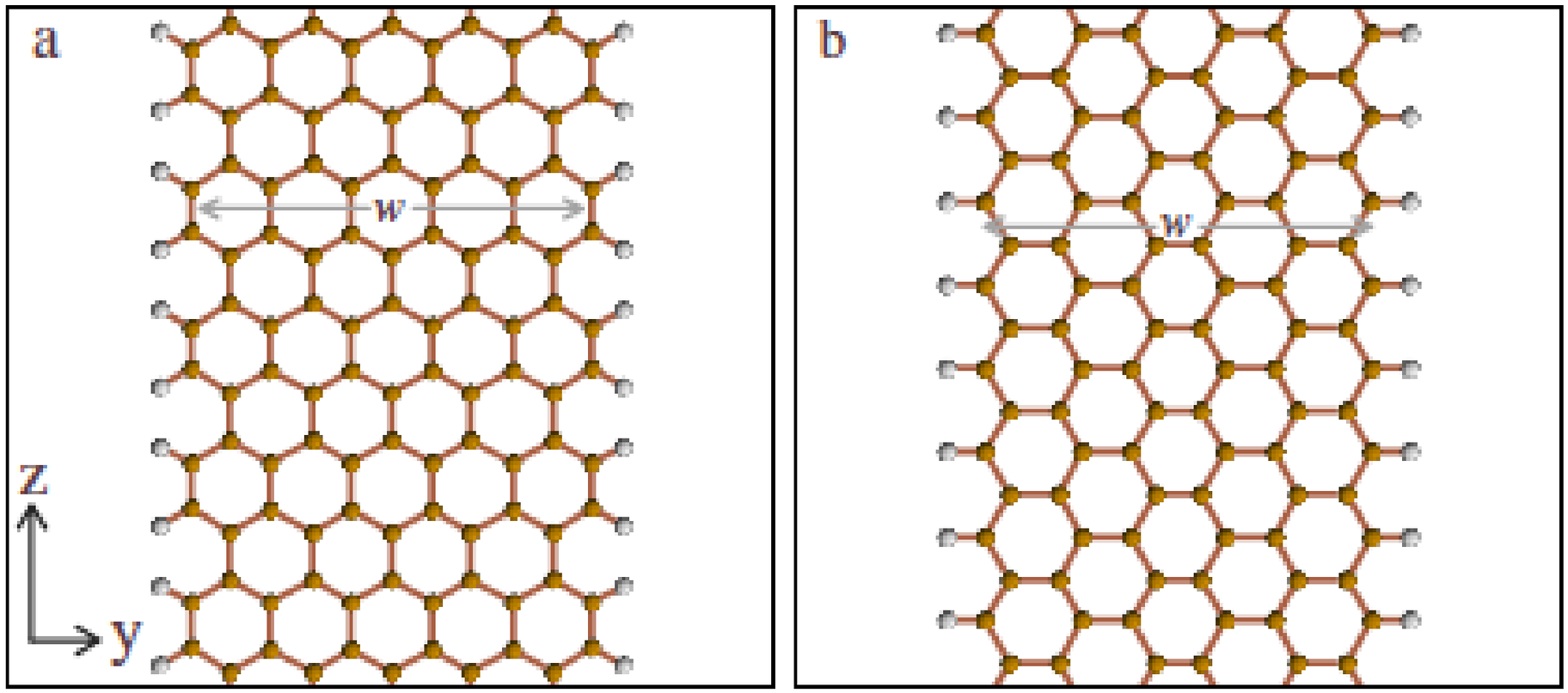


Fasel, Müllen et al., Nature 2010

7-AGNR



11-Armchair

6-Zig-zag

Louie et al., PRL 2007

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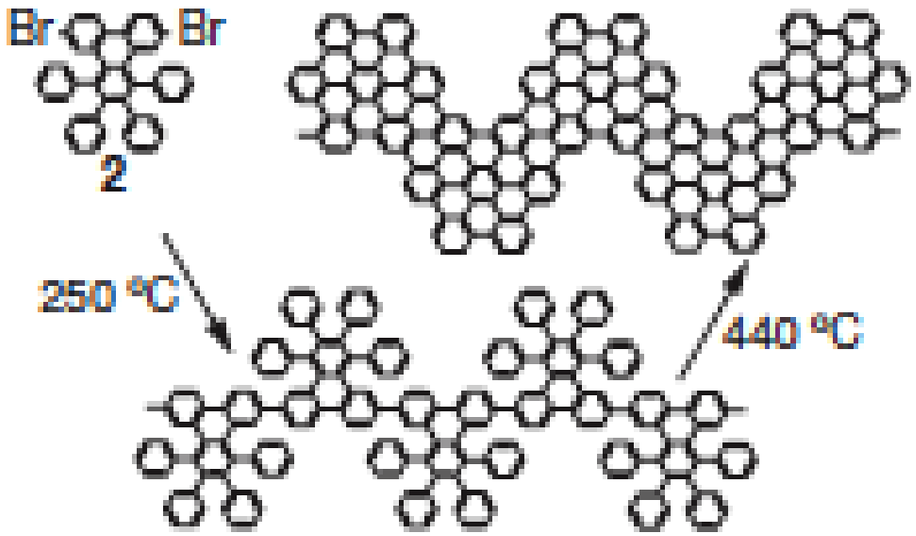

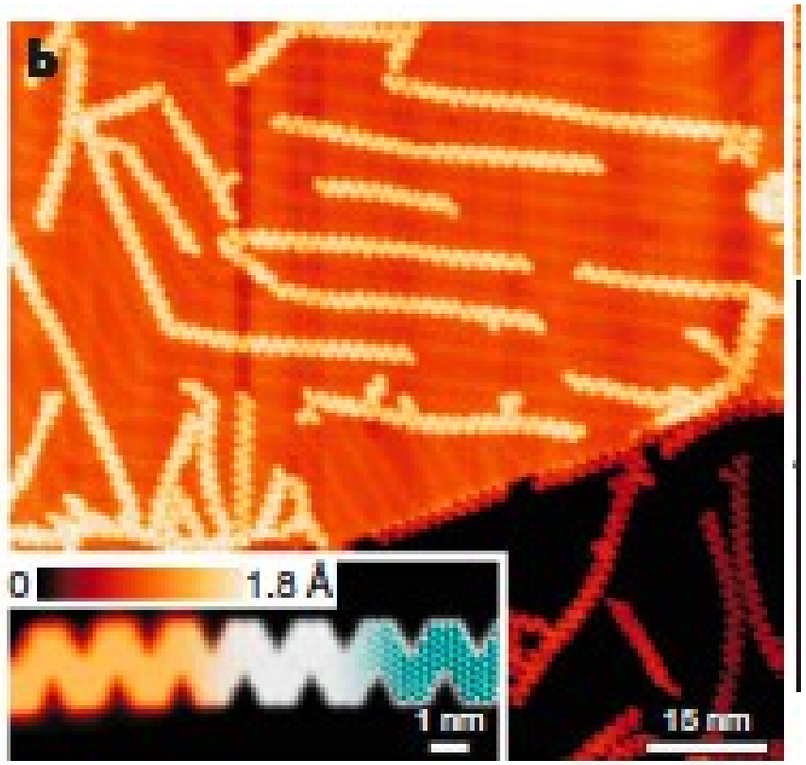

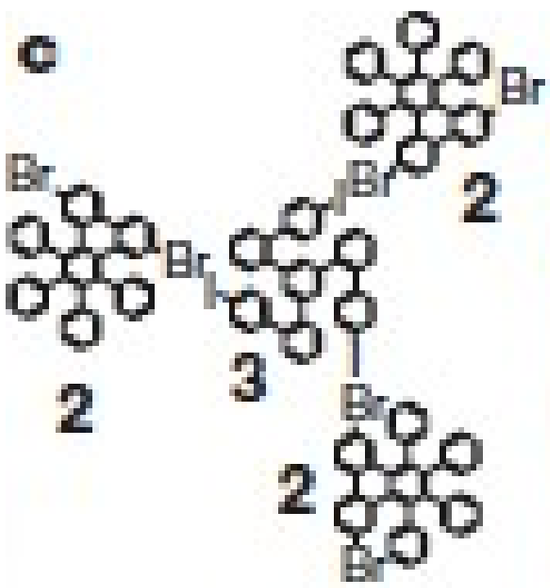

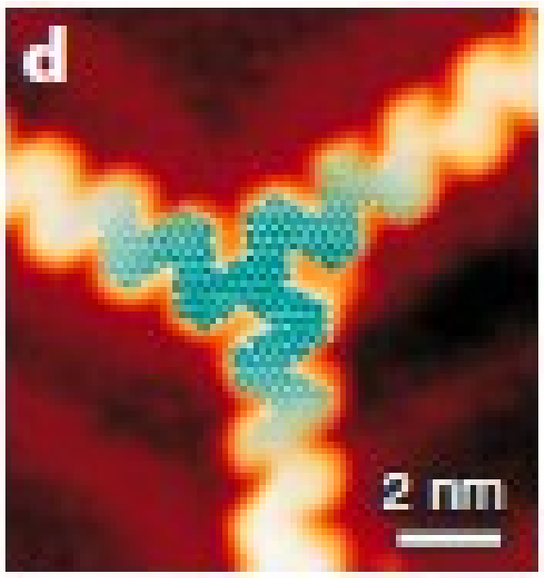

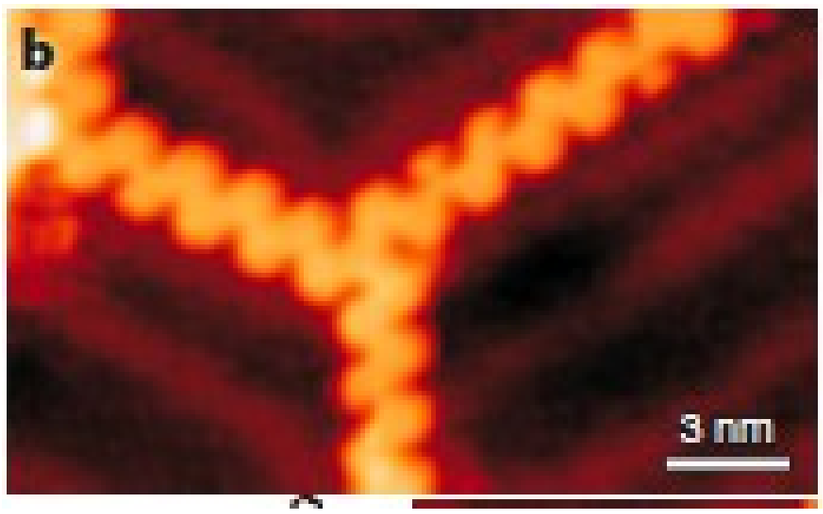

Fasel, Müllen et al., Nature 2010