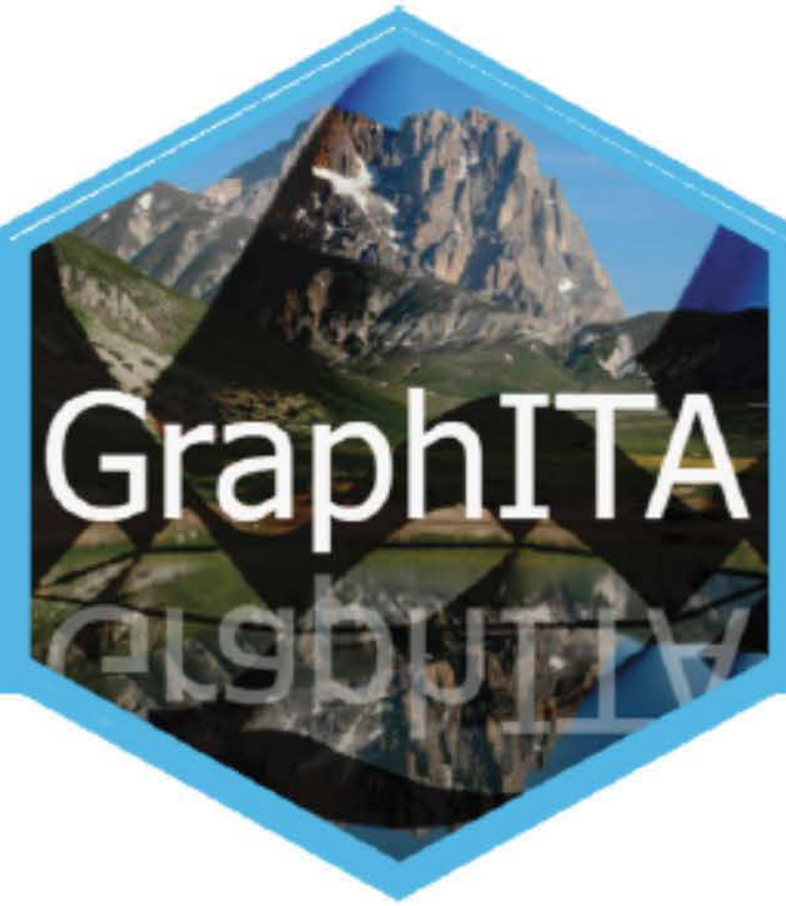
(Thermodynamically stable)

Graphene solutions

Alain Pénicaud

Centre de Recherche Paul Pascal, CNRS, Université Bordeaux-I

penicaud@crpp-bordeaux.cnrs.fr



CNR IMM-Bologna

Università dell'Aquila

A Multidisciplinary and Intersectorial European Workshop on Synthesis, Characterization and Technological Exploitation of Graphene

15-18 May 2011
Gran Sasso National Laboratories
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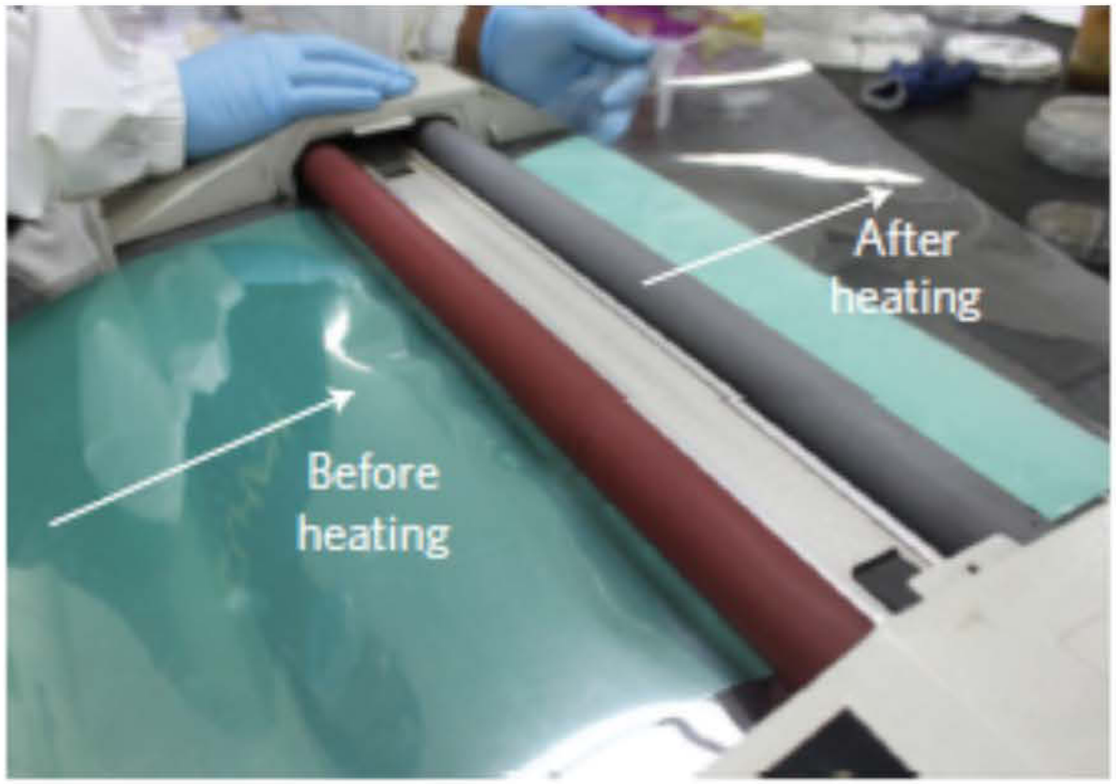

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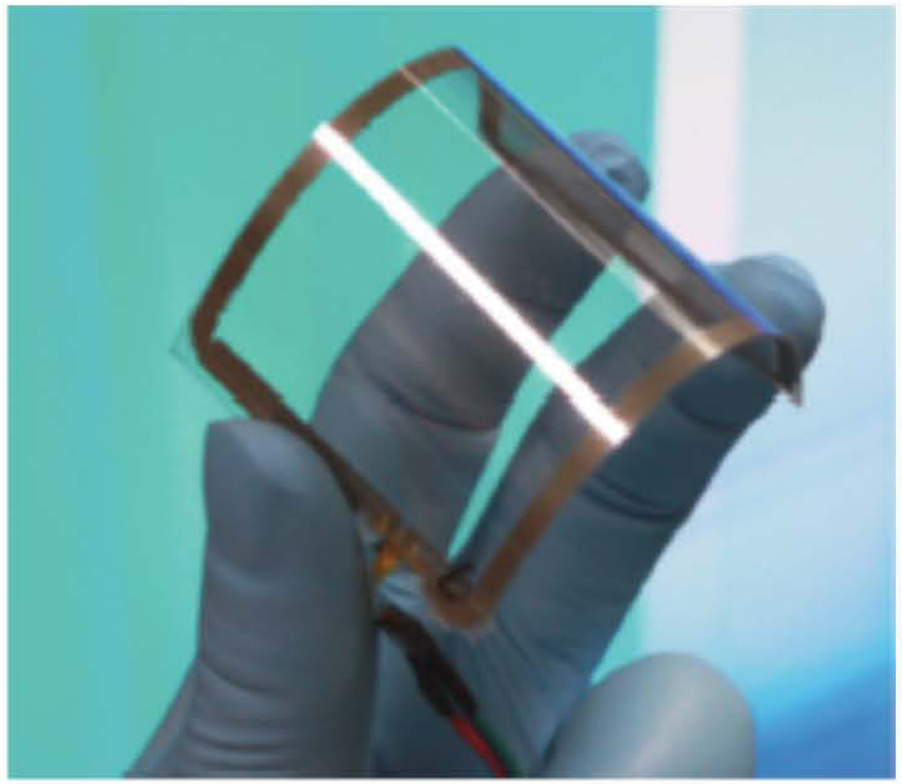

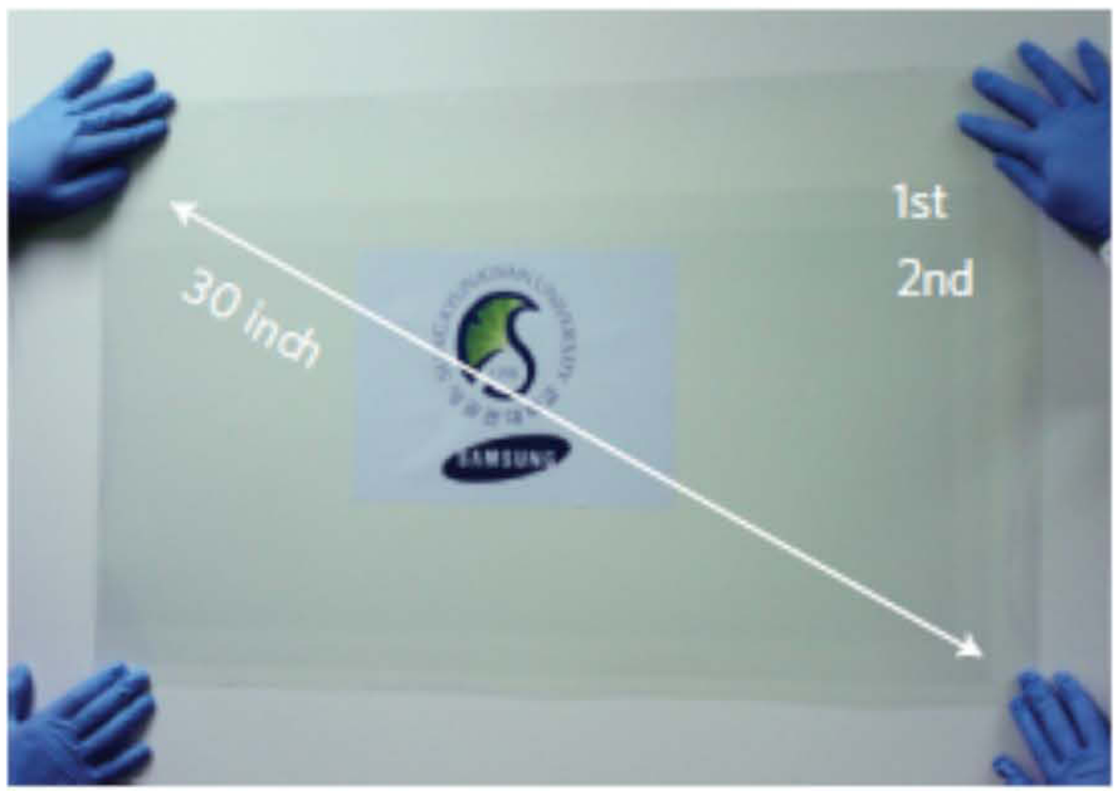

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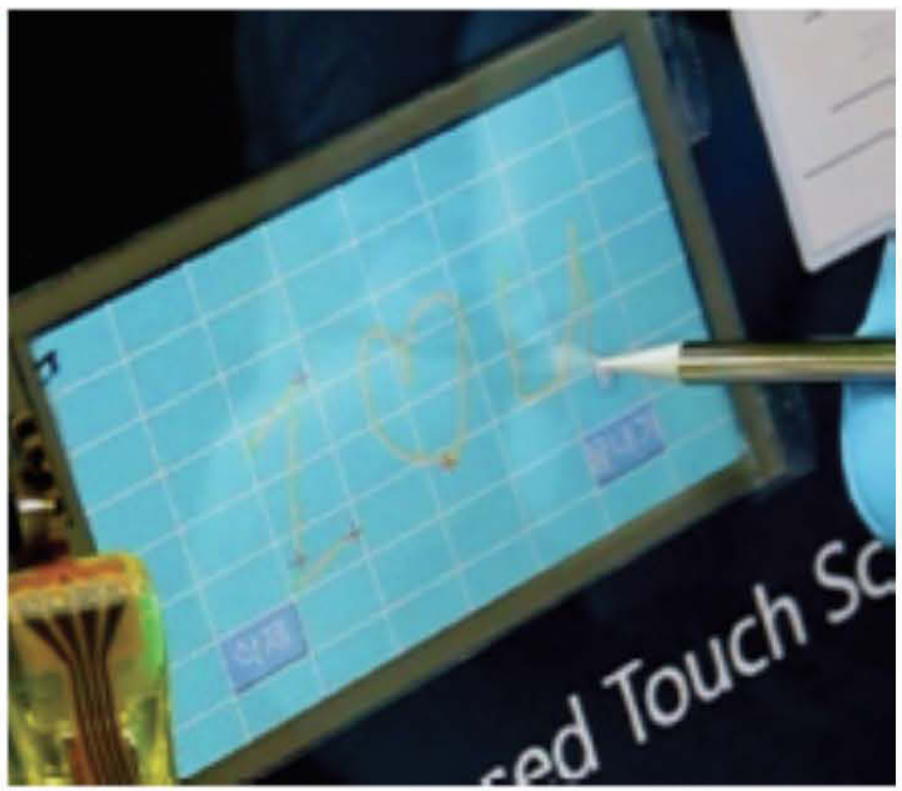
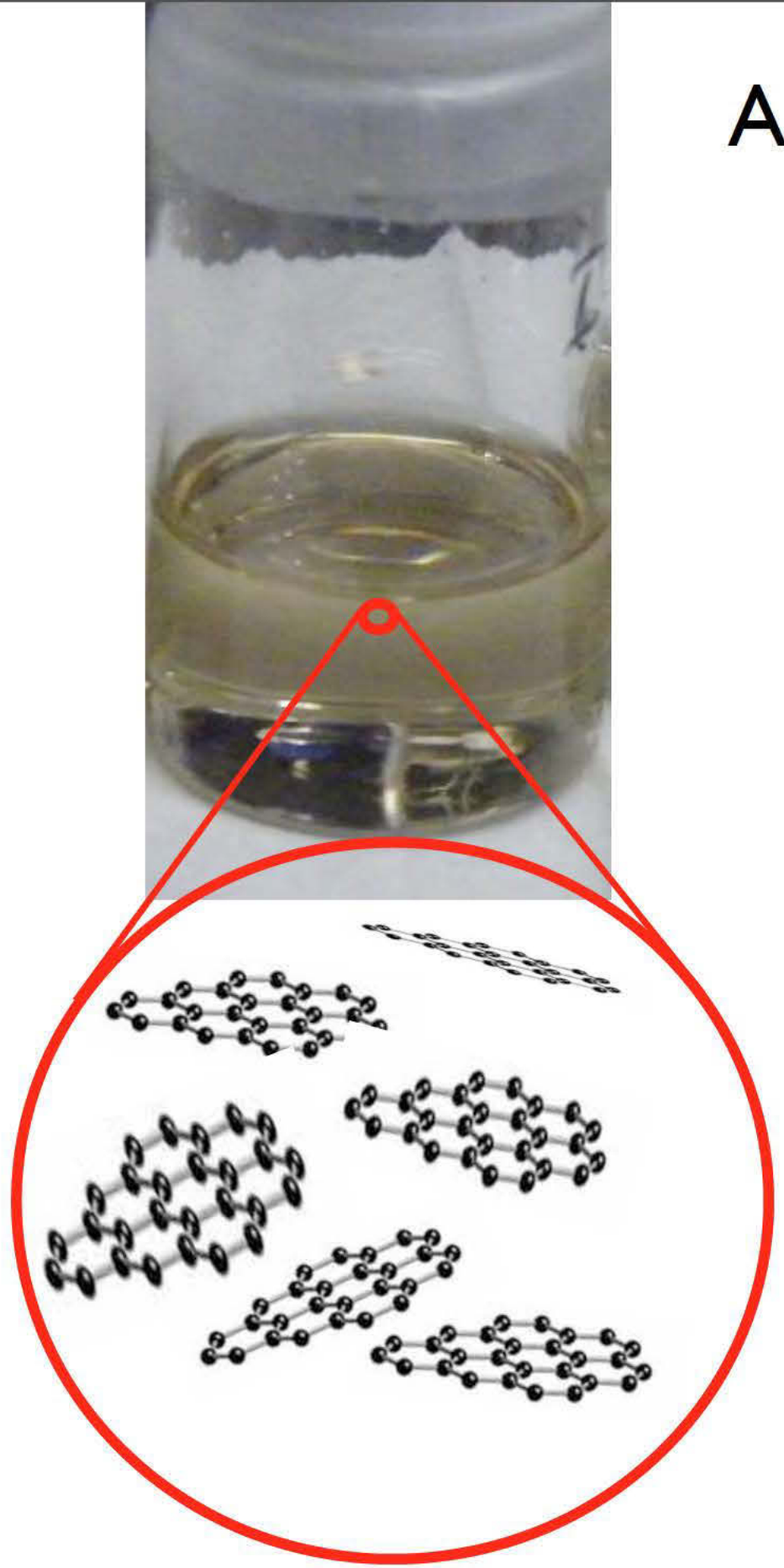


Byung Hee Hong et al., Nature Nanotechnology, 2010

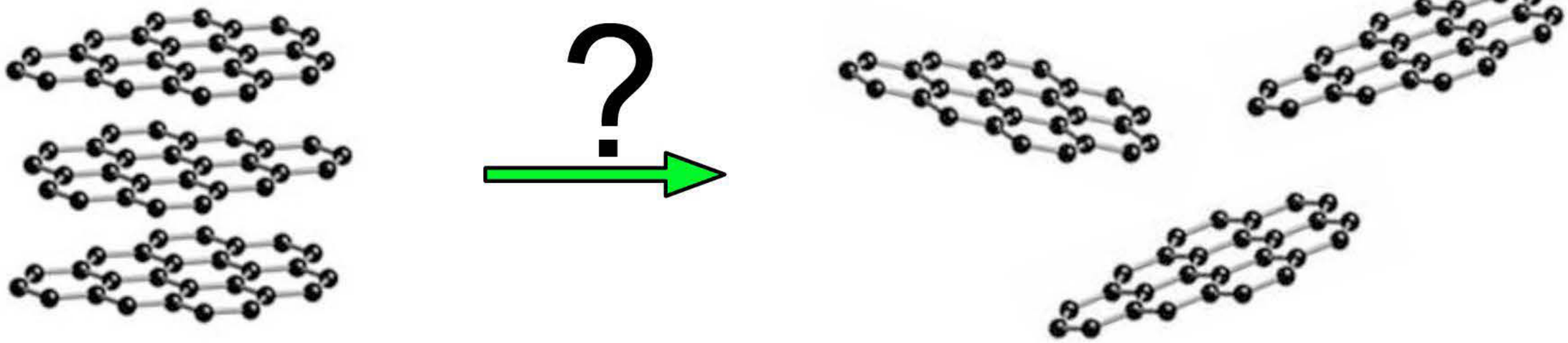


A true graphene solution....

- process large quantities
- assemble on surfaces
- prepare composites
- do chemistry
- ...

Visiting Nacional de Grafite, Minas Gerais, Brazil, 2009

Alain Pénicaud, Centre de Recherche Paul Pascal - CNRS - Université de Bordeaux



Strong van der Waals (cohesive) energy

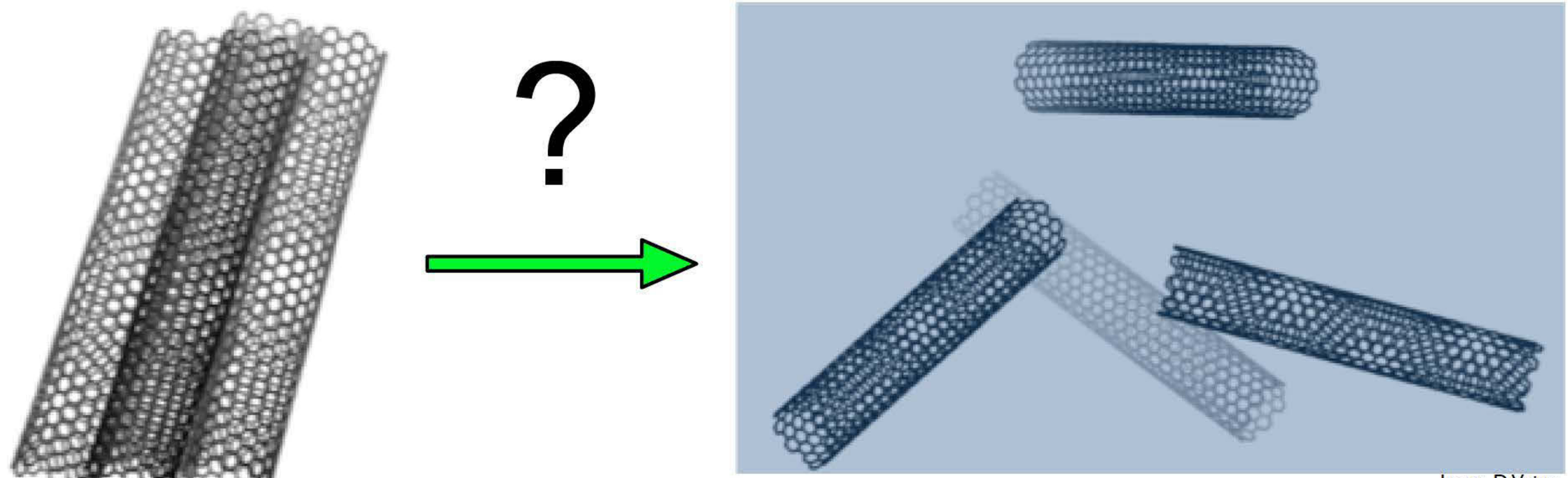


Image D.Voiry

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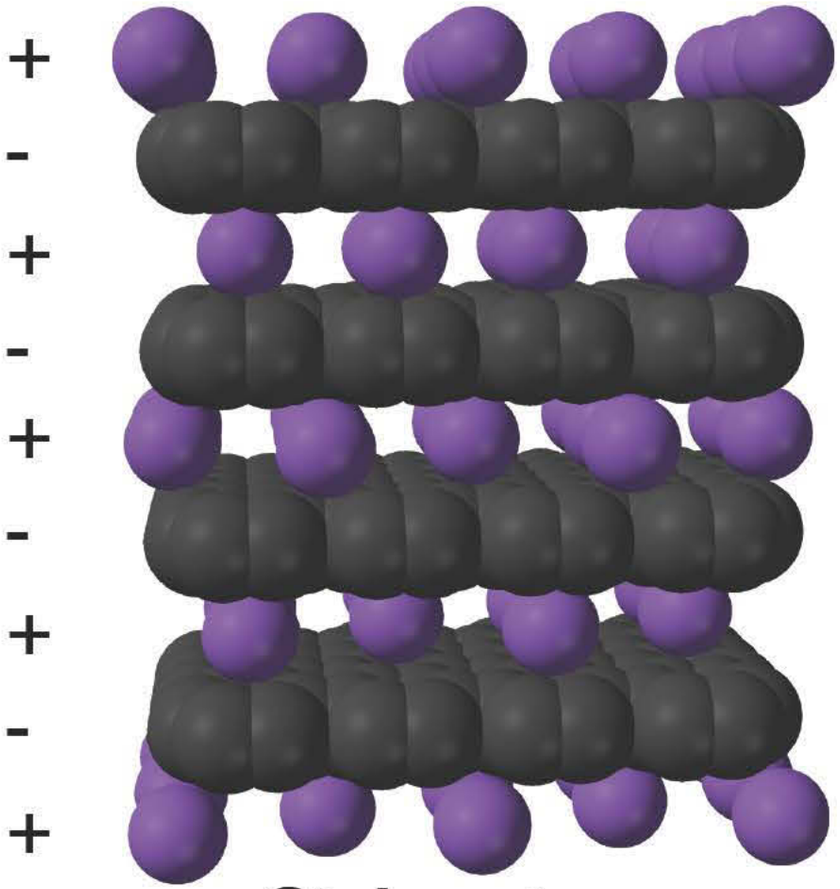
Graphite Intercalation Compounds

Graphite Intercalation Compounds

M. Dumas©Marabout

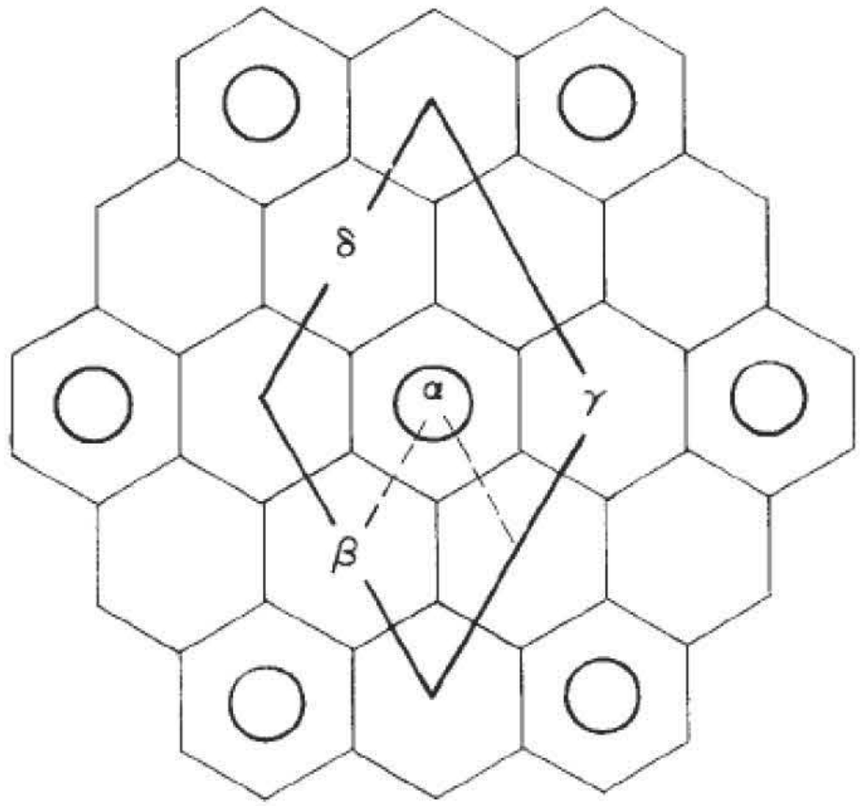
Graphene from Graphite Intercalation Compounds

Model for the structure of KC_8



Side view

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



Top view

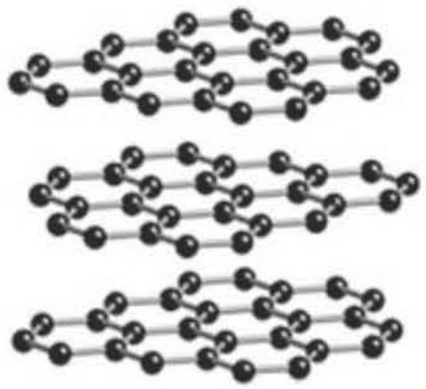
Dresselhaus and Dresselhaus, Adv. in Physics, 1980

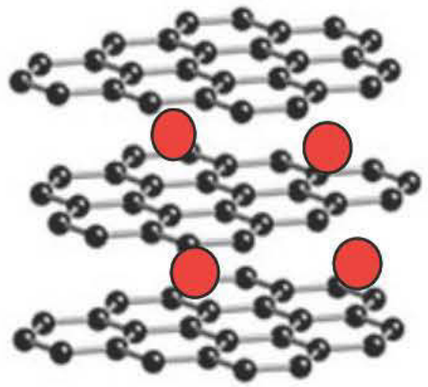
Graphene from Graphite Intercalation Compounds

Thermodynamically stable solutions of graphene:

Nacional de Grafite, Brazil

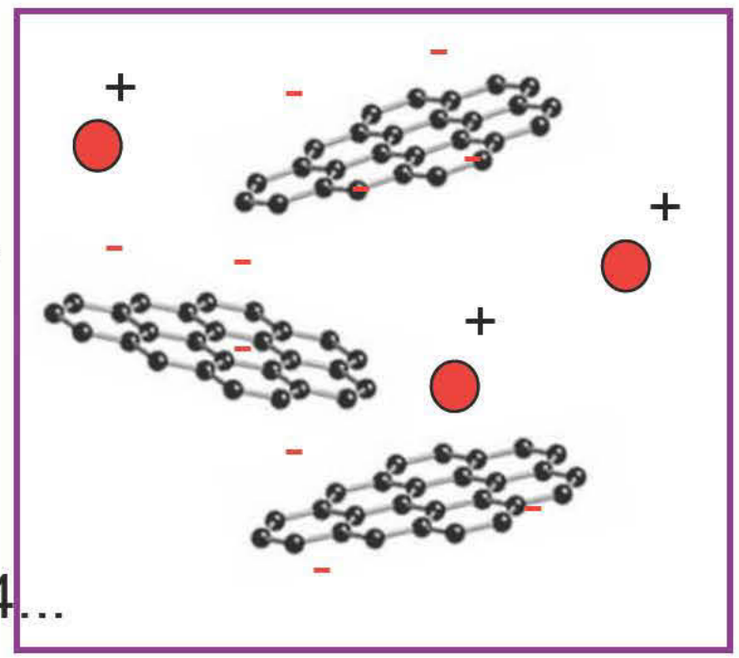
KC_8





GIC

NMP



reported since at least 1954...

Rüdorf and Schulze (1954)

Up to 0.7 mg/ml

C. Vallés et al., Patent (2007),

C. Vallés et al., J. Am. Chem. Soc. **130**, 15802 (2008)

A. Catheline et al. Chem. Commun, 47, 5470 (2011).

Graphene from Graphite Intercalation Compounds

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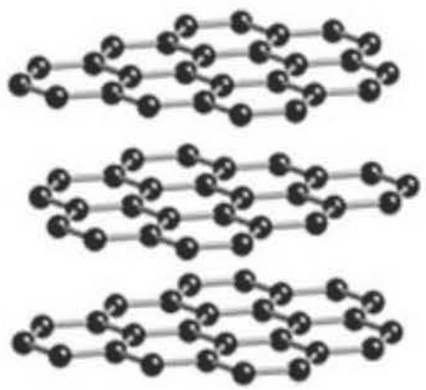
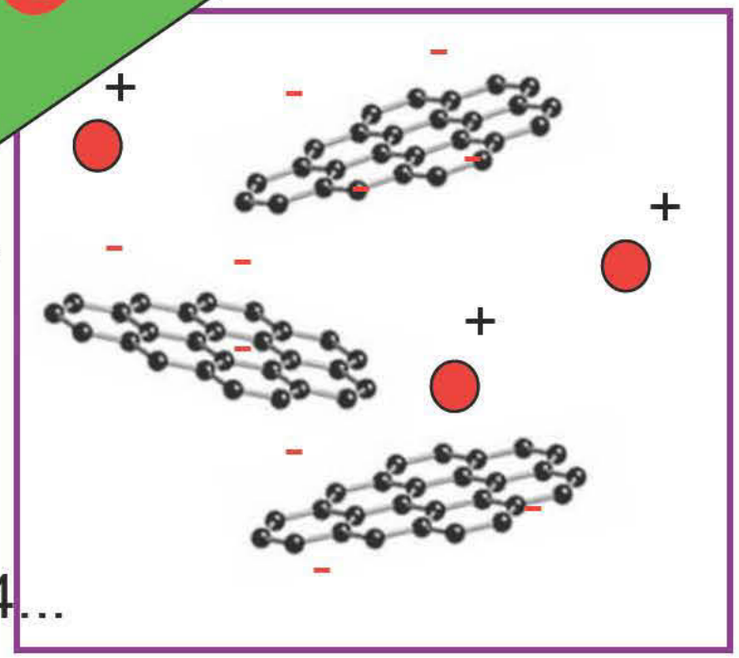


GIC

Sonication free



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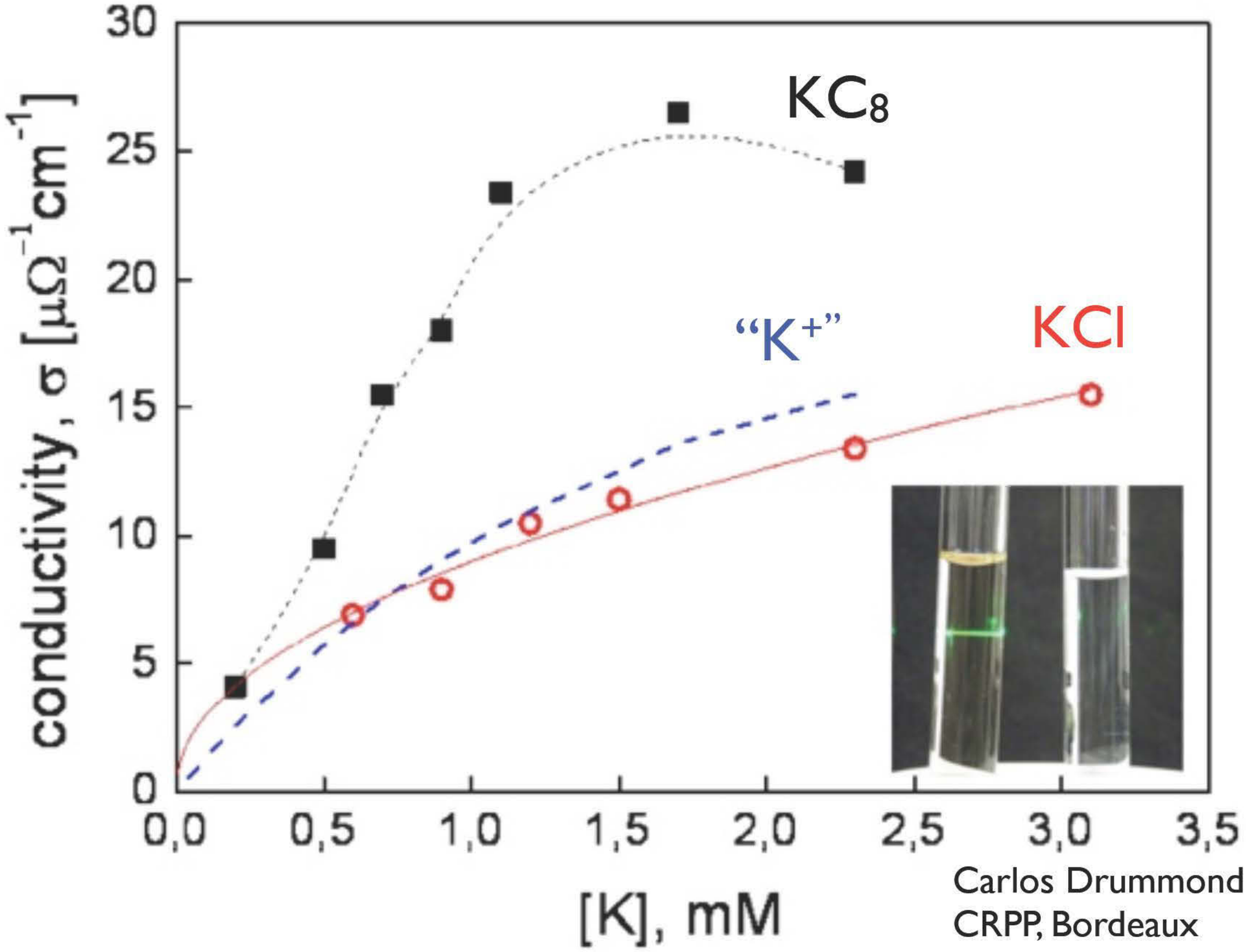
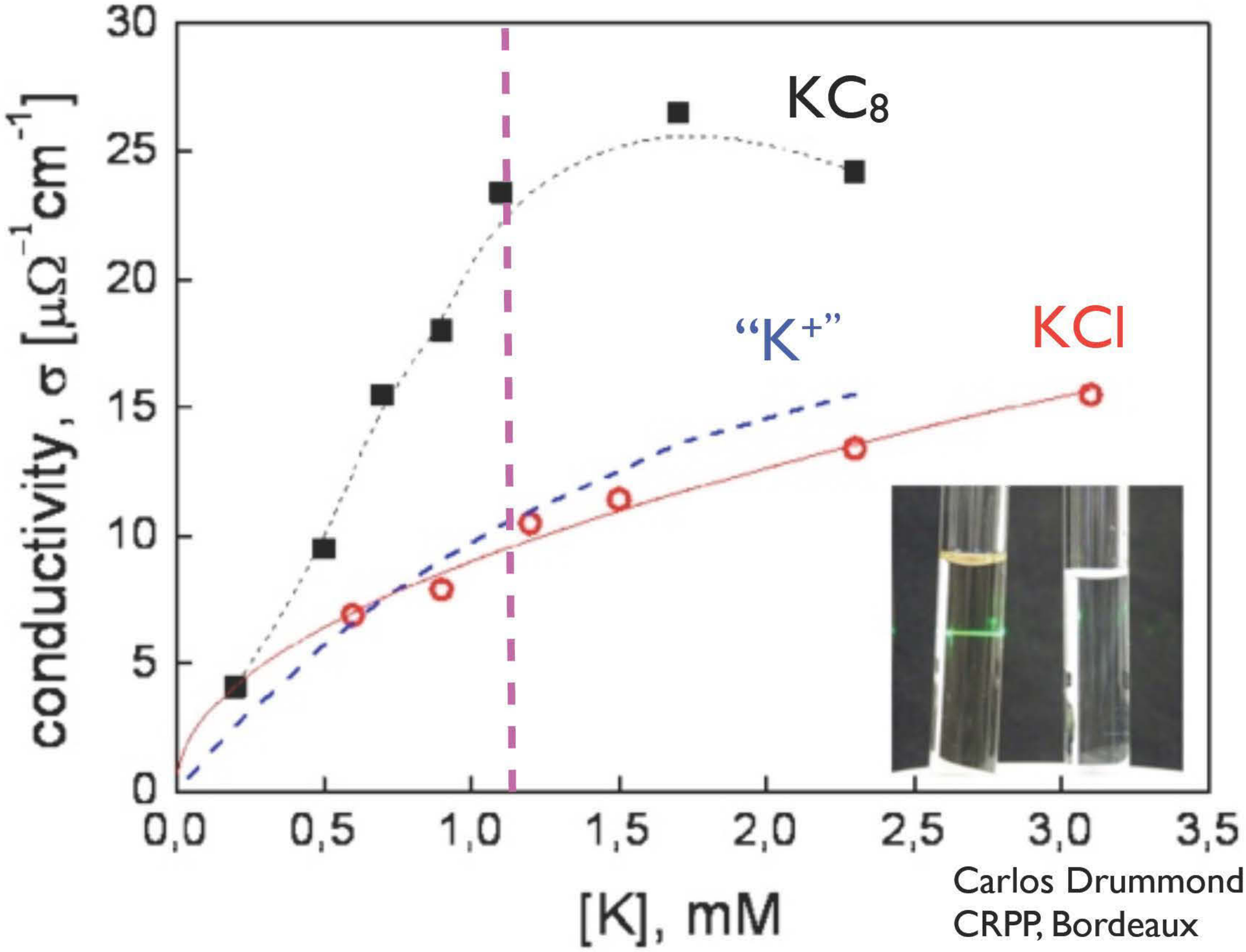
Graphene from Graphite Intercalation Compounds



Carlos Drummond
CRPP, Bordeaux

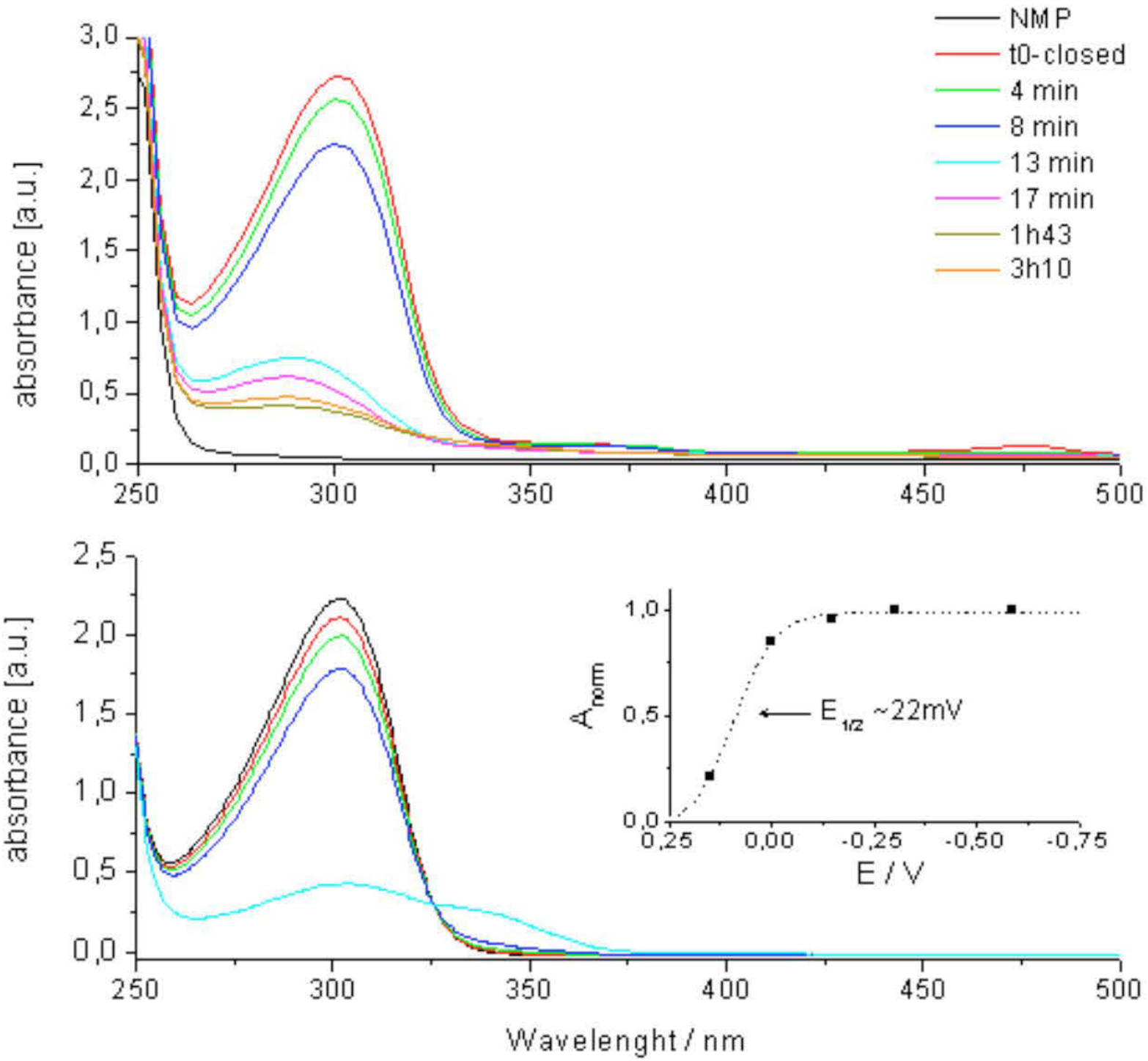
Graphene from Graphite Intercalation Compounds



Carlos Drummond
CRPP, Bordeaux

Oxidation (de-doping)

dry air



electrochemistry

Nernstian behaviour: E° = 22 mV (vs SCE)

Graphene from Graphite Intercalation Compounds

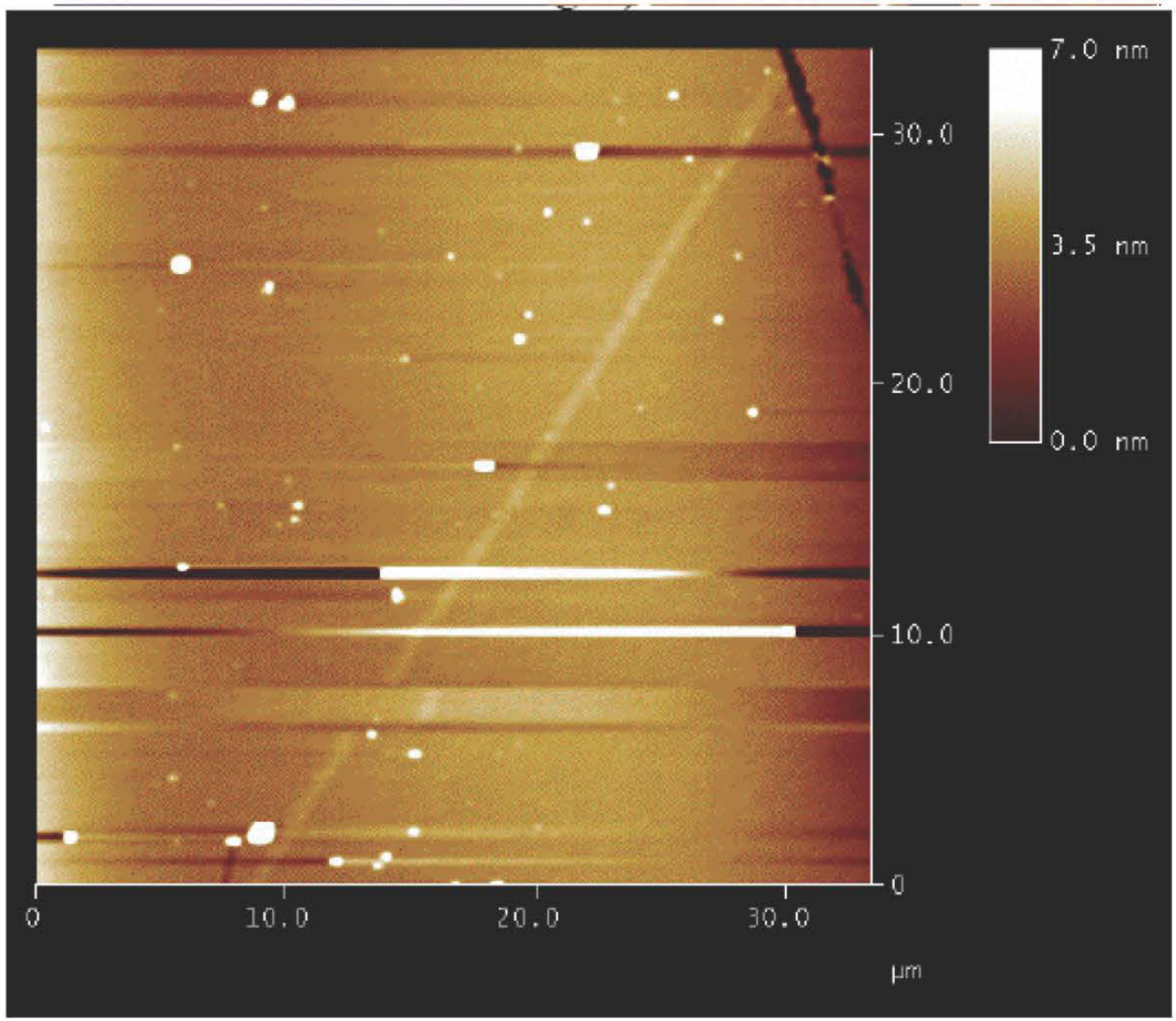
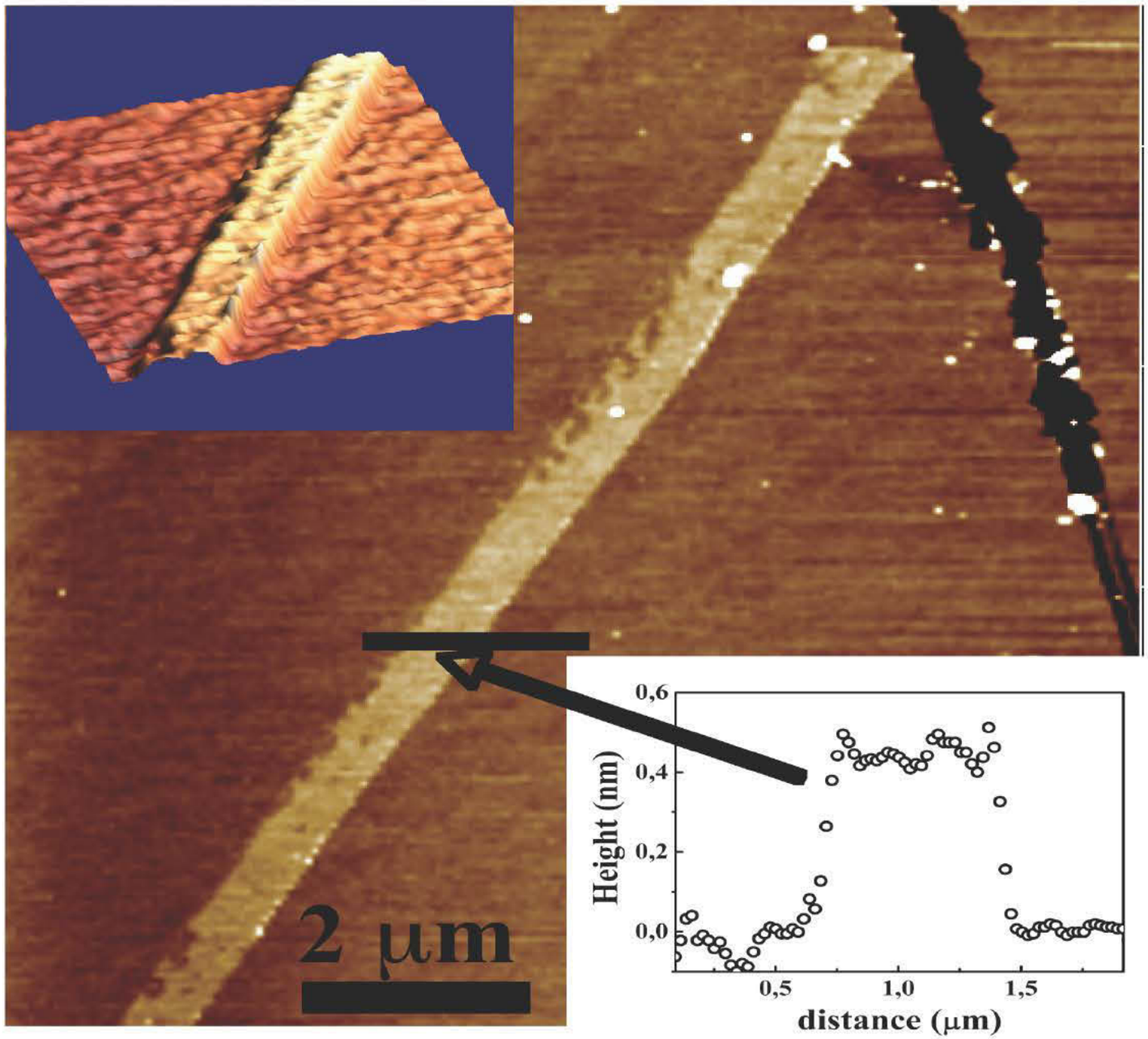


Image by C. Drummond

AFM on mica

End of a graphene ribbon , ca. 40 microns long - ca. 0.4 nm. height

Graphene from Graphite Intercalation Compounds



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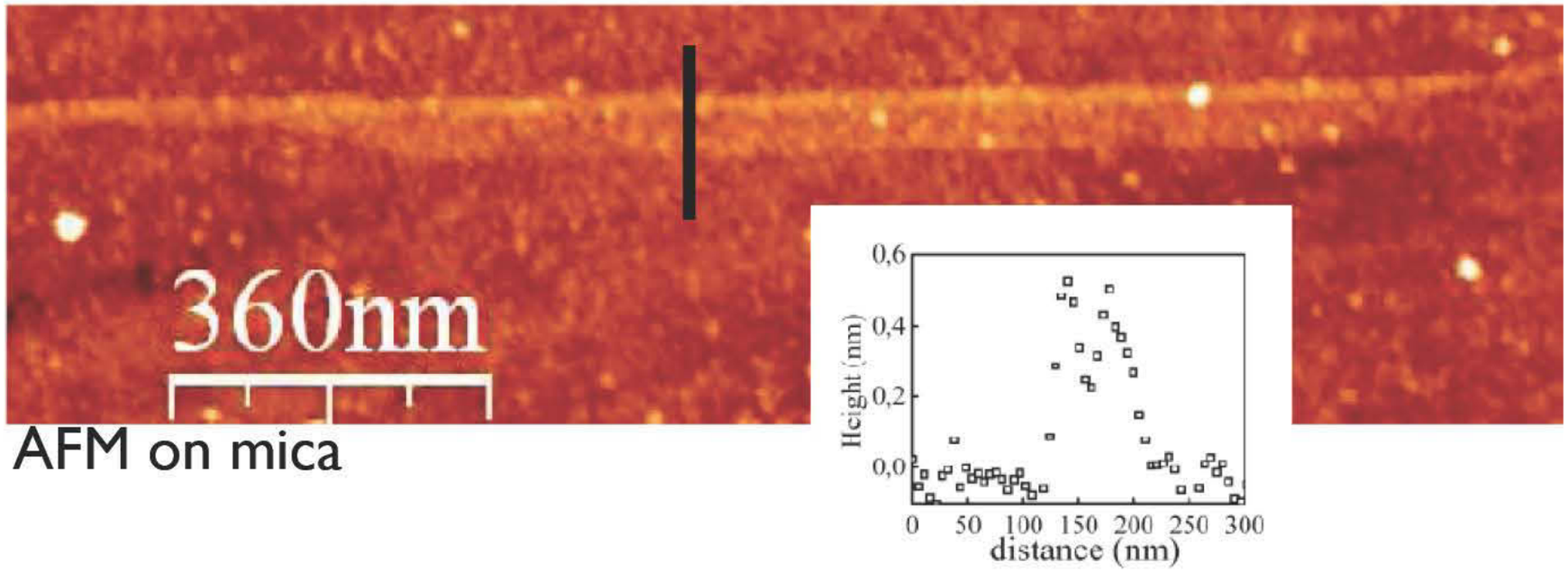

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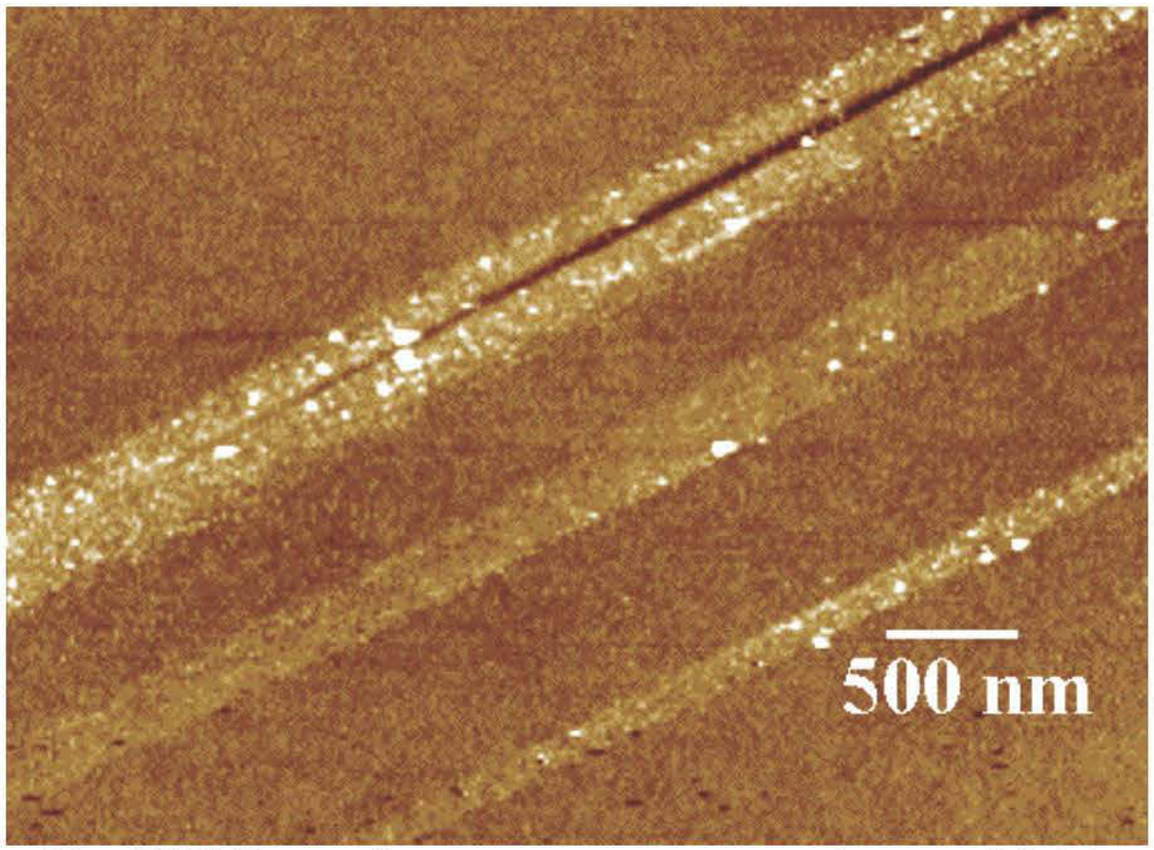


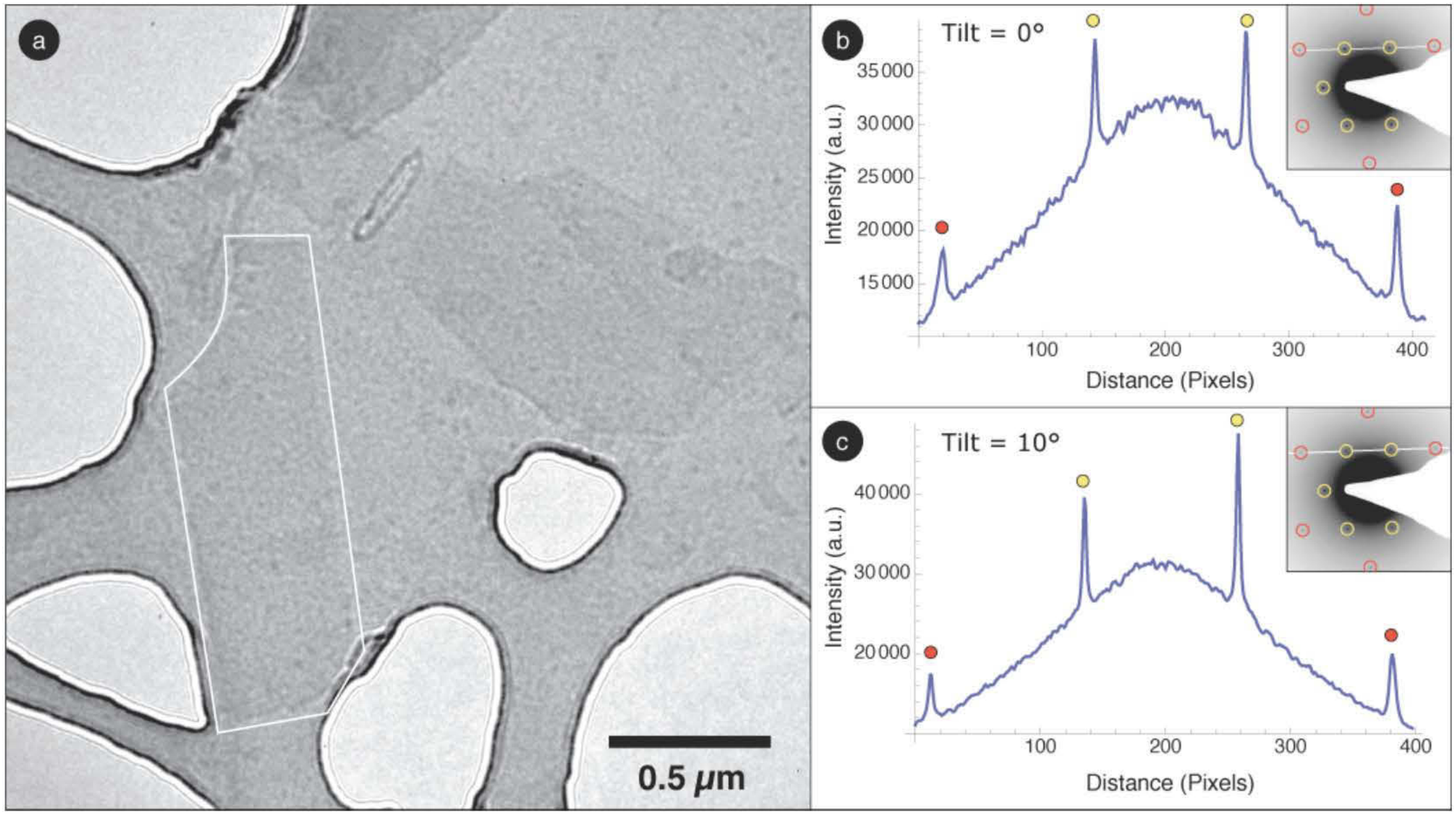
On Si/SiO_2 wafer

Image M. He

From $KC_{24}(THF)_x$

Graphene from Graphite Intercalation Compounds

Transmission electronic microscopy



Luca Ortolani, Bologna, Italy

A. Catheline et al., Chem. Commun., 2011, DOI: 10.1039/C1CC11100K

dispersions or solutions ?

metastable or stable?

Dissolution of Graphene salt or nanotube salt:

Spontaneous process: goes to the lowest energy state

can we go any further ?

Dispersions vs solutions

An ordinary solution is homogeneous whereas a heterogeneous system such as an emulsion of oil in water should be called a mixture.

L. Pauling, . General Chemistry , Dover 1988

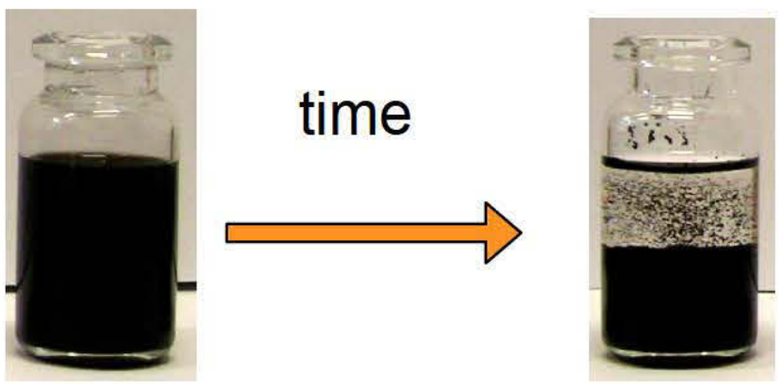
Emulsions (for ex, droplets of oil in water) are dispersions

A powder finely divided in a liquid is also a dispersion (mud)

Dispersion

- Heterogeneous (mixture)
- Metastable :

Biphasic system is energetically more favorable



solutions

- Homogeneous
- Stable :

Solution is energetically more favorable than the biphasic system

Dispersions vs solutions

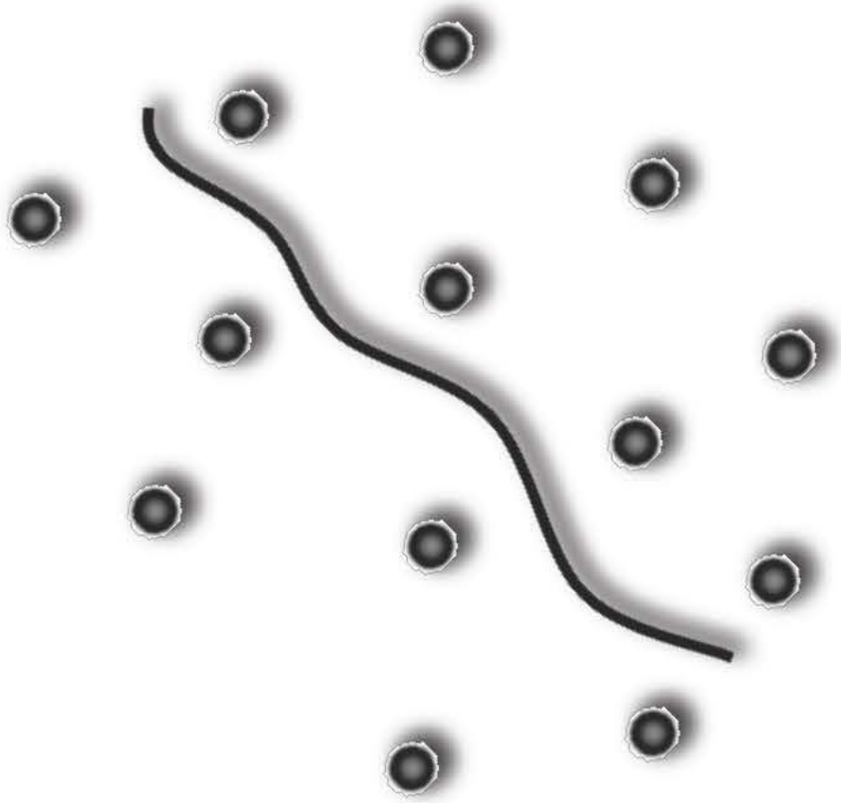
Upon mixing of the ingredients :

Solution will form spontaneously
(think of salt or sugar in water)

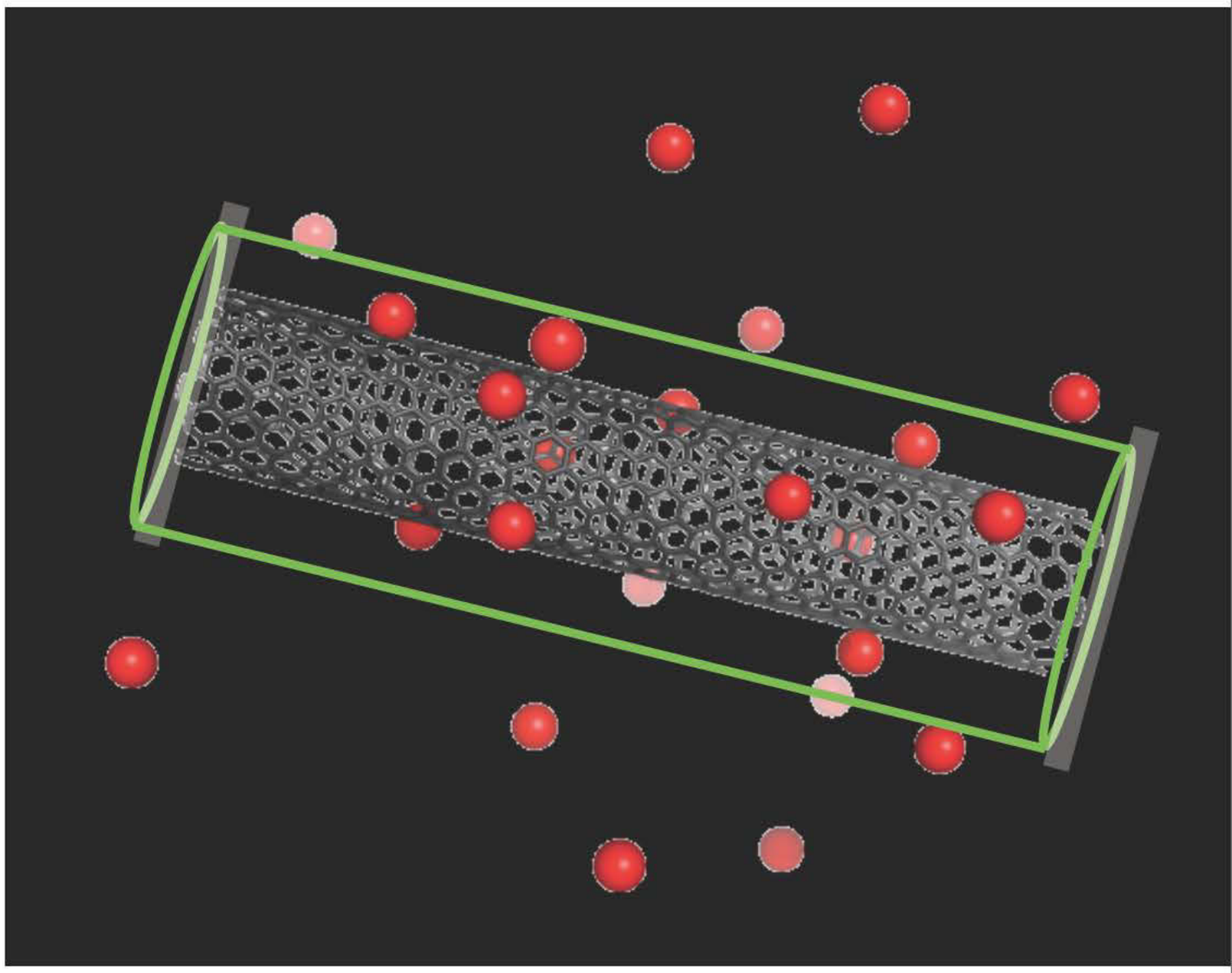
Dispersion will NOT form spontaneously
Think of a mayonnaise

need for stirring, heating, shearing, **sonicating**....

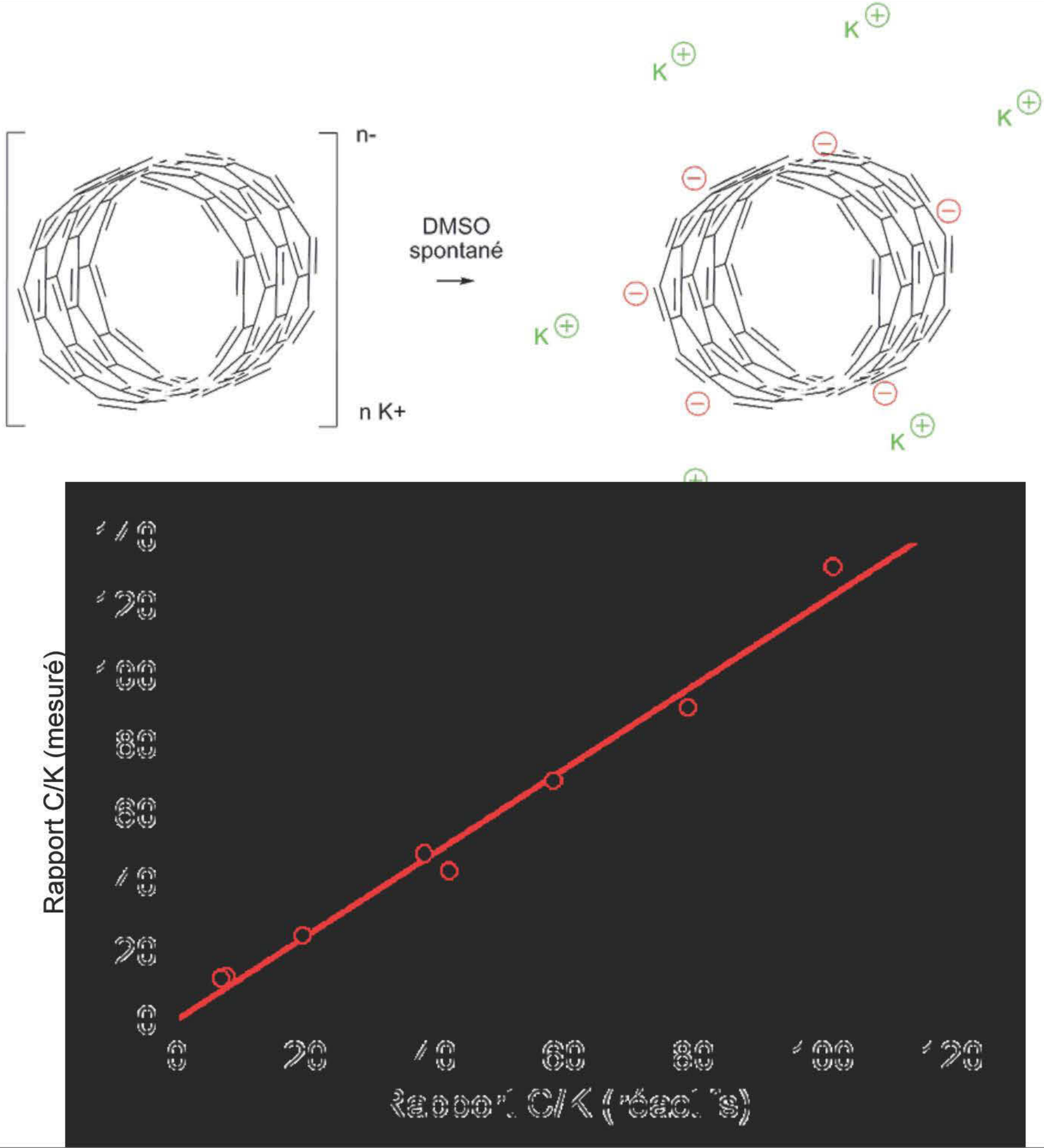
Analogy between reduced nanotubes and polyelectrolytes

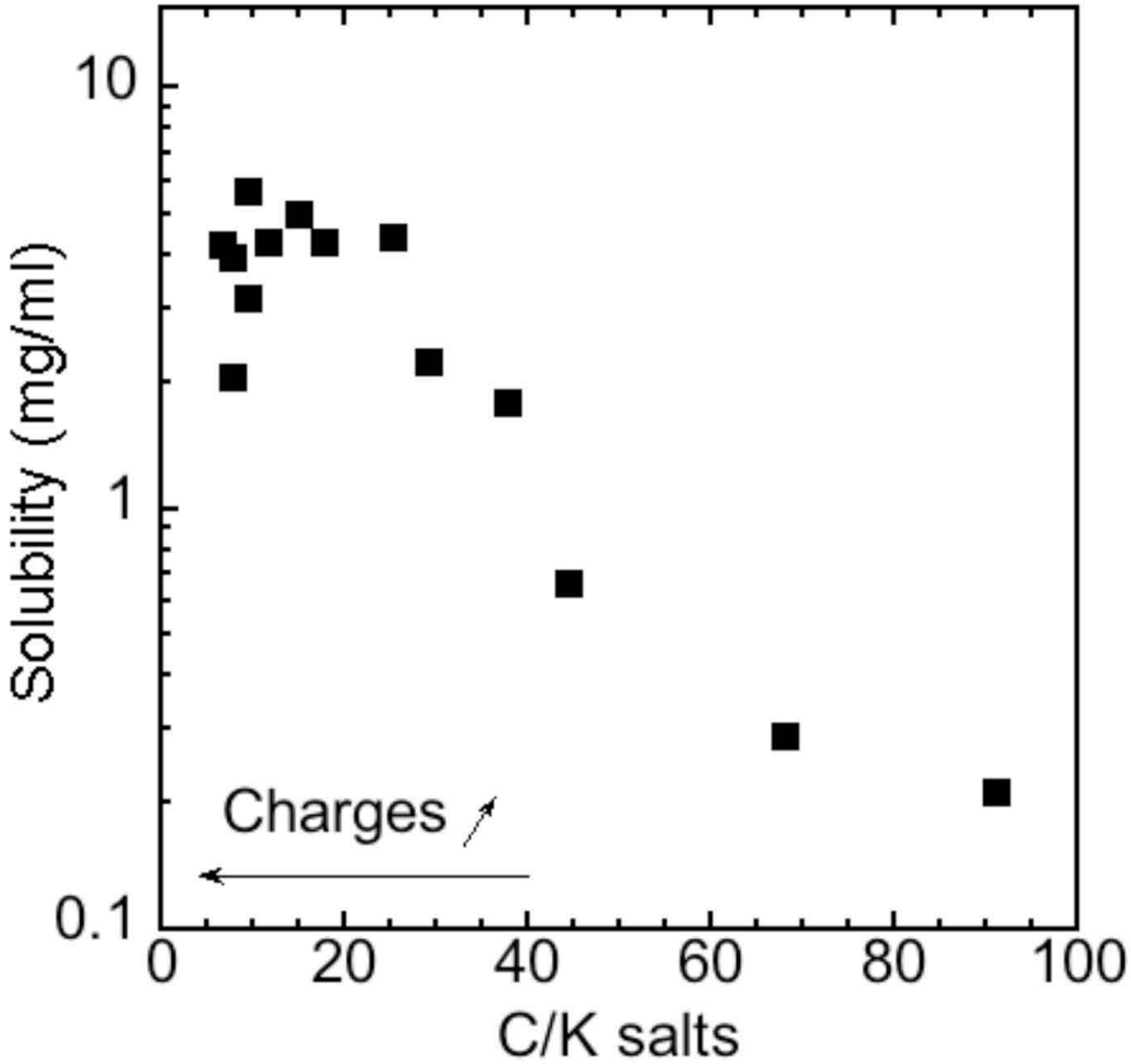


Polyélectrolyte



(reduced graphene: soft 2D polyelectrolyte)


n-
n K+
DMSO
spontané
K
K
K
K
K
Rapport C/K (mesuré)
Rapport C/K (réactifs)
0
20
40
60
80
100
120



can we modelize these results ?

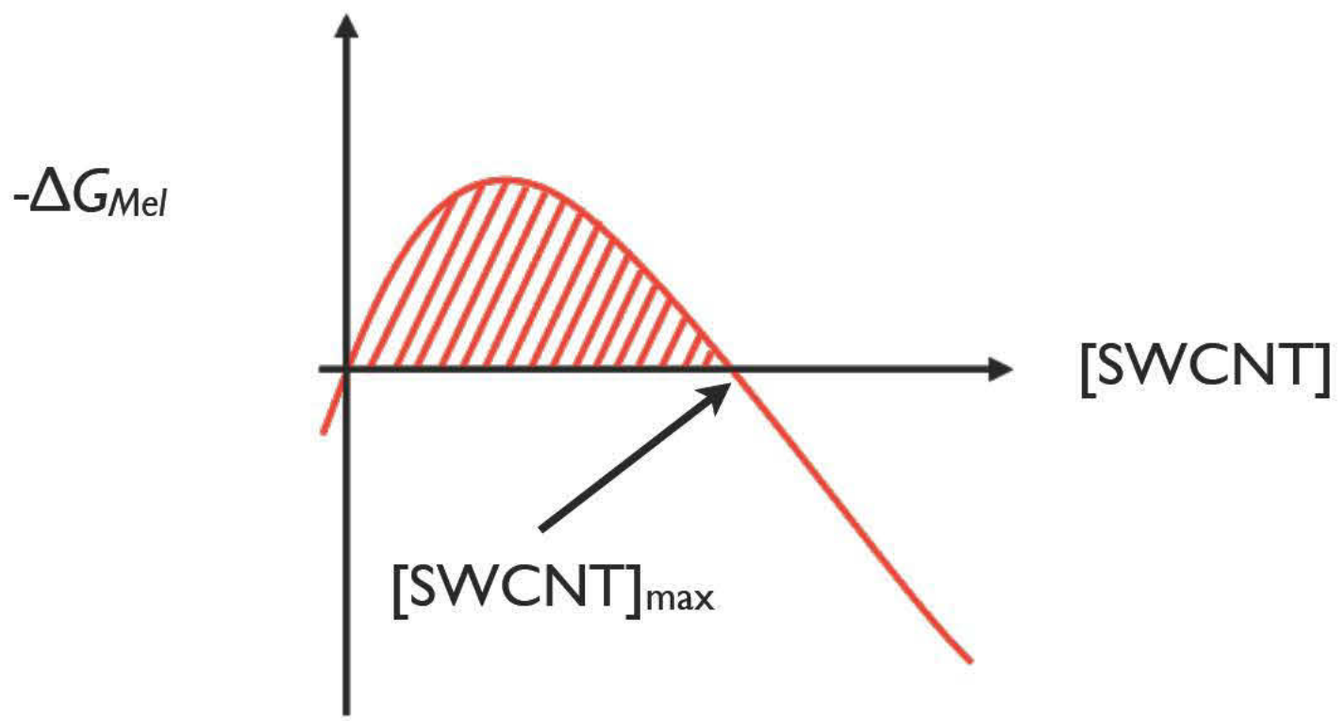
KC_x + solvent

Free energy of mixing:

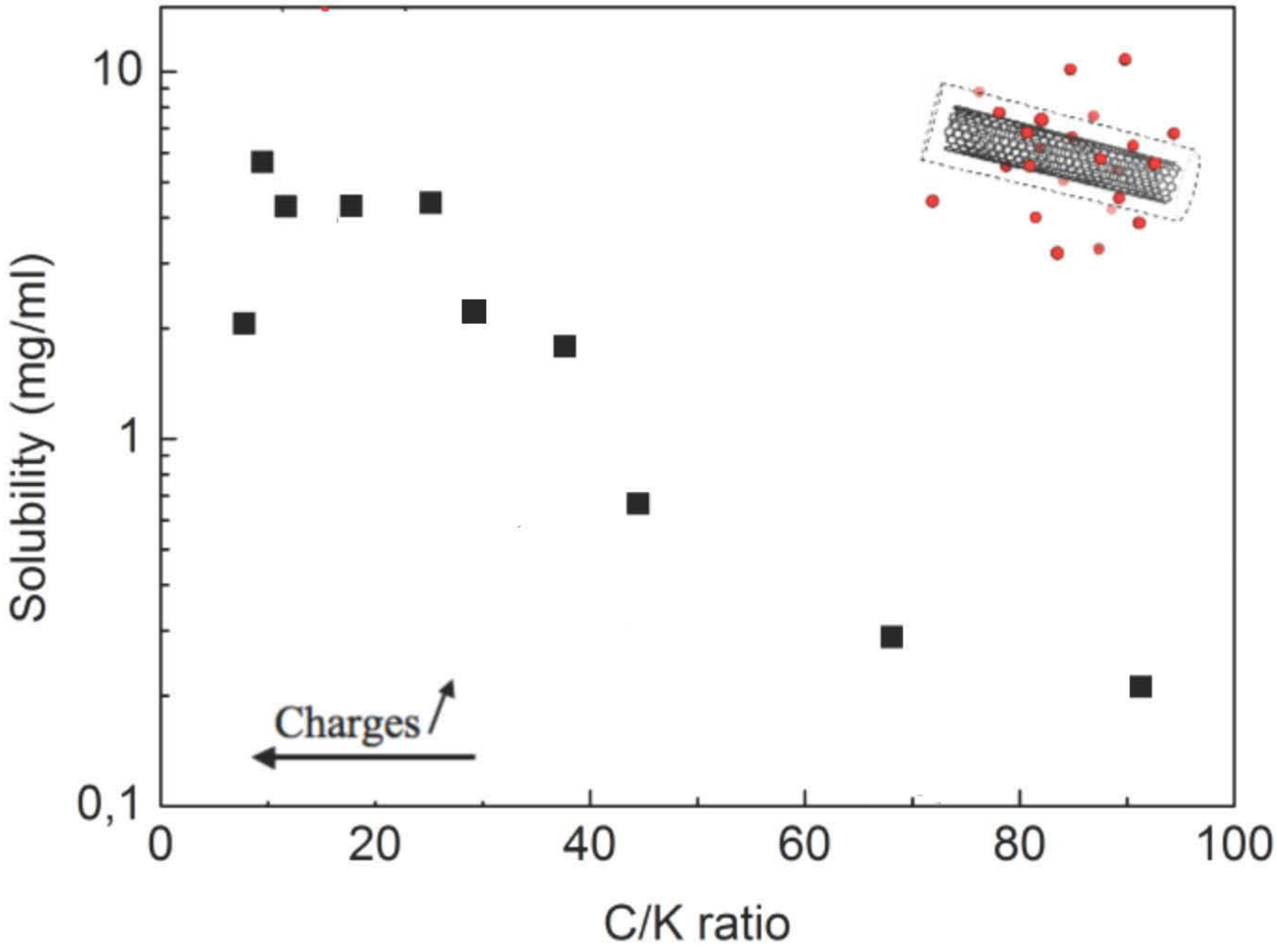
$$\Delta G_{Mel} = \Delta H_{Mel} - T\Delta S_{Mel}$$

mixture is stable if :

$$\Delta G_{Mel} < 0$$



$$\Delta G_{Mel} = \Delta H_{Mel} - T\left[\Delta S_{Mel-SWCNT} + \Delta S_{Mel-Solvant} + \Delta S_{Mel-Contre-ion}\right]$$



D. Voiry
C. Drummond

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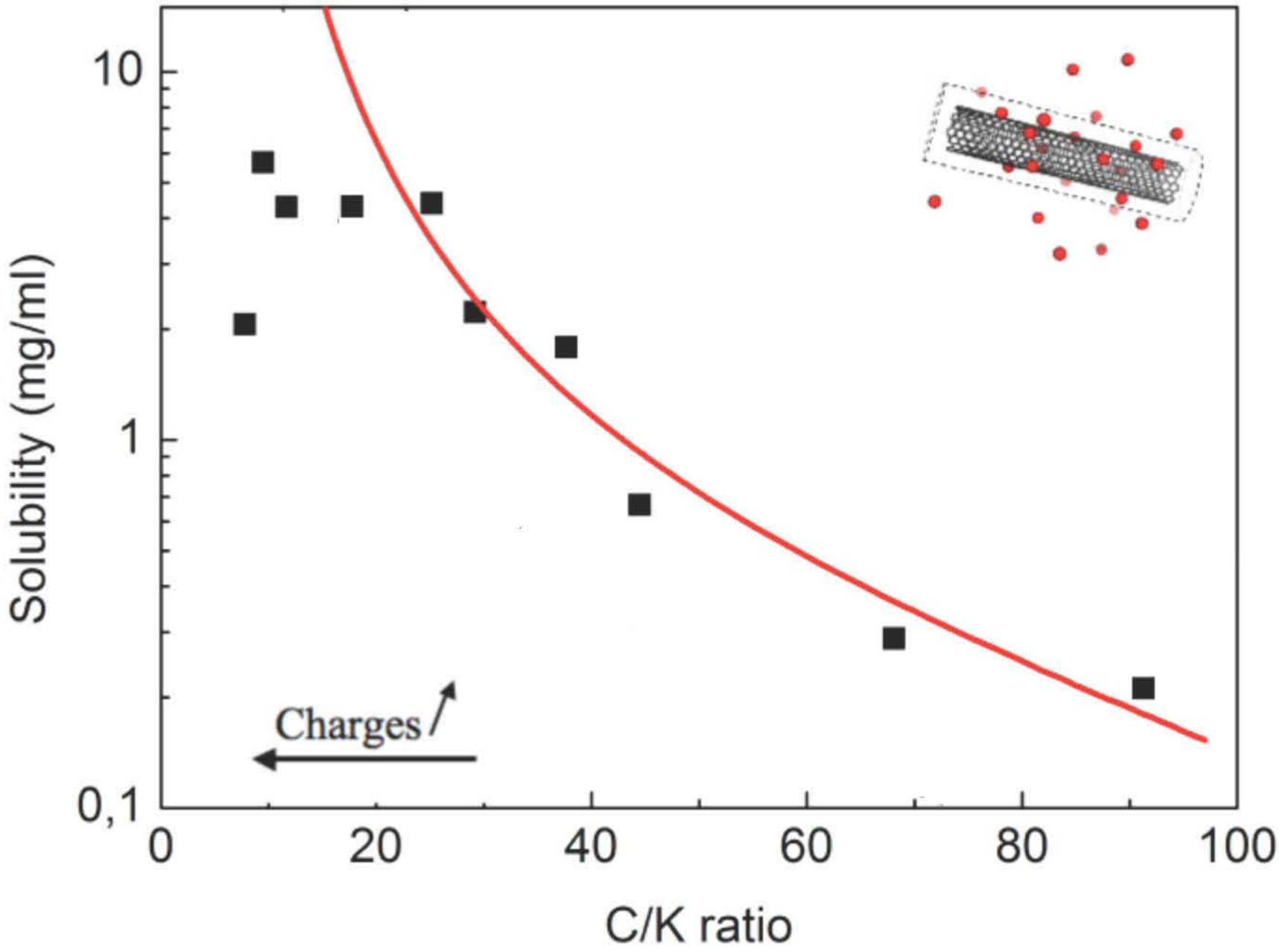

D. Voiry
C. Drummond

Graphene solutions

- ☑ Negatively charged graphene sheets
- ☑ 2D polyelectrolyte

- ☑ Spontaneous dissolution
- ☑ No mechanical energy needed

- ☑ Solutions of graphene 0.7 mg/ml

→ ☑ base for chemistry

The Nanotube team at CRPP, Octobre 2010

Amélie Catheline, **Carlos Drummond**, Hassan Saadaoui (CRPP)
Damien Voiry, Maryse Maugey, Cécile Zakri (CRPP)
Marc Monthioux, (CEMES Toulouse)
Luca Ortolani, Vittorio Morandi **(**CNR Bologna)
Cristina Vallés, CSIC, Zaragoza
C. Furtado, M. Pimenta, C.Fantini, A. Righi, (Belo Horizonte)
F. Paolucci, M. Iurlo, M. Marcaccio, S. Rapino, G. Valenti (Bologna)
Newton Rosas (Nacional de Grafite, Brazil)

ChemOnTubes 2012

Arcachon, France
April 1 – 5, 2012

International Meeting on the Chemistry of Nanotubes and Graphene

Scope

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

Invited speakers

- K. Müllen (Mainz)
- R. Haddon, (U. California Riverside)
- J. Lagerwall (Séoul)
- C. Ewels (Nantes)
- N. Nakashima (Kyushu)

Abstract submission deadline: December 15, 2011
Registration deadline: February 1, 2012

Contact: chemontubes@crpp-bordeaux.cnrs.fr
http://chemontubes2010.crpp-bordeaux.cnrs.fr

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