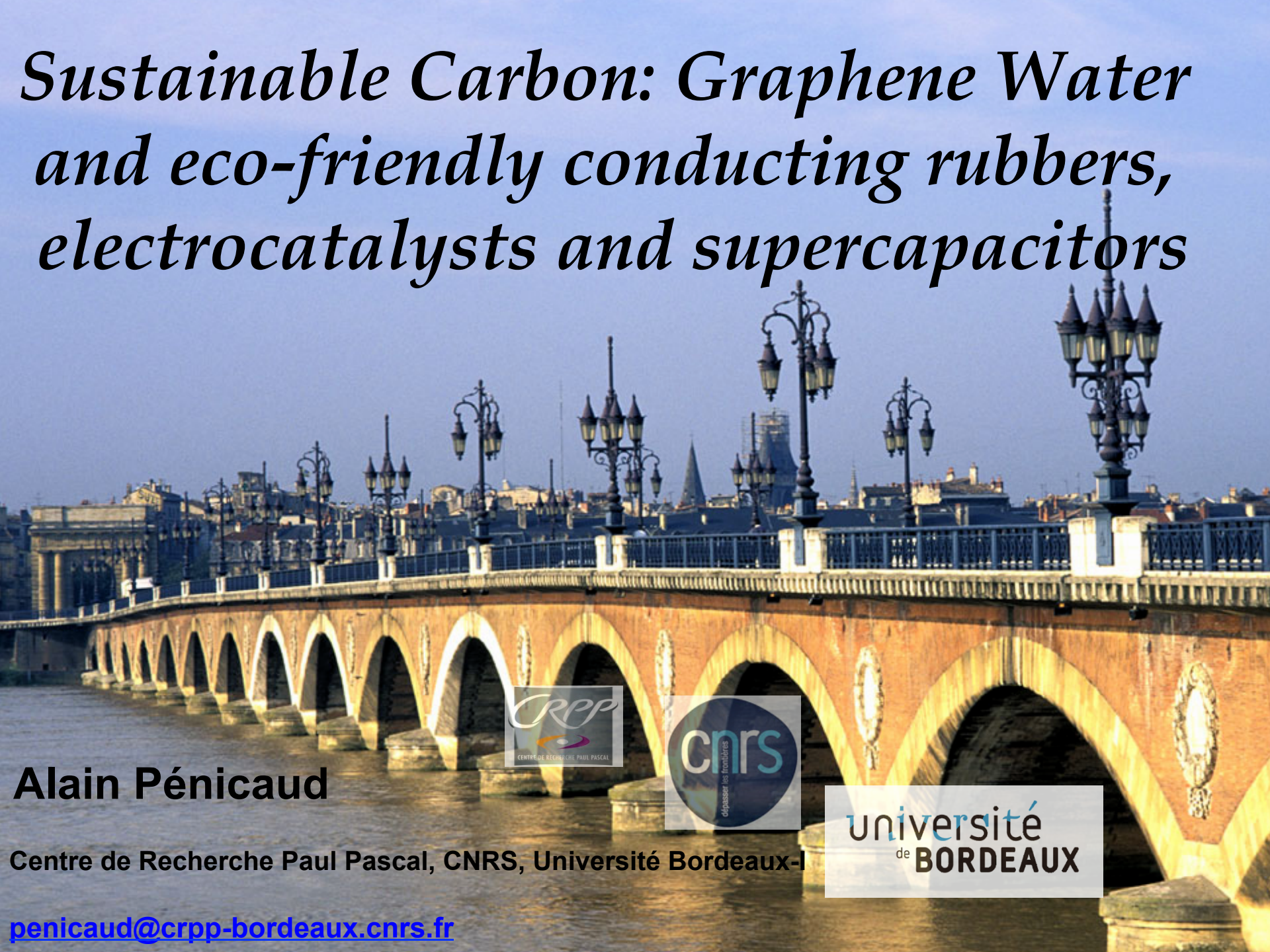
# *Sustainable Carbon: Graphene Water and eco-friendly conducting rubbers, electrocatalysts and supercapacitors*




**Alain Pénicaud**

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

penicaud@crpp-bordeaux.cnrs.fr

# Outline

- Eau de Graphène (graphene water):

  Additive free Single layer graphene in water


- Carbon Waters : the Company

- Multi layer Graphene from food waste ?

  - conducting rubbers
  - electrocatalysts
  - supercapacitors

PLAS•CARB

INNOVATIVE PLASMA BASED TRANSFORMATION OF FOOD WASTE INTO HIGH VALUE GRAPHITIC CARBON AND RENEWABLE HYDROGEN

# Graphene :

## a single layer of hexagonally arranged carbon atoms

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

## The ultimate membrane:

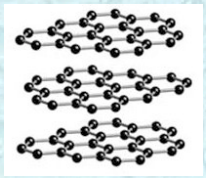
- ☑ All surface material
- ☑ thinnest
- ☑ strongest
- ☑ flexible yet tough
- ☑ electrical conductor
- ☑ Thermal conductor

**Q: How to transfer the property of the individual object to a macroscopic material ?**

A: By **properly** exfoliating graphite

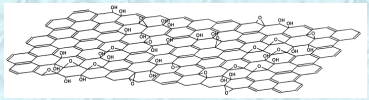
# **Liquid formulations** of graphene

- **Reduced graphene oxide(RGO):**



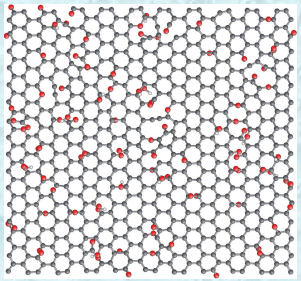
Graphite

Sulfurique acid / $KMnO_4$



GO

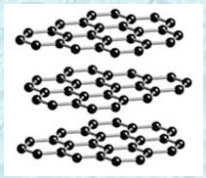
Reduction



RGO

- full exfoliation
- water Soluble
- Defects

- **Mechanical exfoliation in liquids**:



Graphite

Surfactant

Mechanical energy

- Low cost
- Distribution of thickness (1 to 20 layers)
- Concentration < 0.07 g/L
- Surfactants or toxic solvants (NMP)

- **Reductive Dissolution: ….**

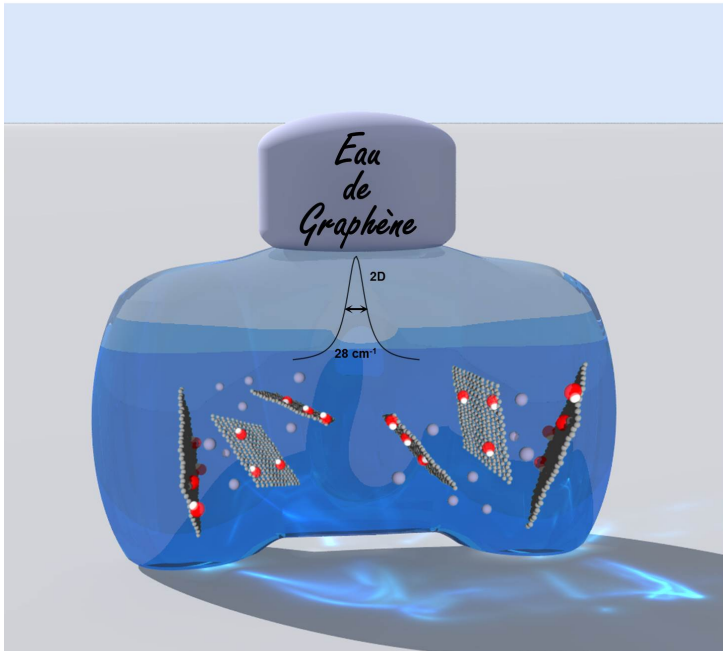
- You ~~cannot~~ can get 100 % single layer graphene in water

Oil

+

Water

George Bepete

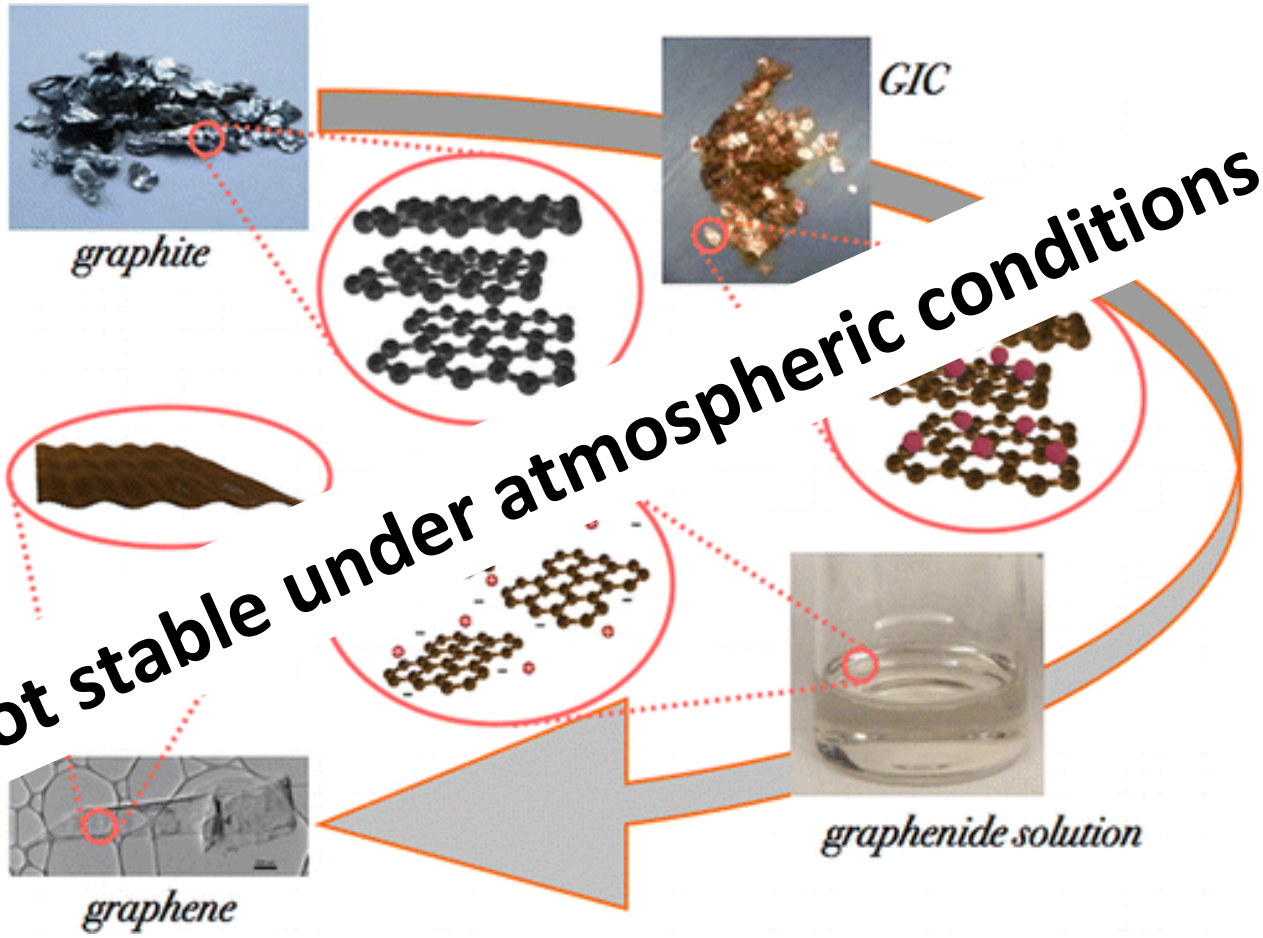



# *Eau de Graphène*

Alain Pénicaud, CNRS-Université de Bordeaux penicaud@crpp-bordeaux.cnrs.fr NanoSpain Bilbao, March 15 2018

# Full exfoliation to SLG

## Dissolution of GICs in aprotic solvents




Drummond & Penicaud., Acc. Chem. Res. (2013)

Valles *et al*., JACS. (2008) Englert *et al*., Nat. Chem. (2011) Catheline *et al.,* Soft Matter. (2012) Milner et al., JACS. (2012)

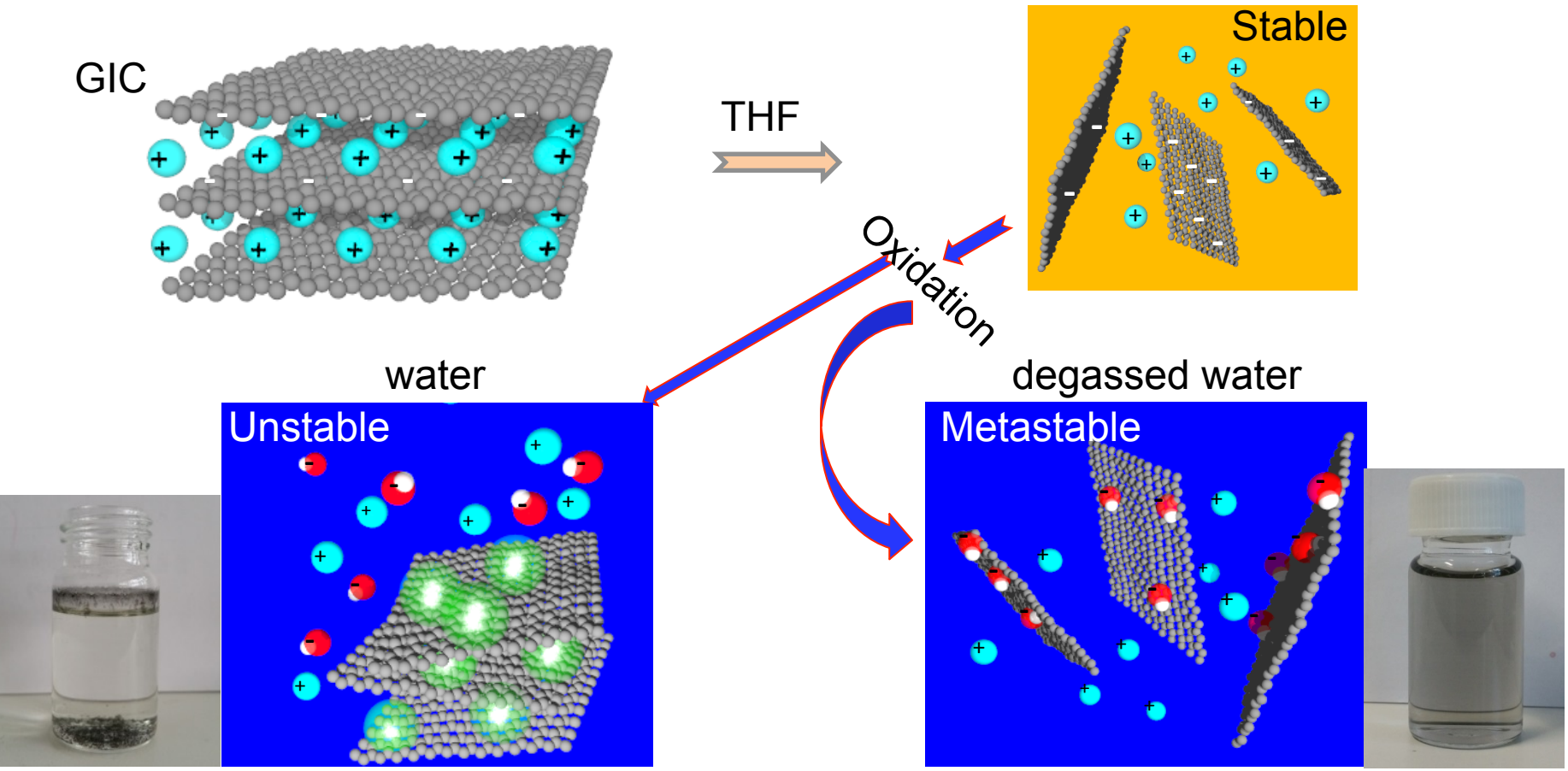
nature chemistry

ARTICLES

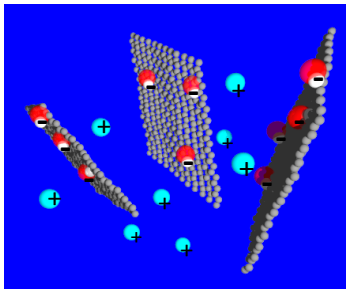
PUBLISHED ONLINE: 28 NOVEMBER 2016 | DOI: 10.1038/NCHEM.2669

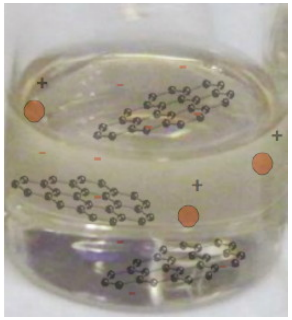
# Surfactant-free single-layer graphene in water

George Bepete[1,2], Eric Anglaret[3], Luca Ortolani[4], Vittorio Morandi[4], Kai Huang[1,2], Alain Pénicaud[1,2]* and Carlos Drummond[1,2]*




Bepete *et al.*, Nature Chem, 2017, J. Phys. Chem C, 2016, Phys. Status Solidi RRL 2016





Oxidation

Addition of water

$+ O_2$ → $+ K^+O_2^-$ → $+ KOH$

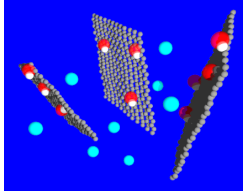
Normal water

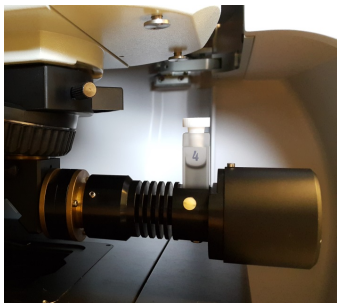
pH = 11

Degassed water

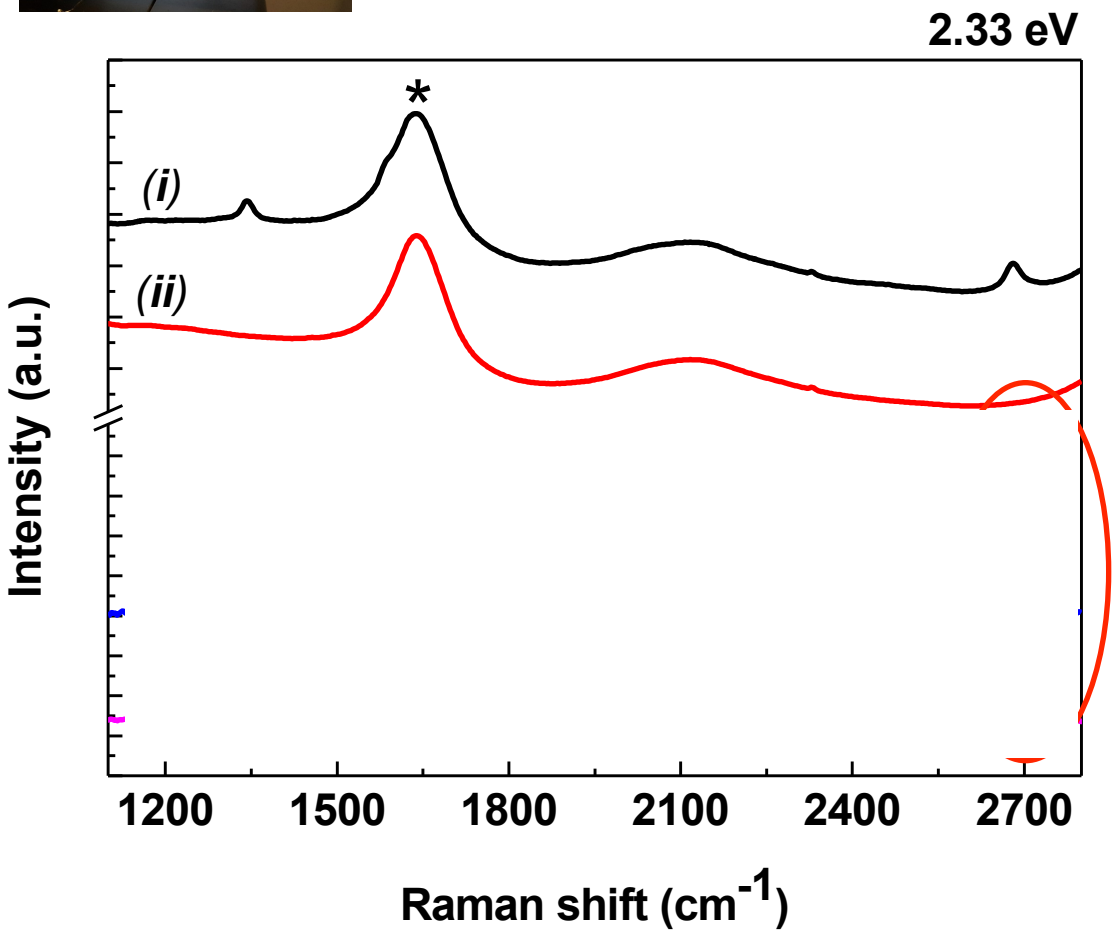
pH = 8

# Raman signatures of graphene in water





## In liquid !



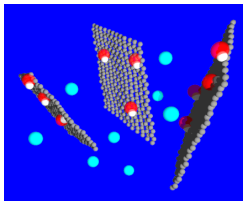

**Graphene in water**

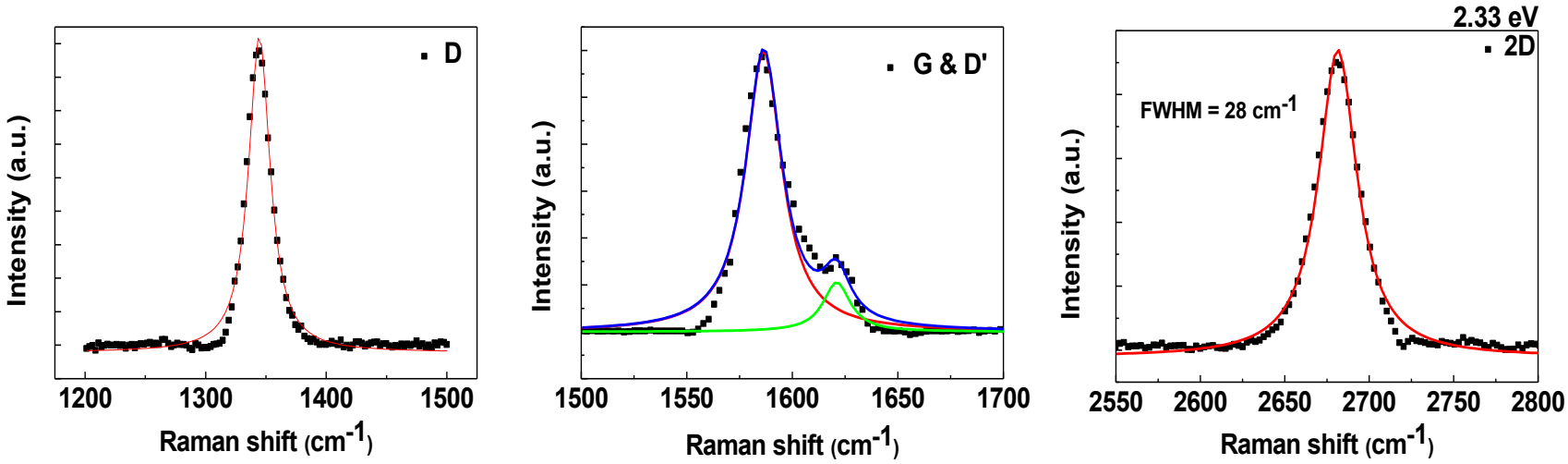
**Water**

**Graphene in water after water substraction**

**NaC stabilized graphene After water substraction**

# Raman signatures of SLG in water





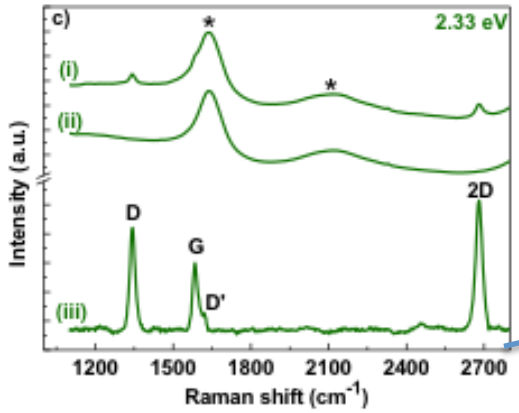

| ExcitationEnergy (eV) | D | | G | | D' | | 2D | |
|---|---|---|---|---|---|---|---|---|
| | ω | Δ | ω | Δ | ω | Δ | ω | Δ |
| 2.33 | 1345 | 27 | 1586 | 21 | 1620 | 16 | 2681 | 28 |

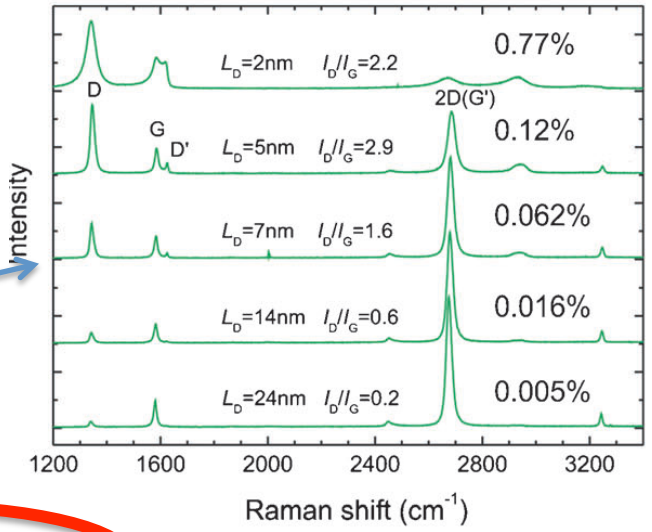
**Symmetric, narrow and intense 2D band**
→signature of SLG

Bepete et al., J. Phys. Chem C, 2016

# D band : concentration of defects ?

Lucchese Carbon (2010)



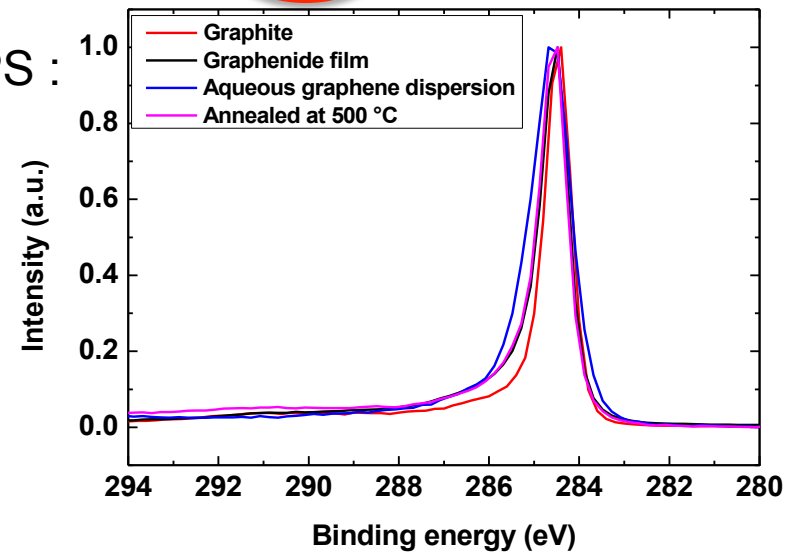



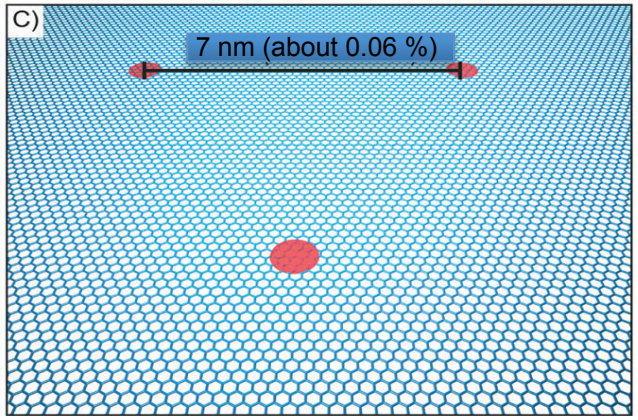

Cançado et al.. Nano Lett. (2011)

| $E_L$/ eV | ID/IG | ID/ID' |
|---|---|---|
| 2.33 | 1.6 | 9.0 |

600 ppm defects

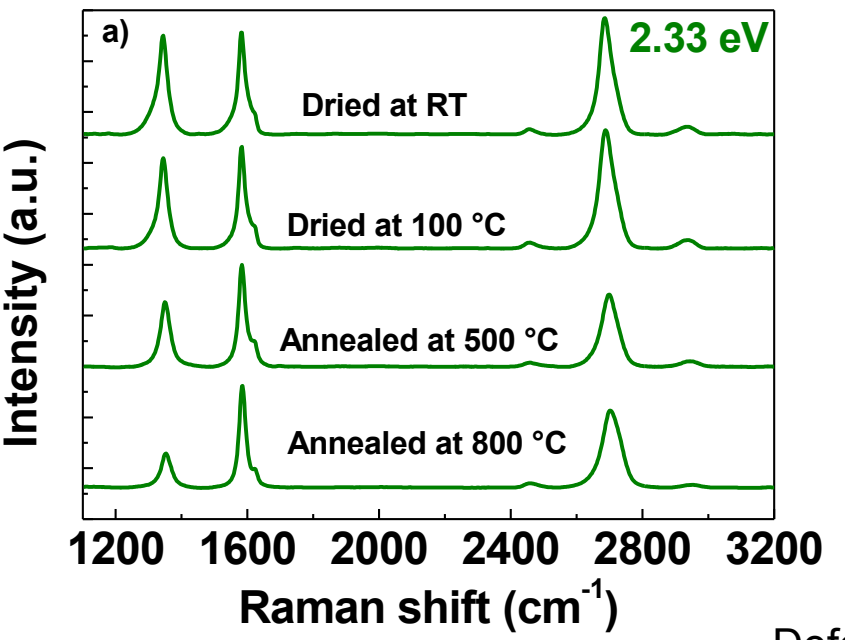
XPS :




Adapted from:Eigler & Hirsch Angew. Chemie (2014)

# Films from EdG at 2.33 eV




| Film Treatment | 2D | | $A_D/A_G$ | $I_D/I_{D'}$ |
|---|---|---|---|---|
| | $\omega$ | 2G | | |
| Aqueous dispersion | 2681 | 28 | 1.5 | 9.0 |
| As made film | 2688 | 51 | 1.3 | 7.1 |
| 100 °C film | 2691 | 55 | 1.1 | 6.1 |
| 500 °C film | 2699 | 59 | 0.9 | 4.0 |
| 800 °C film | 2705 | 65 | 0.5 | 3.0 |

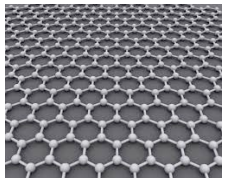
Defect analysis : Casiraghi et al. Nanolett. 2012, PRB 2013

**After annealing, all sp3 defects removed: only edges left**

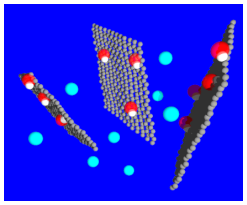
σ = 32 kS/m -> ρ= 0.003 Ω.cm

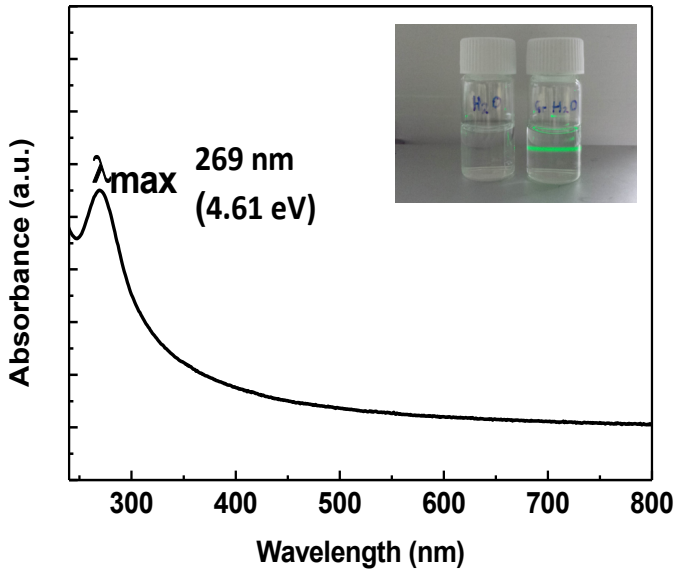
(carbon inks ρ= 10 Ω.cm, Ag inks $10^{-6}$ Ω.cm)

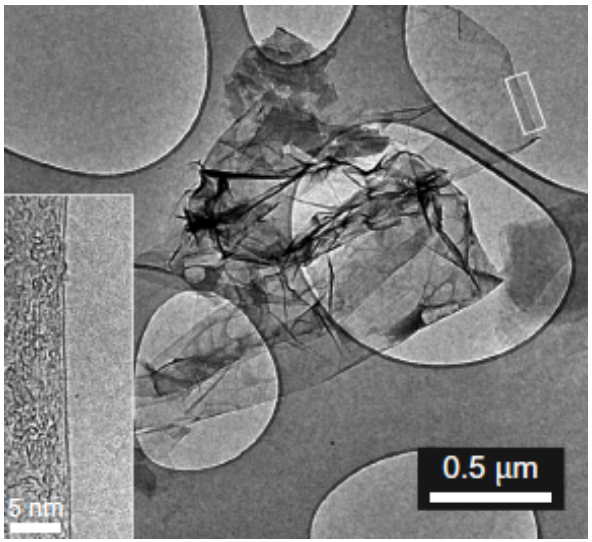
Light, flexible, inert, conductive coatings

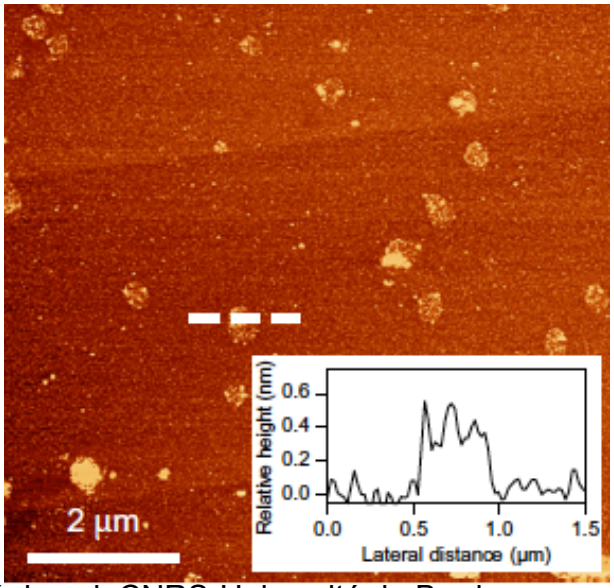


# *Other evidences of SLG in "eau de graphene"*






**SLG in *degassed* water**
**(no surfactant/organic additives)**

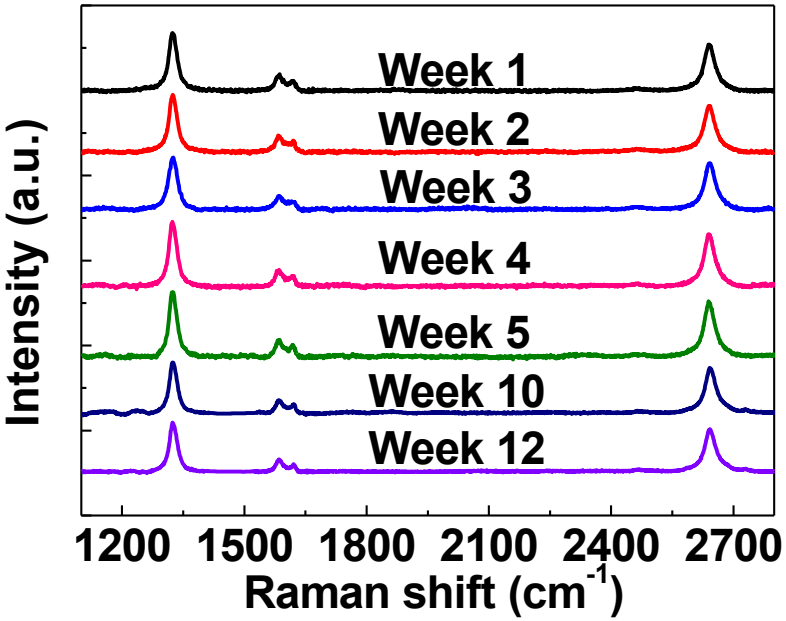
**c=0.16 g/L≈ 200 m²/L , pH=8**

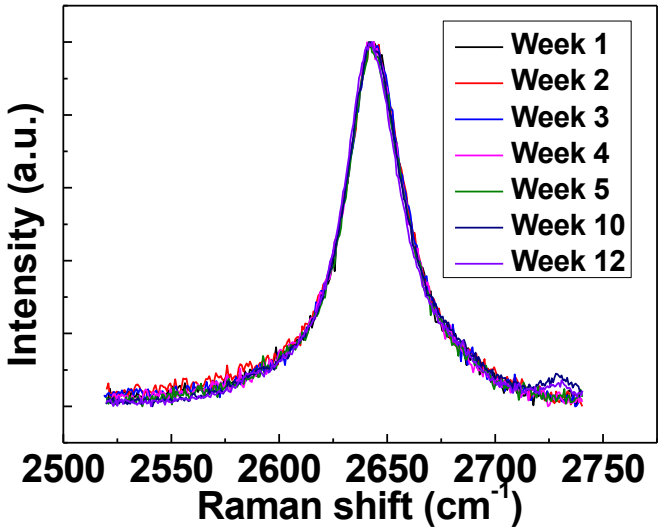
**Typical flake size 100 nm-1 µm**

*Bepete et al., Nature Chemistry, 2016*

# Stability of SLG dispersions

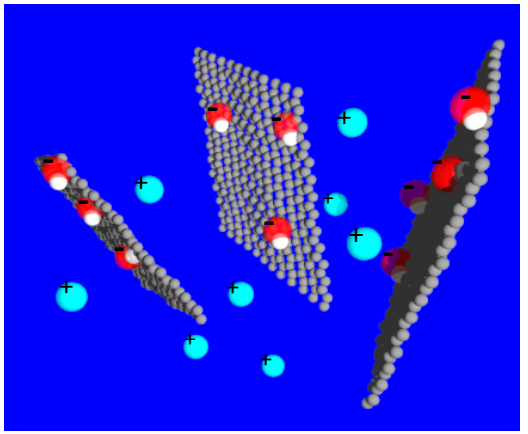
## Raman spectroscopy

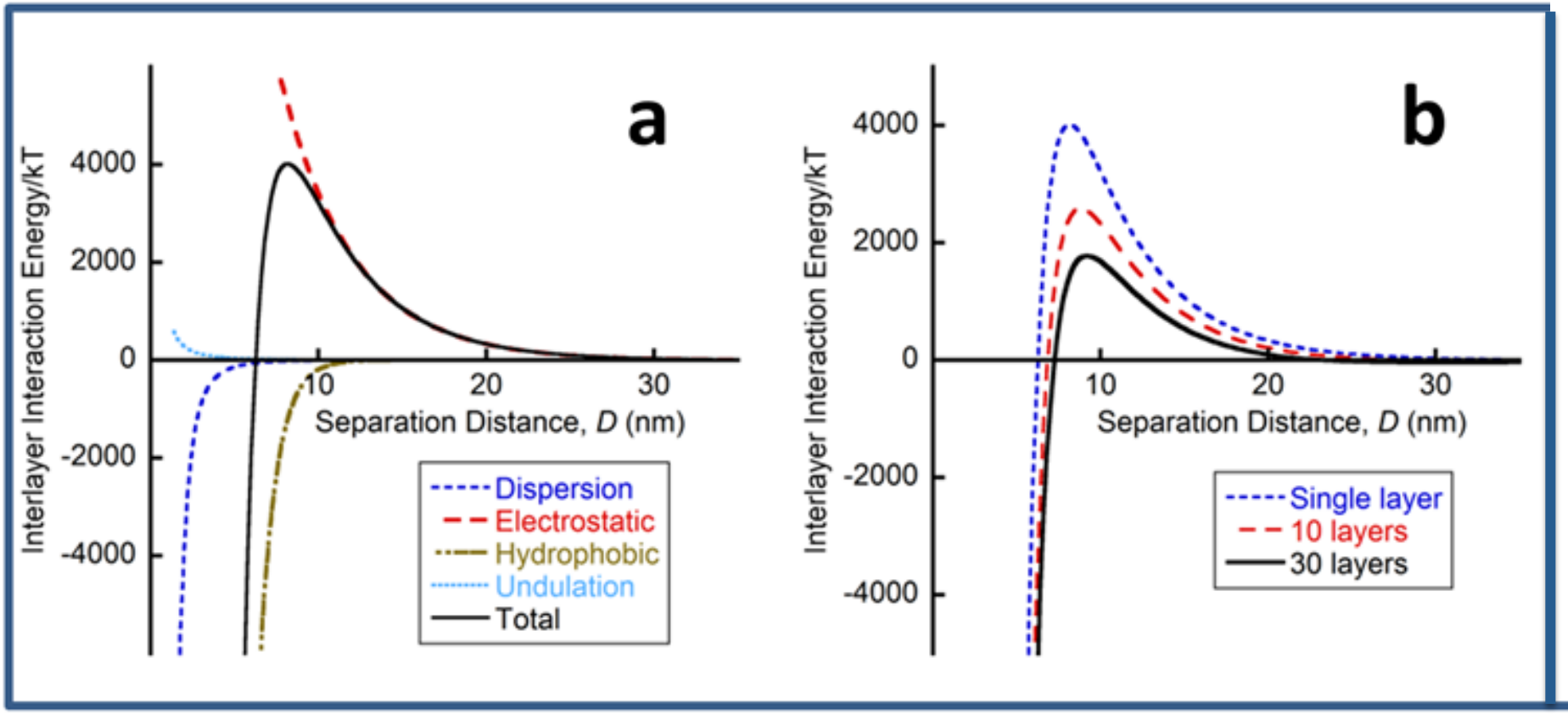



Same 2D linewidth after **12 weeks…**

# The ingredients behind (meta)stability. I



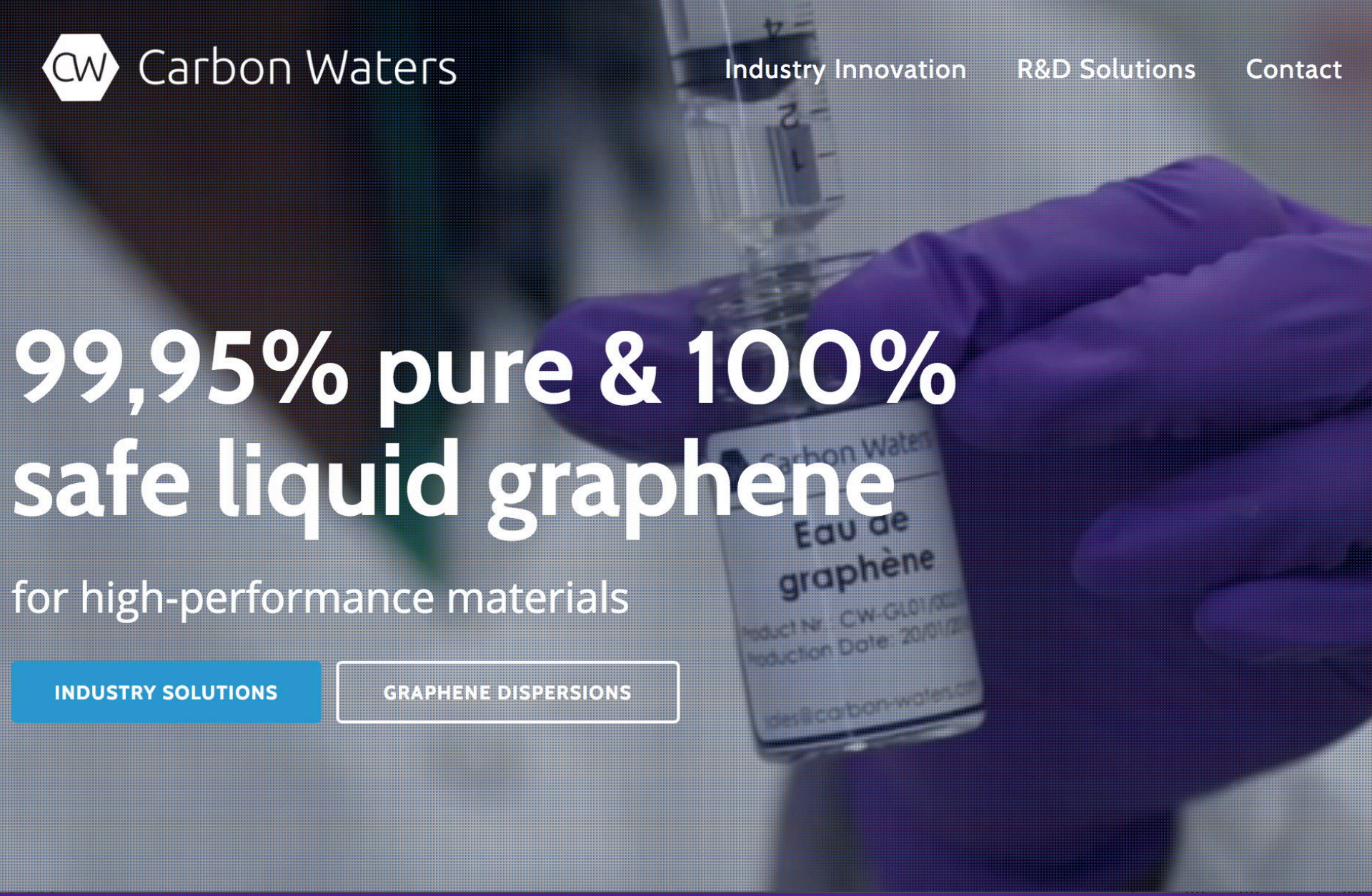


# Eau de Nanotube

(Nanotube Water)

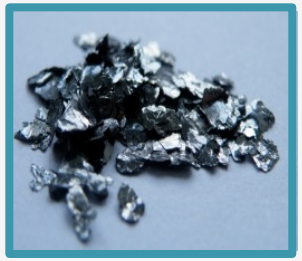
See Eric Anglaret's talk

Alain Pénicaud, CNRS-Université de Bordeaux penicaud@crpp-bordeaux.cnrs.fr 




https://www.carbon-waters.com/

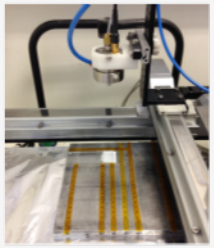
# Carbon Waters : Graphene processing for industry



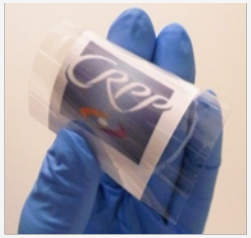
***Exclusive licensing of 3 patents,***

- No free nanoparticles
- No chemical agents
- Extremely stable
- Very high quality and no defect materials
- Can be printed on several surfaces
- Easy to scale-up

Liquid organic nanomaterial solution



Surface printing



Surfaces with enhanced and reinforced properties

**Carbon Waters : production and sales of nanocarbons and nanocarbon printed surfaces**

# Multilayer graphene from food waste

Food Waste

Anaerobic Digestion:
BIOGAS: $CH_4$ & $CO_2$

microwave plasma process: biogas to C & $H_2$

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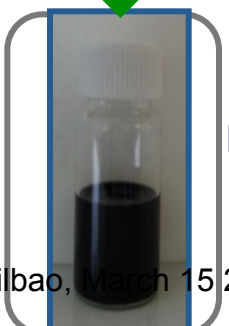
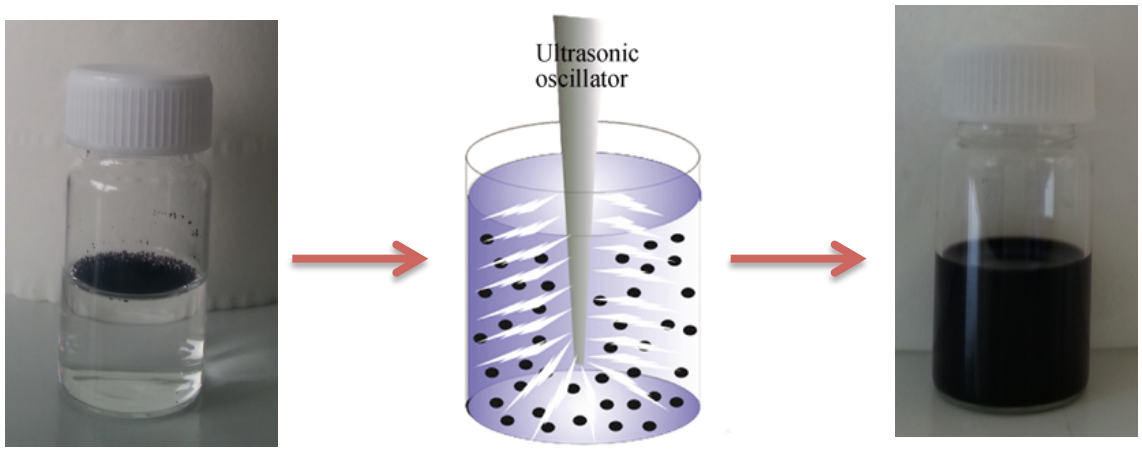
Conducting rubbers
Conducting inks
Supercapacitors
...

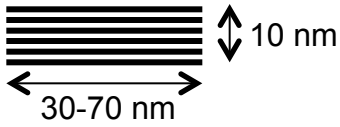


Nanocarbon dispersion




# Graphitic nanocarbon :

- Graphitic nature (turbostratic)
- High conductivity (σ~100 S/m)
- Nanopucks of ca 20-30 graphene layers
- Size distribution:
  - Average thickness = 10 nm
  - lateral size = 30 - 70 nm




Carbon Nanopucks

Conductive inks of graphitic nanoparticles from a sustainable carbon feedstock,Hof, Kampioti, Huang et al., **Carbon** 111 (2017) 142.

# Applications : Rubber Composites

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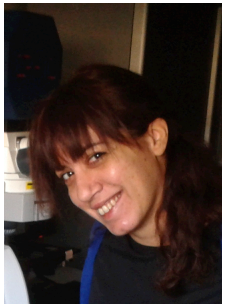
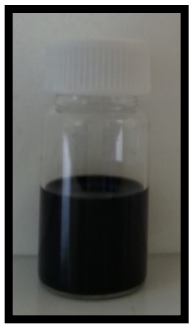


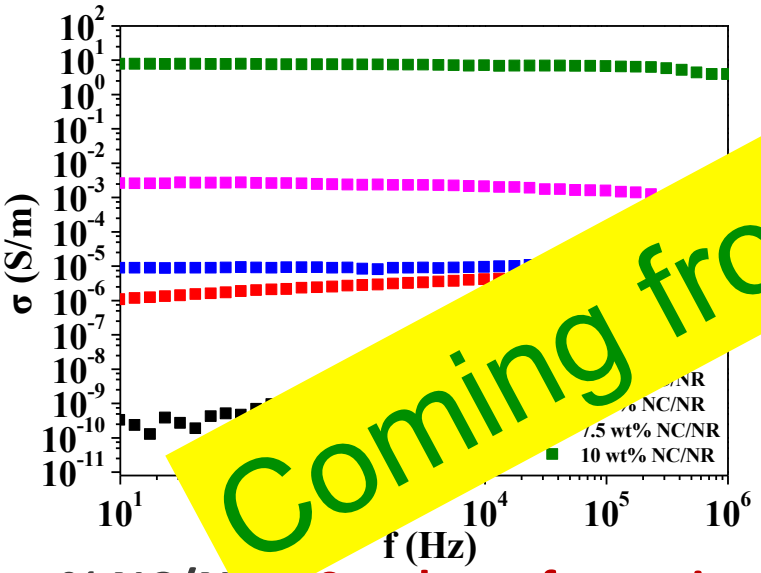
Katerina Kampioti

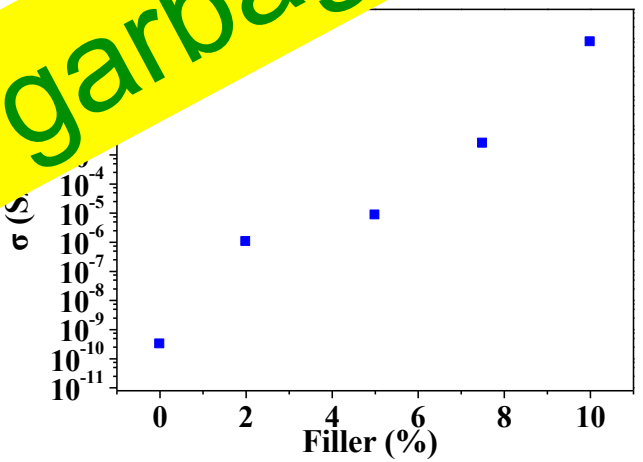
NR

NC



R/NC nanocomposites




Coming from garbage !

**10 wt% NC/NR : 10 orders of magnitude better electrical conductivity !!!**

Kampioti et al., ACS Omega 2018

Collab. Aldo Zarbin's group, Curitiba, Brazil

YouTube : **From compost to composites: An eco-friendly way to improve rubber**

# Applications : Inks

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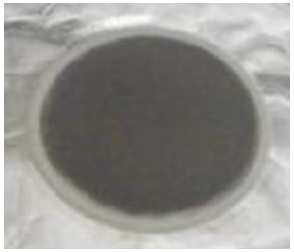
## Filtration

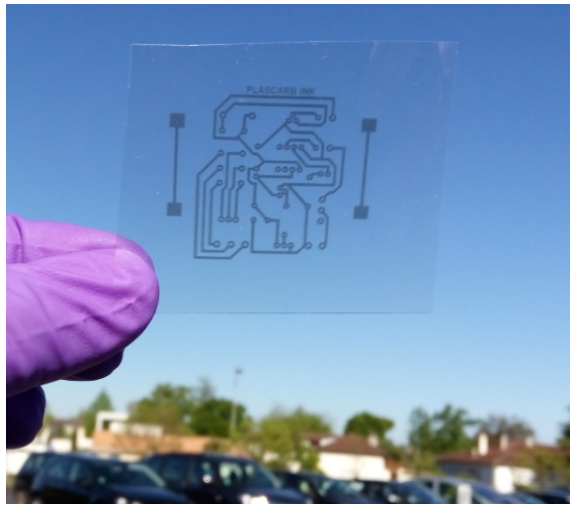
filtration on membrane



ρ= 2 Ω.cm

(carbon black inks ρ= 1 Ω.cm)

## Ink-jet printing



20 prints on PET

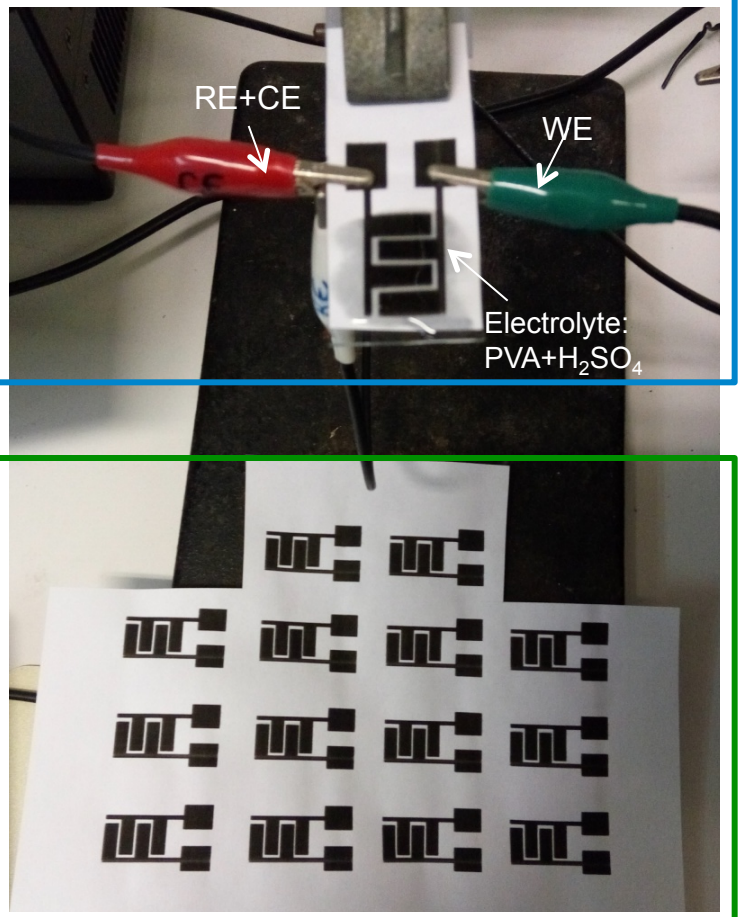
Hof, Kampioti, Huang et al., Carbon 2017

# Flexible micro supercapacitor by inkjet printing

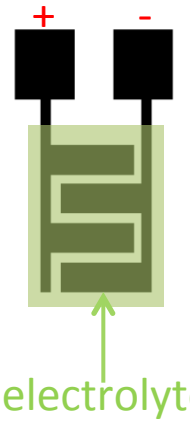
Kai Huang

Canon printer

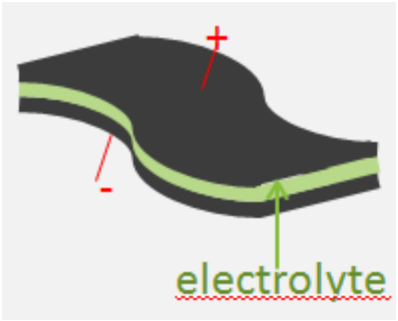

Cyclic voltrammetry testing set-up




In-plane MSC

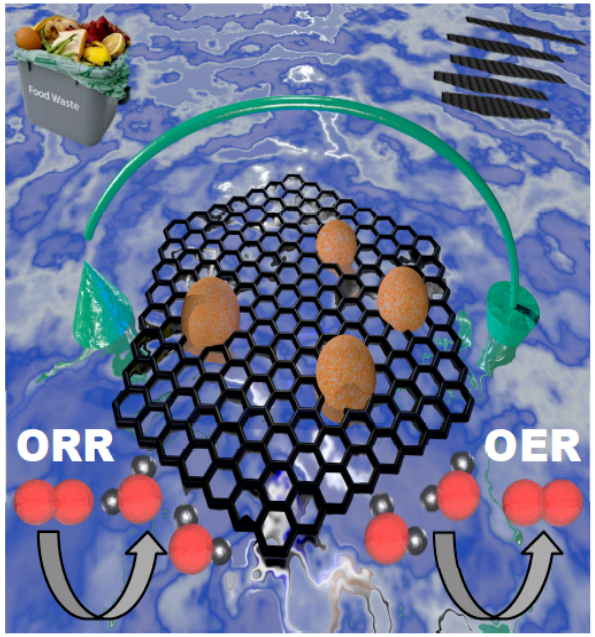



Sandwich MSC



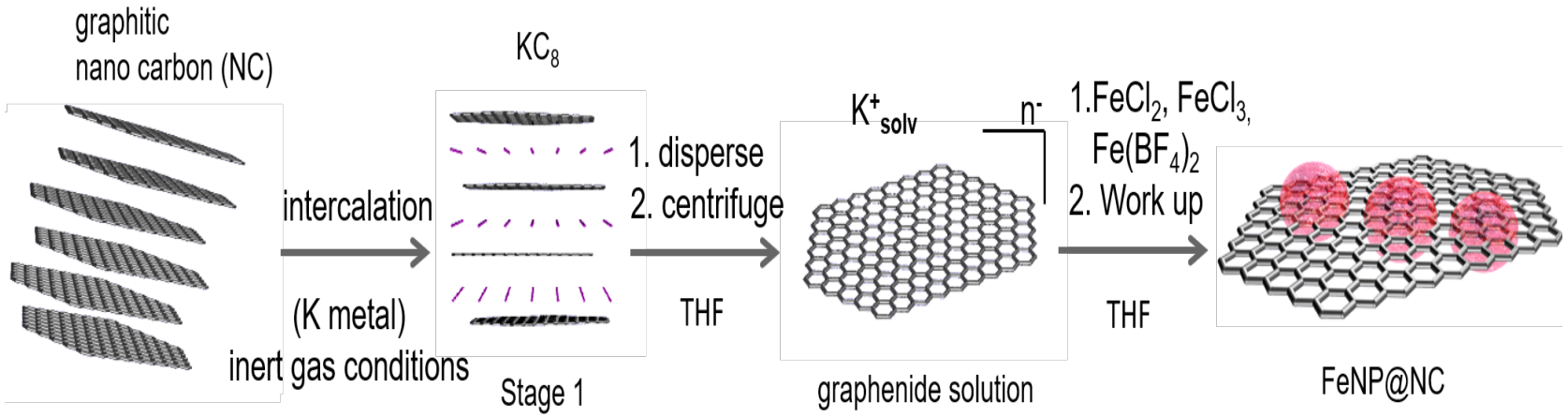

Printed micro supercapacitors on A4 paper

Alain Pénicaud, CNRS-Université de Bordeaux penicaud@crpp-bordeaux.cnrs.fr NanoSpain Bilbao, March 15 2018




# From Food Waste to Efficient Bifunctional Nonprecious Electrocatalyst

Ferdinand Hof



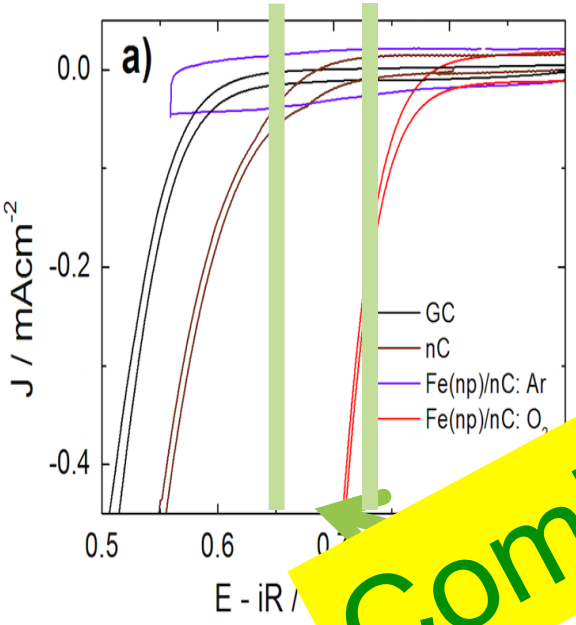

Hof, F. et al. Chem. Eur. J. 2017

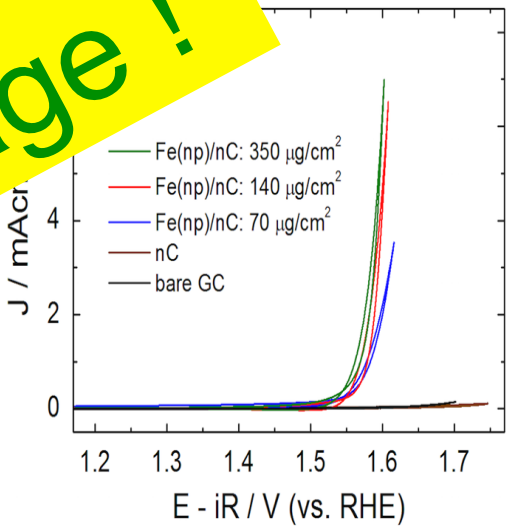
# Oxygen reduction reaction (ORR)

# Oxygen evolution reaction (OER)

$O_2 + 4H^+ + 4e^-$ $2\ H_2O$

$2\ H_2O$




Coming from garbage !

Commercial Pt catalysts
for fuel cells exhibit an overpotential
of 0.5 - 0.6 V vs RHE
theoretical value: E° = 1.22 V vs RHE

**GC** bare glassy carbon
**nC** graphitic nano carbon

Hof, F. et al. Chem. Eur. J. 2017

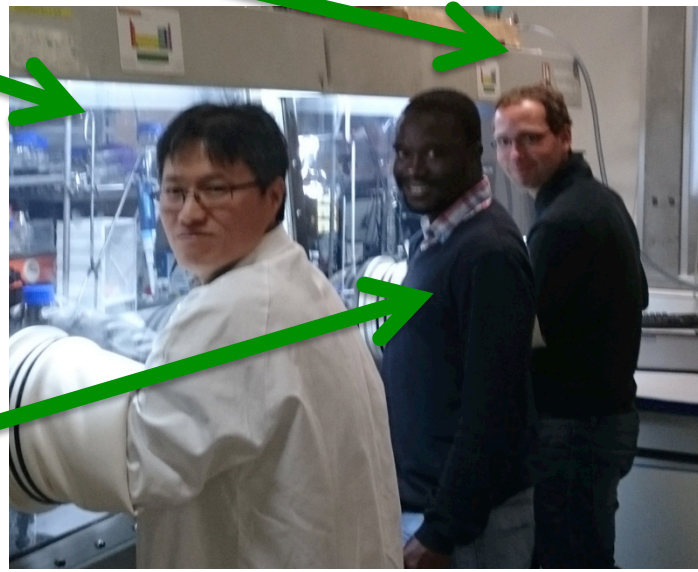
# Conclusion

- **Single layer Graphene can be stabilized in water** with no additives.
- **Raman signature of graphene in a liquid**

- **Carbon Waters** company

- Few layer graphene from **food waste**
- **Eco friendly Conducting inks, rubbers, supercapacitors, …**

**Plascarb project :**
**Katerina Kampioti**
**Dr Ferdinand Hof**
**Dr Kai Huang**



**Rubber composites**
Prof. A. Zarbin (Curitiba)
Dr Carolina Matos (“)

**Eau de Graphène:**
**Dr George Bepete**
**Dr Carlos Drummond**
**Prof. Eric Anglaret** (Montpellier University)
Dr Luca Ortolani (CNR Bologna)
Dr Vittorio Morandi (CNR Bologna)

**Carbon Waters project:**
**Dr A. Chesneau, Dr. F. Dragin, Dr. J. Messner**

ChemOnTubes 2018

April 22 – 26, 2018
Biarritz, France

# International Meeting on the Chemistry of Graphene and Carbon Nanotubes

**Still time to submit a poster or to attend**

## Scope

**All sessions will be devoted to both graphene and carbon nanotubes**

- Functionalization, dispersion, sorting
- Electrochemistry, devices
- Composites, foams, coatings
- Energy storage, conversi
- Nanomedicine, bio
- Functional m
- Catalys embranes
- O ics

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**Abstract submission deadline:** December 15th, 2017
**Registration deadline:** February 2, 2018
**Inquiries:** chemontubes@crpp-bordeaux.cnrs.fr

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