



# Bionanocomposites based on chitosan and few layers graphene. The effect of tailor made functionalization

Maurizio Galimberti

V. Barbera, S. Guerra, G. Prioglio, F. Margani, E. Testa, M. Zambito Marsala,

Politecnico di Milano, Department of Chemistry, Materials and Chemical Engineering “G. Natta”

*2<sup>nd</sup> Global virtual summit on Carbon, Graphene, 0D, 1D, and 2D Materials*  
*November 15-16, 2021*

# Items of the presentation

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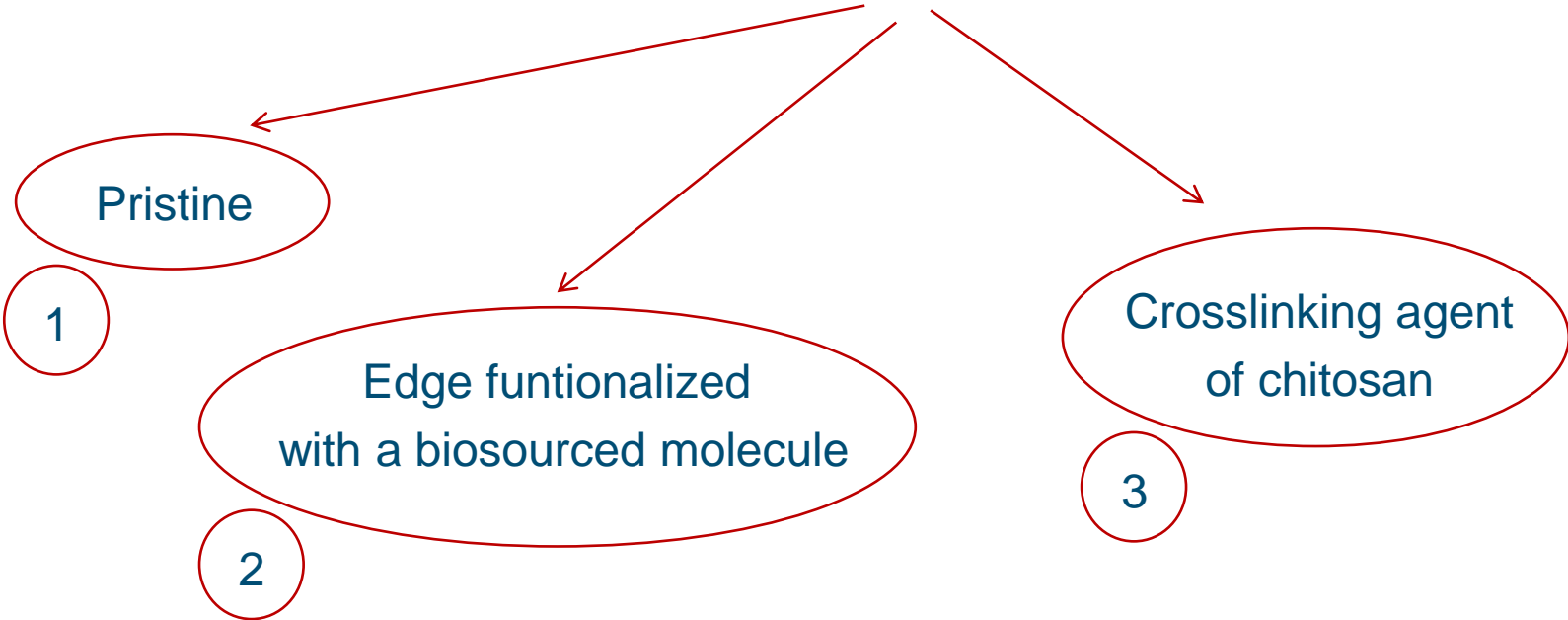
- ➡ Bionanocomposites and graphene layers
  - ➡ Introduction
  - ➡ The role of the structure of the graphene layers

# Items of the presentation

- Bionanocomposites and graphene layers

  - Introduction

  - The role of the structure of the graphene layers

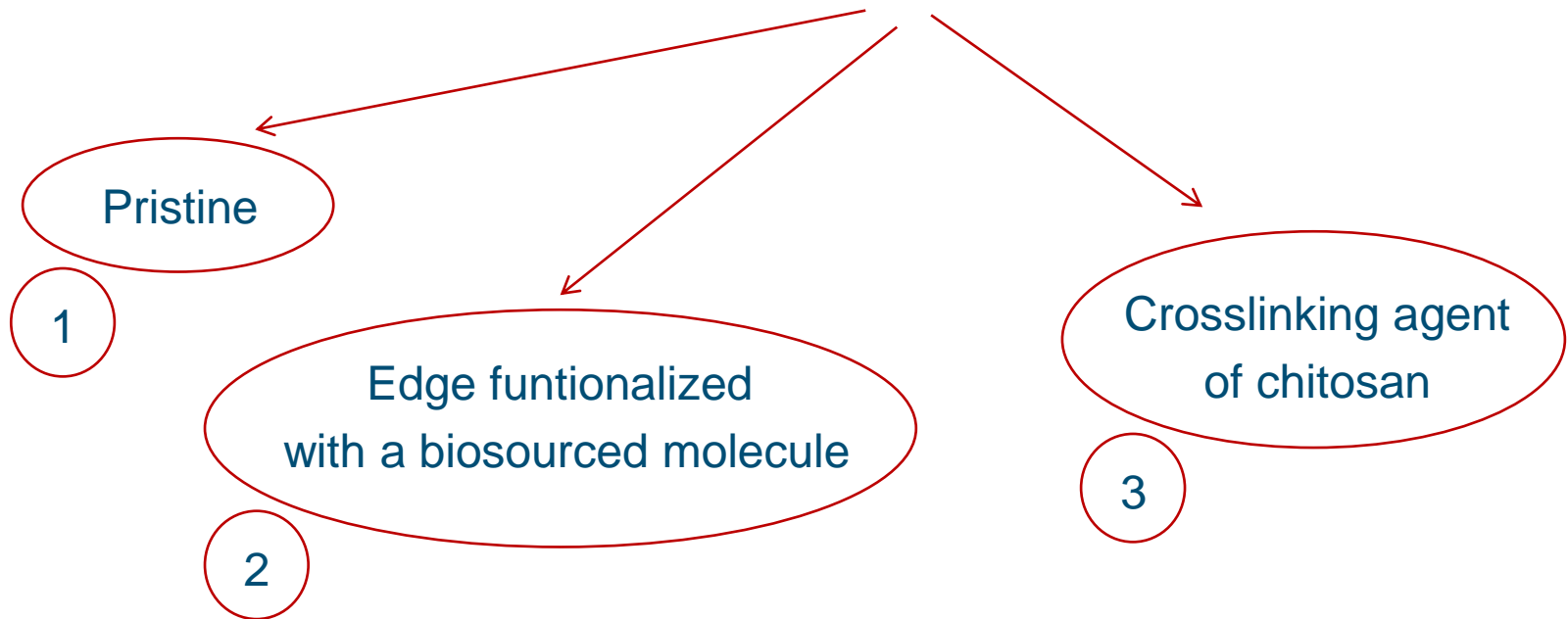


# Items of the presentation

## 👉 Bionanocomposites and graphene layers

### 👉 Introduction

### 👉 The role of the structure of the graphene layers



### 👉 Tailor made edge functionalization of graphene layers

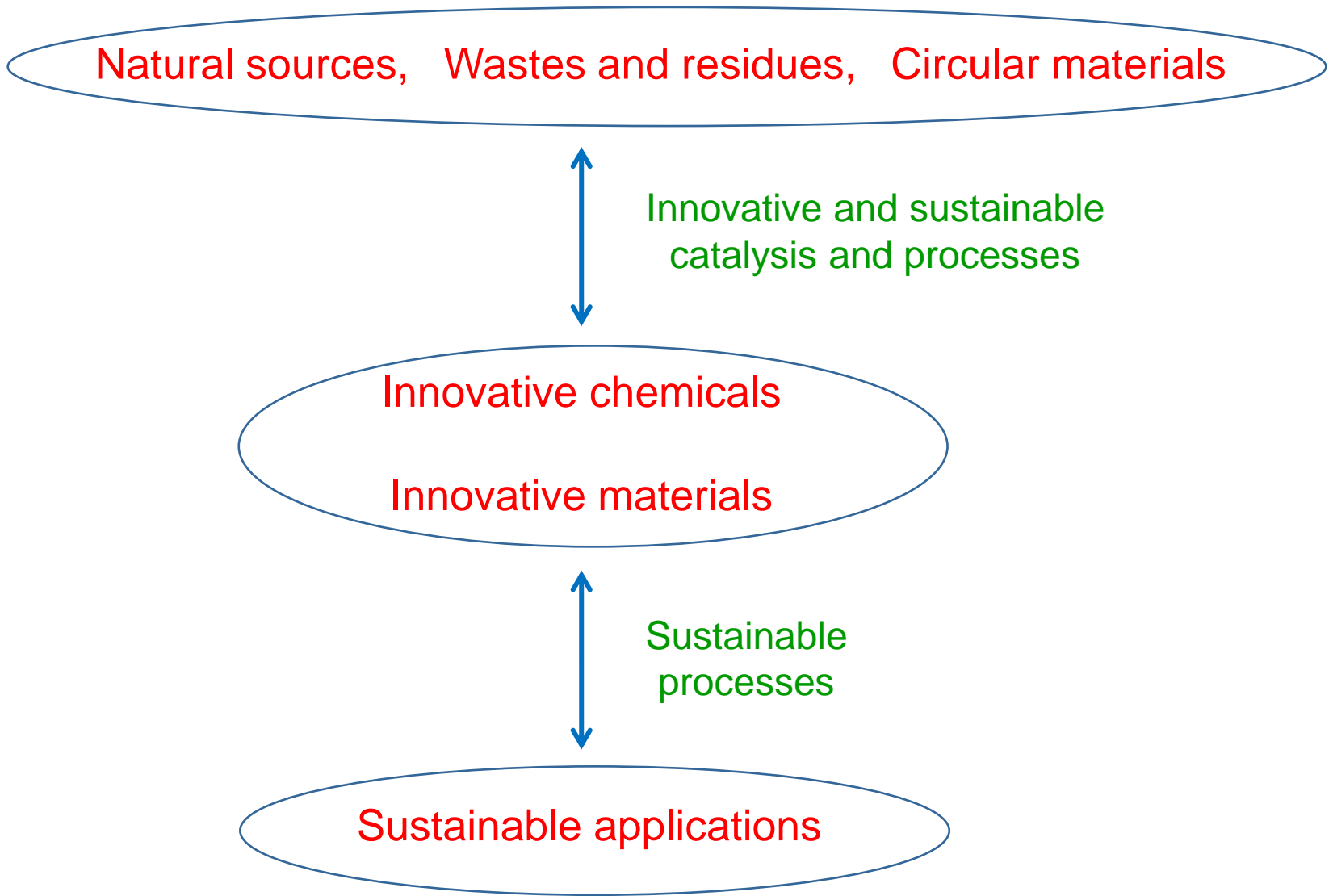


## **ISCaMaP**

*Innovative **S**ustainable **C**hemistry and **M**aterials and **P**roteomics  
Group*

Politecnico di Milano, Department of Chemistry, Materials and Chemical Engineering “G. Natta”

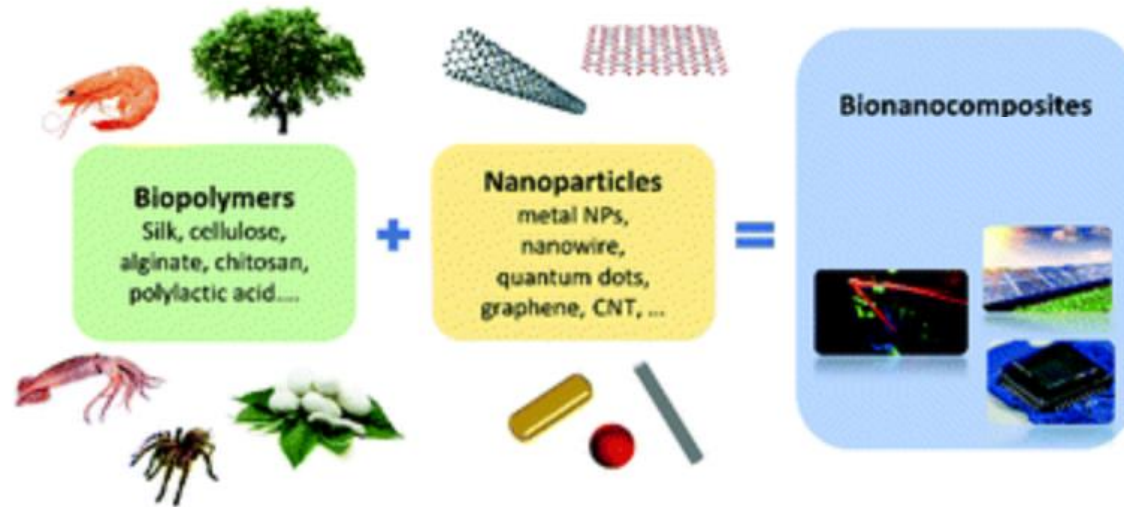
# ISCaMaP Strategy: sustainability for innovation



# Why bio-nanocomposites?

Searching *bio-nanocomposites* on Google Scholar: 20.600 results

- Emerging class of hybrid materials consisting of biopolymers and solids with at least one dimension in the nanometer range



*J. Mater. Chem. C*, 2021, 9, 5578

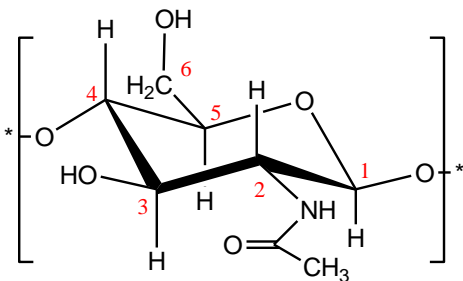
Packaging, optics, photonics, electronics, filtering, absorption, catalysis ...



# Why chitosan?

Searching chitosan on Google Scholar: 1.290.000 results

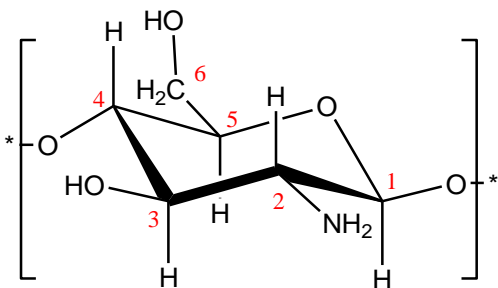
## Chitin



2-acetamido-2-deoxy-β-D-glucopyranose

deacetylation

## Chitosan



2-amino-2-deoxy-β-D-glucopyranose

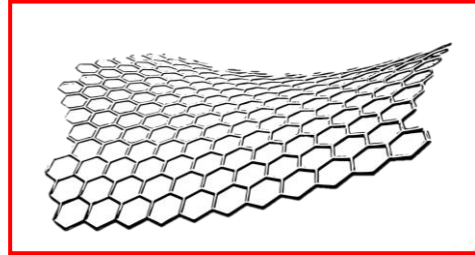
Chitin is the second most abundant polysaccharide in nature, behind only cellulose

Non toxic materials. Environmentally friendly. Low cost



# Why graphene?

Searching chitosan on Google Scholar: 1.920.000 results



The thinnest material on earth

## Top properties



**Thermal conductivity**  
> 5300 W/mK @RT



**Mechanical properties**  
The single graphene  
layers is the most resistant  
tested material: 42 N/m

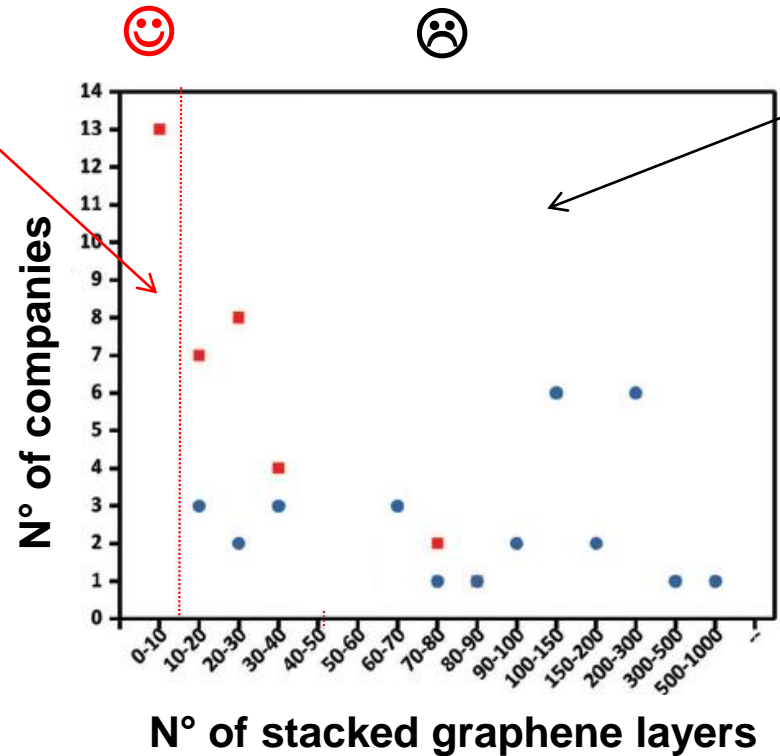


**Electrical resistivity**  
 $1 \cdot 10^{-8} \Omega \cdot \text{m}$ ,  
a very low value

# Graphene on the market. Flake or fake?

graphene

few layer  
graphene



graphite

50% of the product

90% of the product

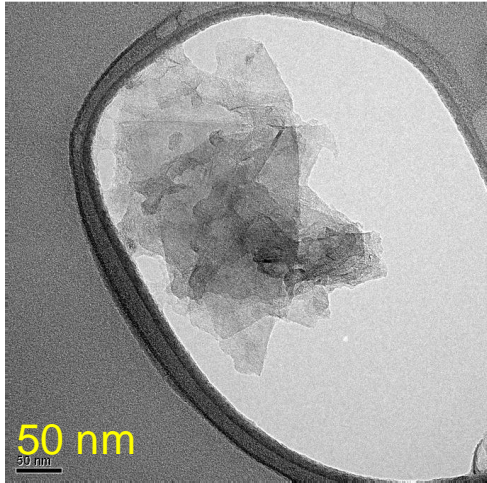
Study on 60 products / companies

# Graphene in the real world ... ?



*death valley*

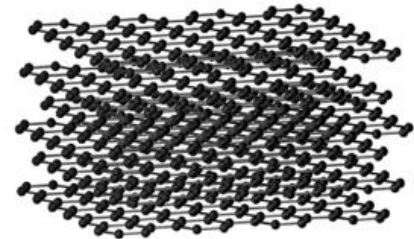
# High surface area graphite - HSAG



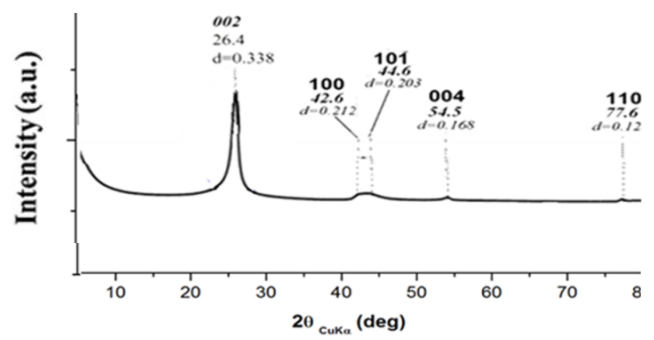
High surface area graphite (HSAG)

Surface area: 300 m<sup>2</sup>/g

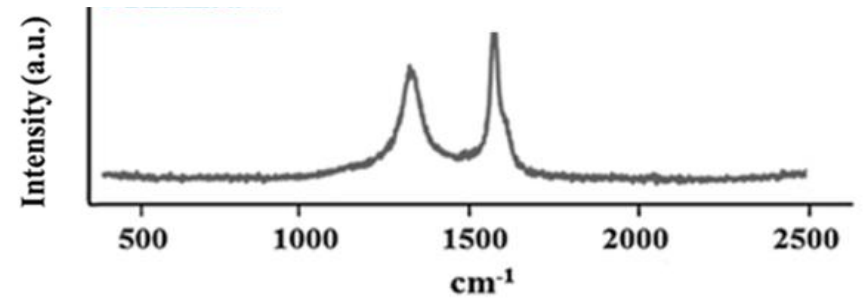
Number of stacked layers: ca 35



WAXD

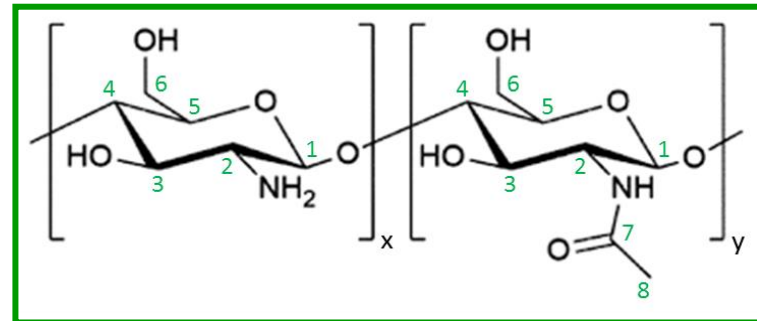
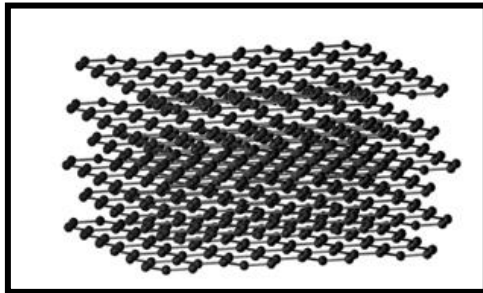


Raman

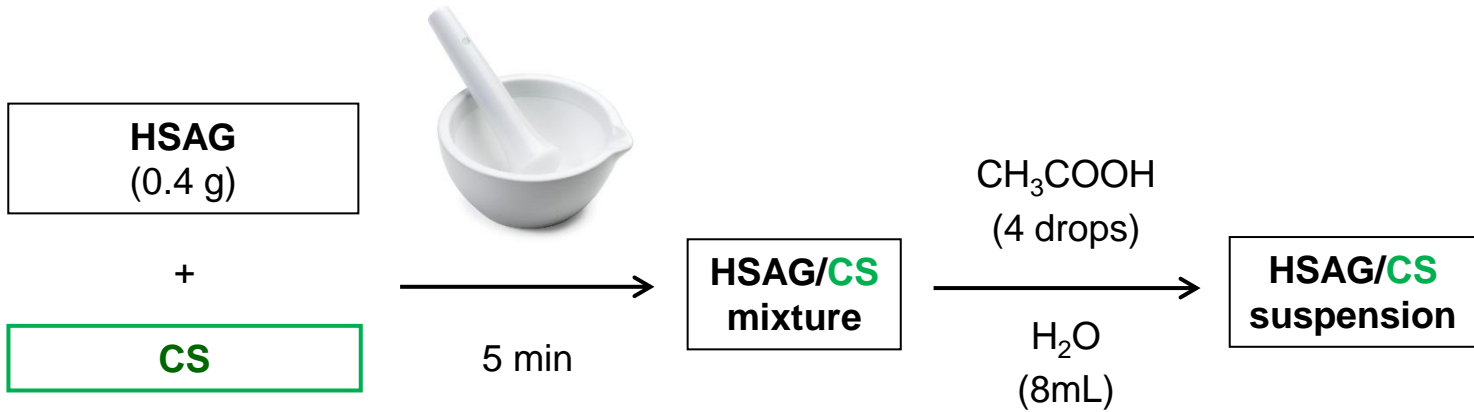


## Bionanocomposites based on Graphene layers and Chitosan

### Direct Preparation from High Surface Area Graphite

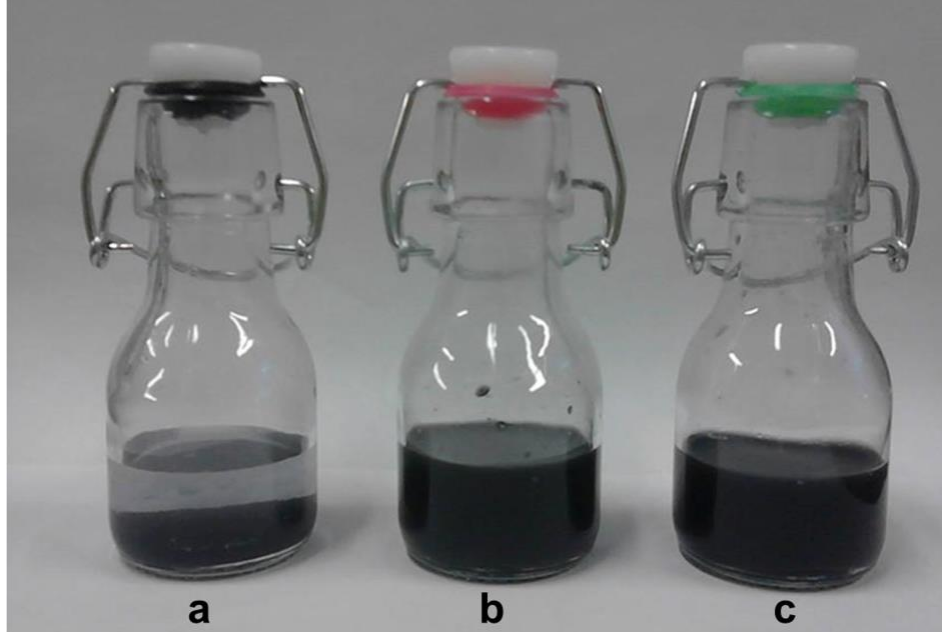


# Water suspensions of adducts of HSAG with chitosan



**HSAG/CS = 1/1, 2/1, 4/1, 6/1**

# stability of water dispersions of HSAG/CS adducts



HSAG/CS = 1/1

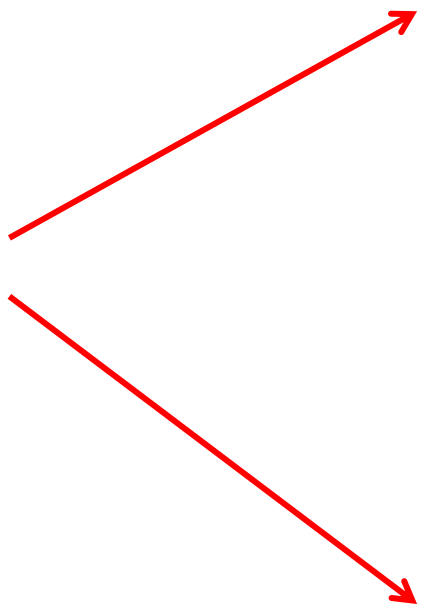
Concentration  
1 mg/mL

HSAG

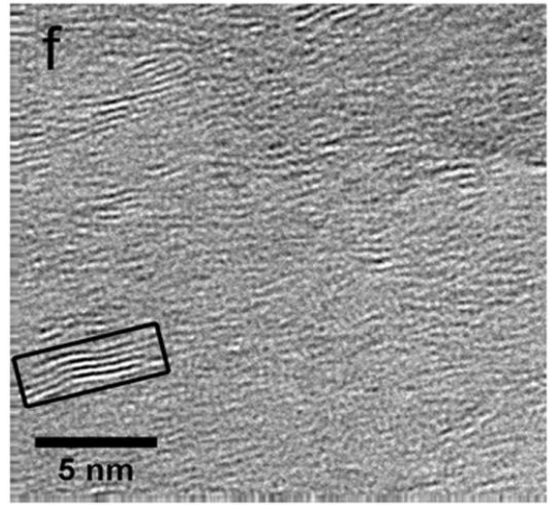
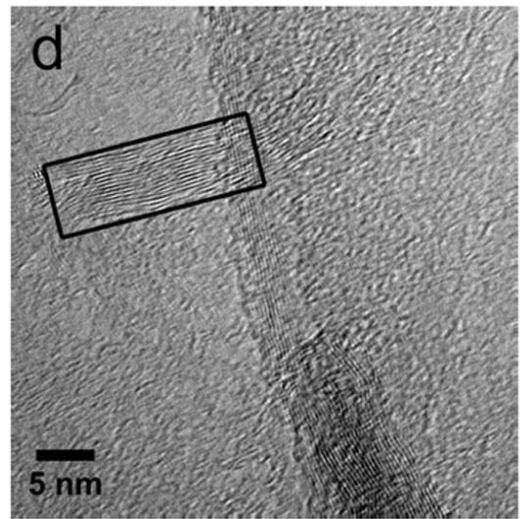
HSAG/CS  
after 1 month storage

HSAG/CS  
after 30 min centrifugation at 9000 rpm

# Few layers graphene from HSAG/CS adducts



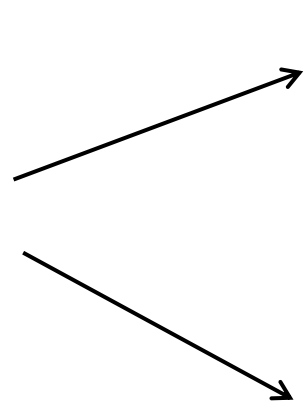
HRTEM analysis





# Aerogels and carbon papers from HSAG/CS adducts

HSAG/CS = 1/1



HSAG/CS Hydrogel

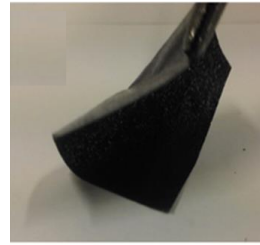
-50°C, 5mbar

HSAG/CS Aerogel



Casting on a glass plate

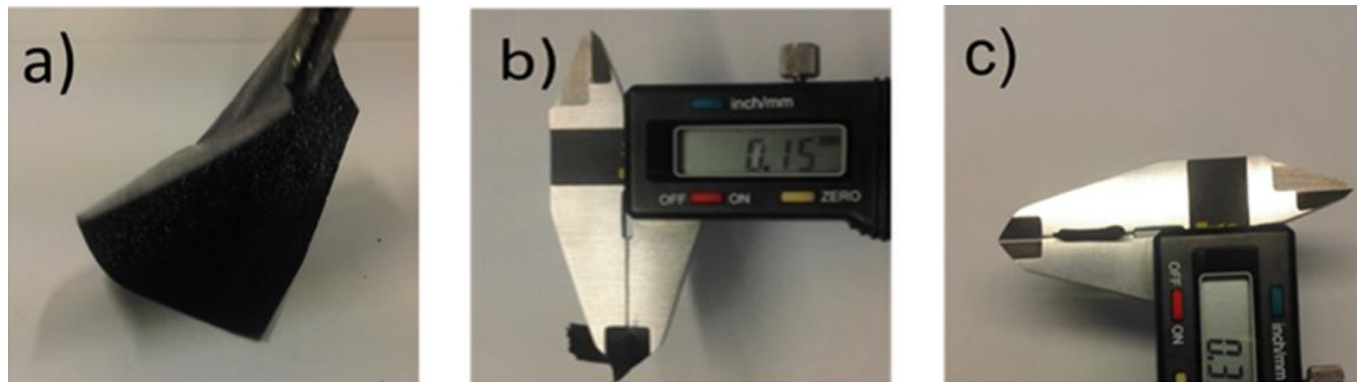
evaporation  
RT, 24 h



HSAG/CS Carbon paper

# Carbon papers from HSAG/CS adducts

HSAG/CS = 1/1

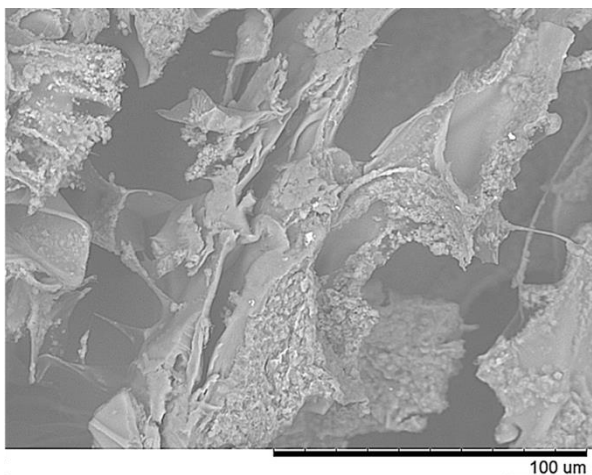


free-standing (thickness = 0.15 mm).

Very flexible and perfectly foldable

Curvature radius close to 180° without the appearance of cracks

# Aerogels from HSAG/CS adducts



Well-developed highly porous structure:  
low density:  $0.026 \text{ gcm}^{-3}$ .

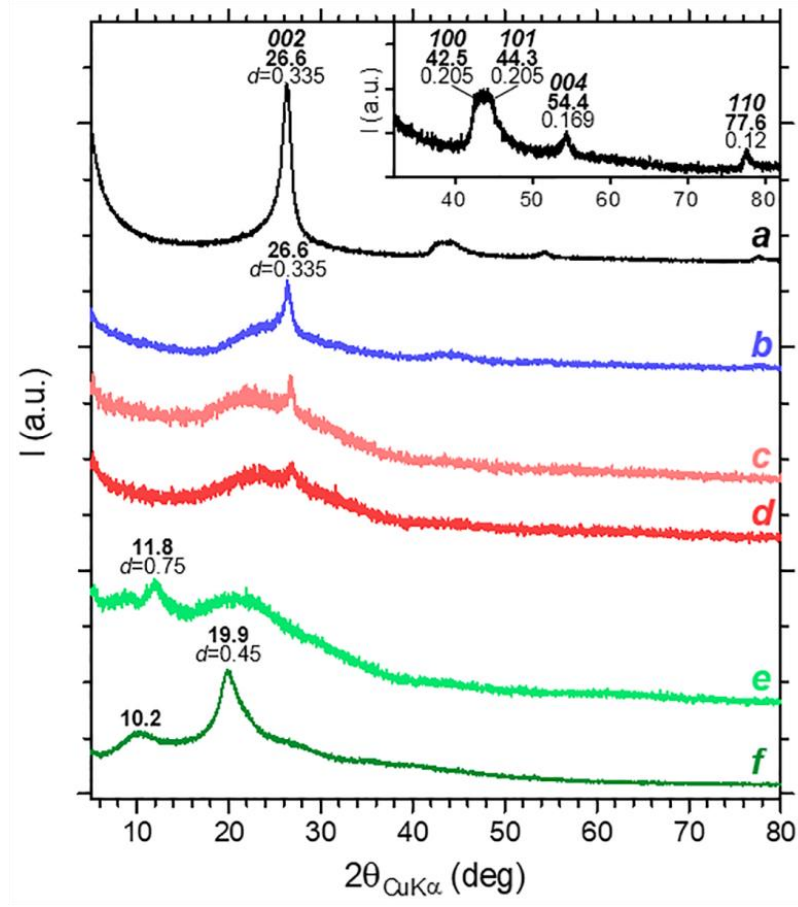
honeycomb structure

HSAG agglomerates and continuous HSAG networks

The aerogel formation does not disrupt the connectivity of the nanofiller

# Structure of HSAG/CS adducts

## X-Ray diffraction



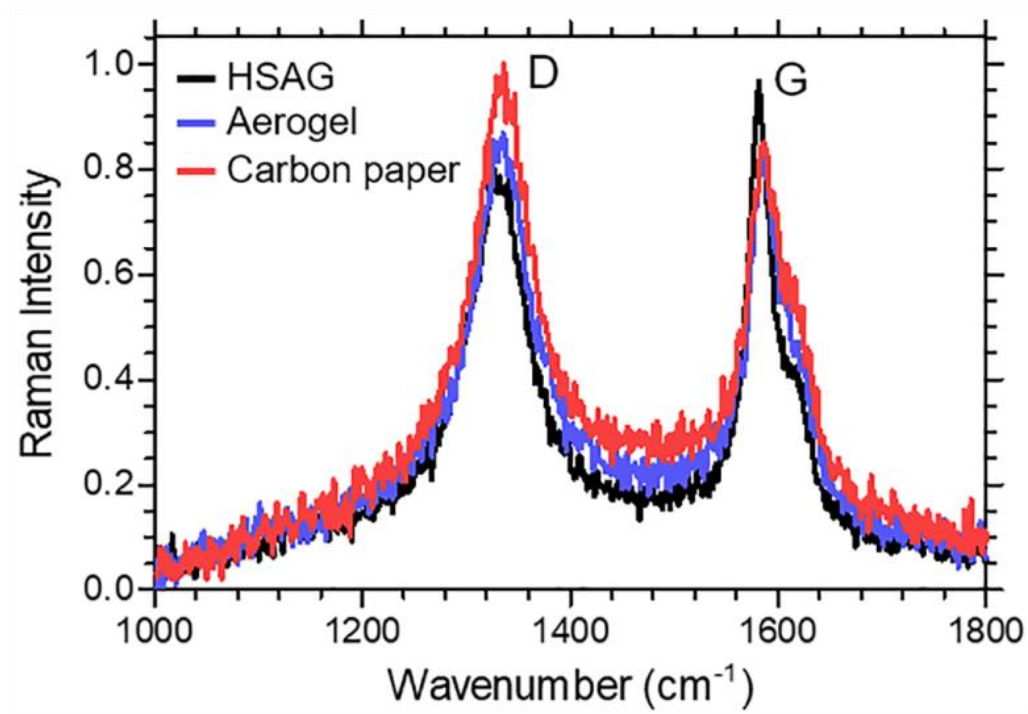
- pristine HSAG (a),
- HSAG/CS 1:1 aerogel
- HSAG/CS 1:1 paper
- HSAG/CS 1:1 paper (with more water)
- CS film in acetic acid
- chitosan powder (f).

Detectable (002) reflection due to stacking of graphene layers

# Structure of HSAG/CS adducts

HSAG/CS = 1/1

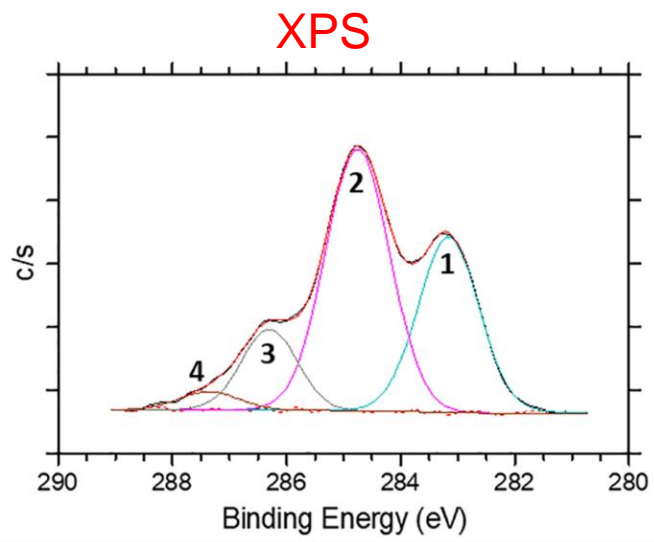
## Raman spectra



Detectable increase of  $I_D/I_G$ : ascribed to a further structural disorder induced by the preparation of the sample

# HSAG/CS adducts. The interaction of CS with the graphene layers

HSAG/CS = 1/1



high resolution C1s spectrum and its deconvolution for HSAG/CS 1:1 paper



binding energies shifted to lower values with respect to pure CS

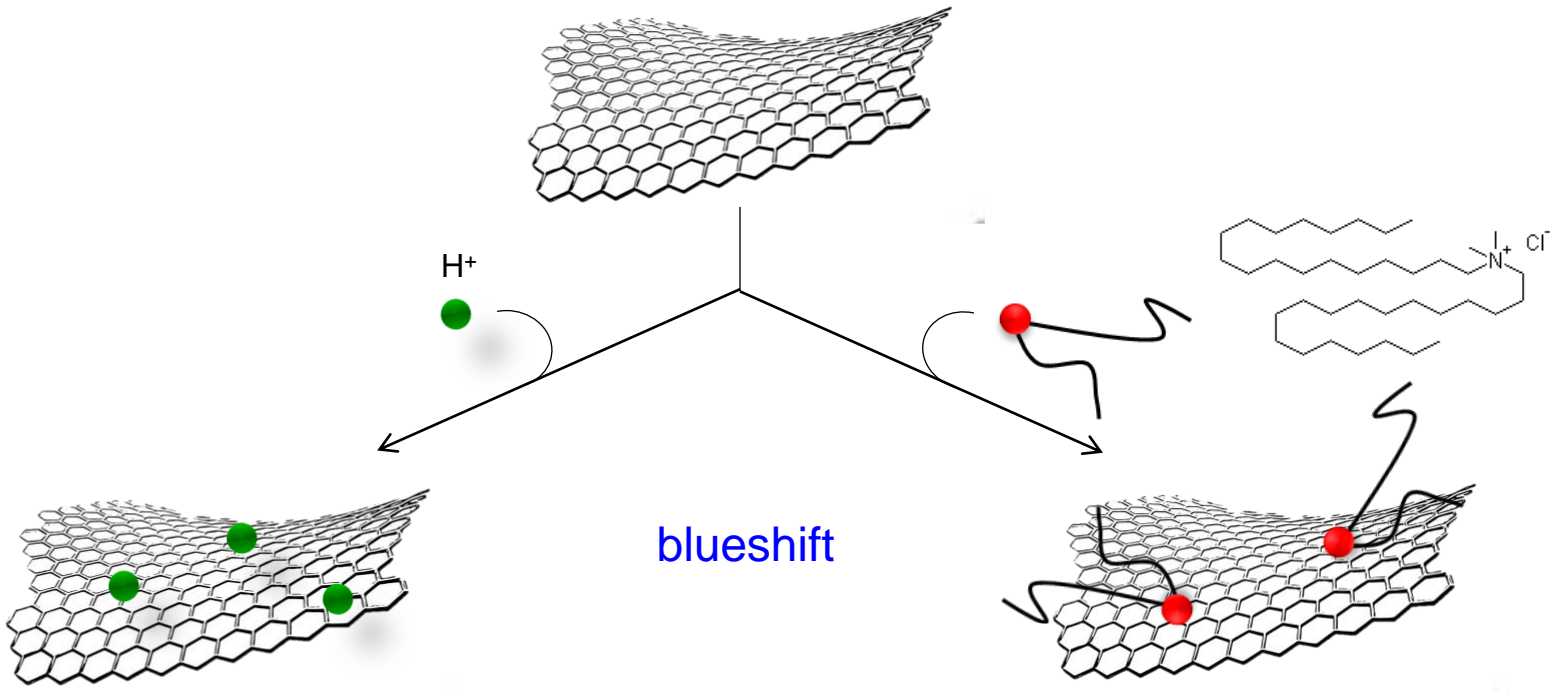


charging effects on the surface of CS attributed to HSAG.



CS is at the surface of the carbon paper and covers HSAG  
strong interactions between the graphite layers and the biopolymer

# HSAG adducts. UV spectroscopy

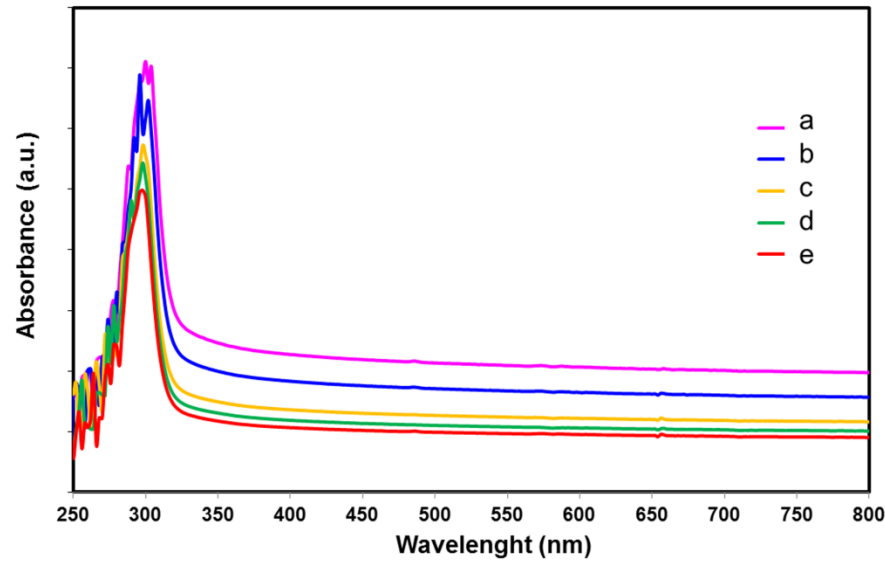


Sample	Molar ratios <sup>a</sup>	Absorbance	Wavelength (nm)
HSAG	/	0.9	300
HSAG/H <sup>+</sup>	1:2	0.8	286
HSAG/2HTCI	1:2	0.6	284

<sup>a</sup> considering the moles of C6 rings as the moles of the graphitic substrate

# HSAG/CS adducts. The interaction of CS with the graphene layers

Blueshift due to chitosan

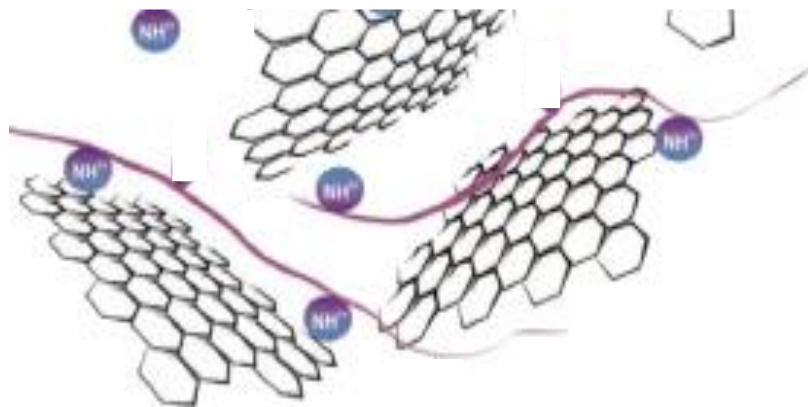


Redshift due to the dilution



# HSAG/CS adducts. The interaction of CS with the graphene layers

No evidences of covalent bond between CS and graphene layers



## Cation- $\pi$ interaction

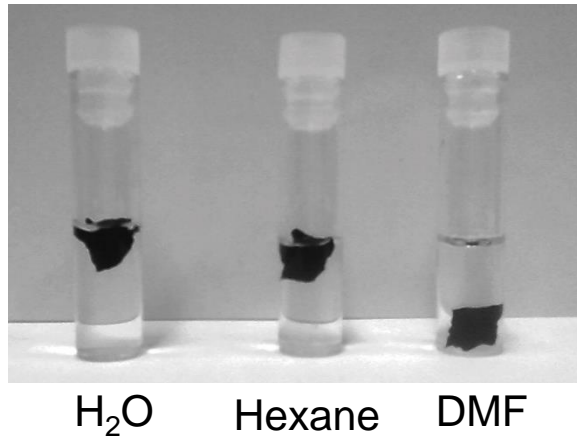
Protonated CS chains interact with graphene

Protonated polymeric chains repulse each other  
and facilitate distribution of graphene

# Carbon papers and aerogels from HSAG/CS adducts. stability to solvents and pH

HSAG/CS = 1/1

after 2 months storage



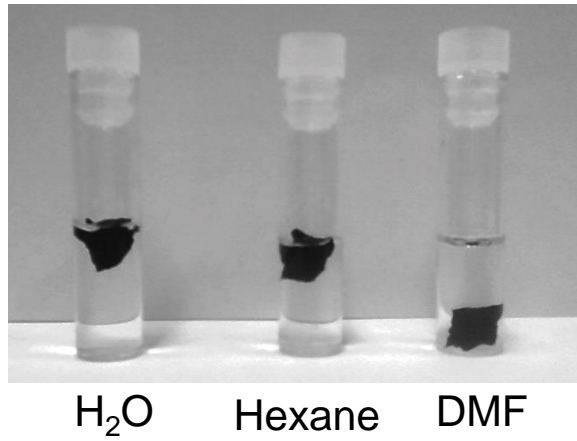
stability  
in H<sub>2</sub>O and solvents

negligible swelling, TGA analysis did not reveal any mass loss

# Carbon papers and aerogels from HSAG/CS adducts. stability to solvents and pH

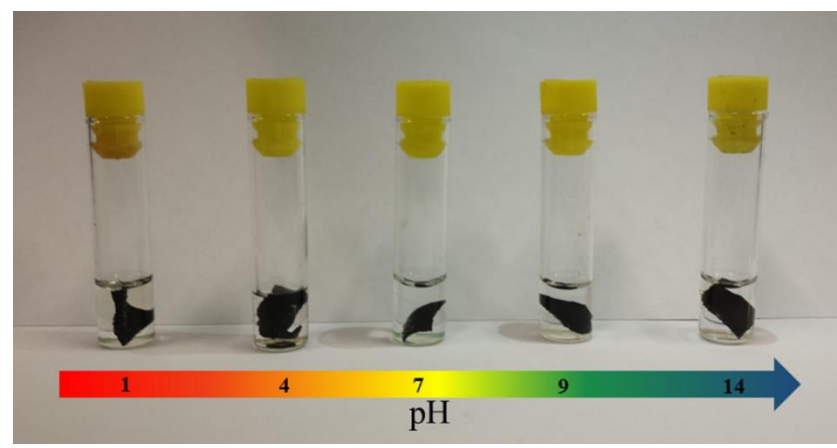
HSAG/CS = 1/1

after 2 months storage



stability  
in H<sub>2</sub>O and solvents

negligible swelling, TGA analysis did not reveal any mass loss



pH stability

swelling

stability

*Pictures are for carbon papers*

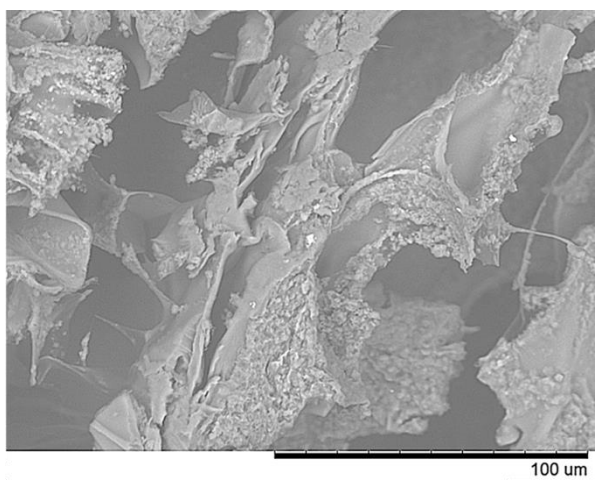
Carbon papers and aerogels from HSAG/CS adducts. Electrical conductivity

carbon papers



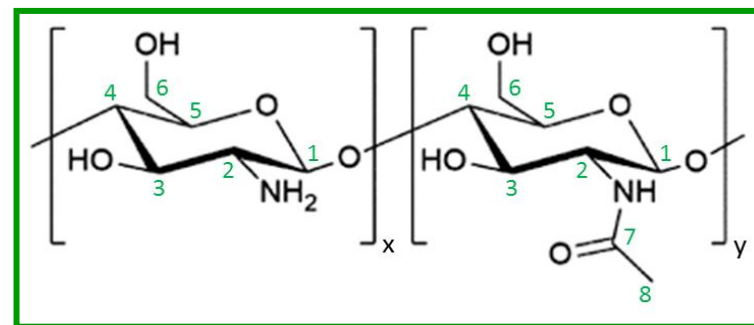
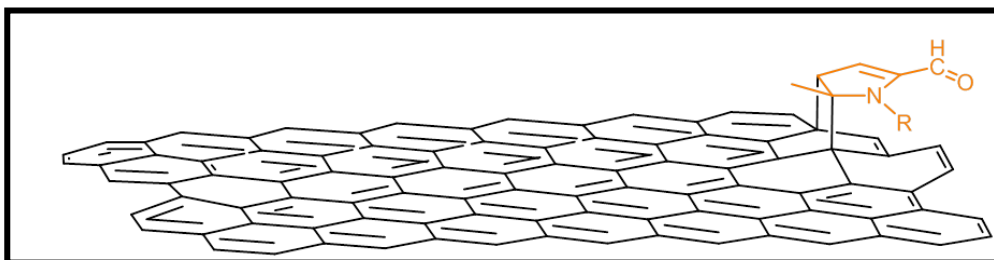
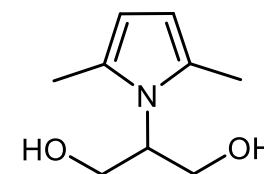
HSAG/CS ratio	$\sigma$ (S/m)
Chitosan	1 E <sup>-8</sup>
1:1	8.27 E <sup>-5</sup>
2:1	1.05 E <sup>-4</sup>
4:1	1.56 E <sup>-3</sup>
6:1	1.9 E <sup>-2</sup>

aerogels



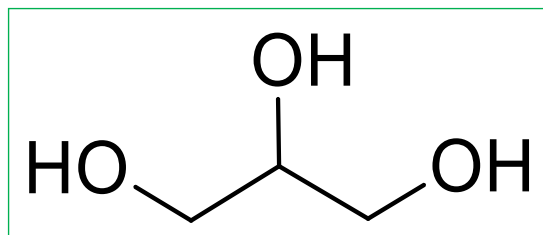
HSAG/CS ratio	$\sigma$ (S/m)
Chitosan	1 E <sup>-8</sup>
1:1 <sup>c</sup>	3.3 E <sup>1</sup>

# Bionanocomposites based on Graphene layers modified with serinol pyrrole (SP) and Chitosan

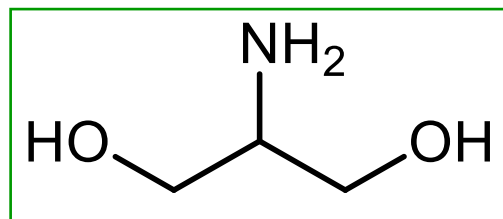


S. Guerra, V. Barbera, A. Vitale, R. Bongiovanni, A. Serafini, L. Conzatti, L. Brambilla, M. Galimberti,  
"Edge Functionalized Graphene Layers for (Ultra) High Exfoliation in Carbon Papers and Aerogels in the Presence of Chitosan" *Materials* 2020, 13, 39

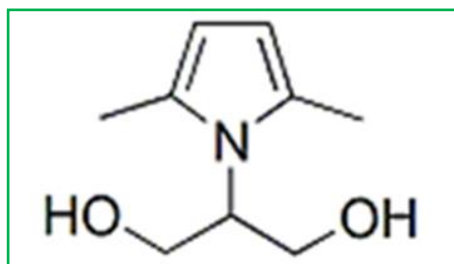
# Glycerol as the C3 building block. From glycerol to serinol to serinol pyrrole



Propane-1,2,3-triol

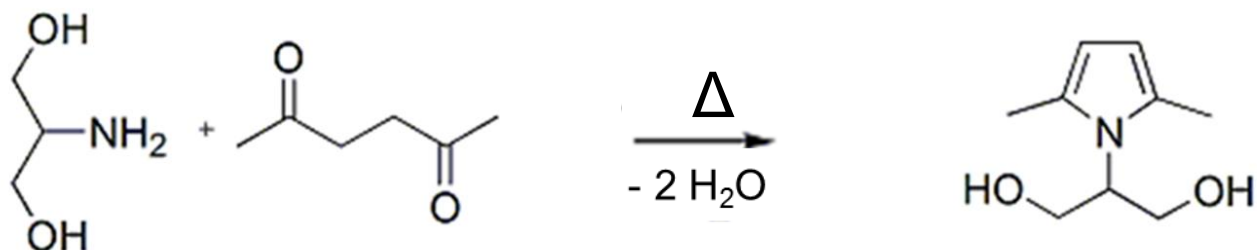


2-Amino-1,3-propanediol



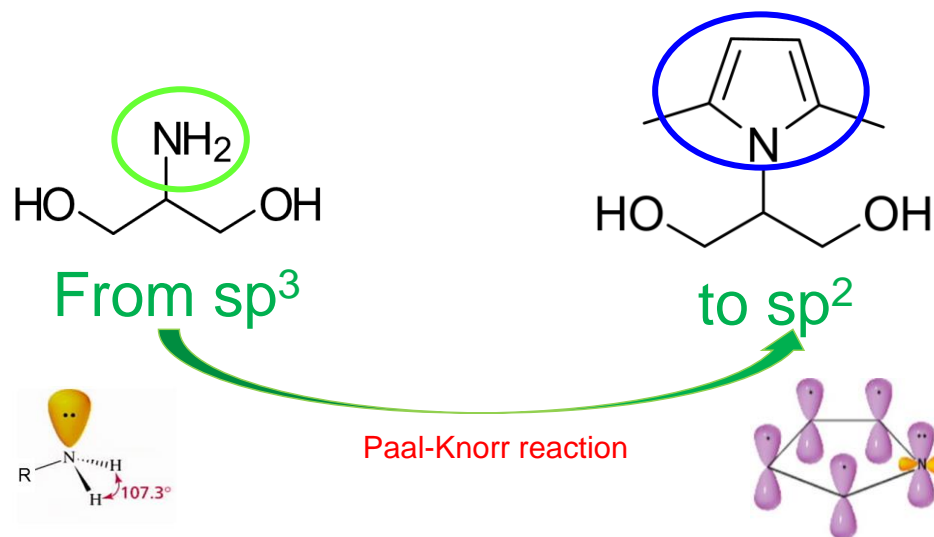
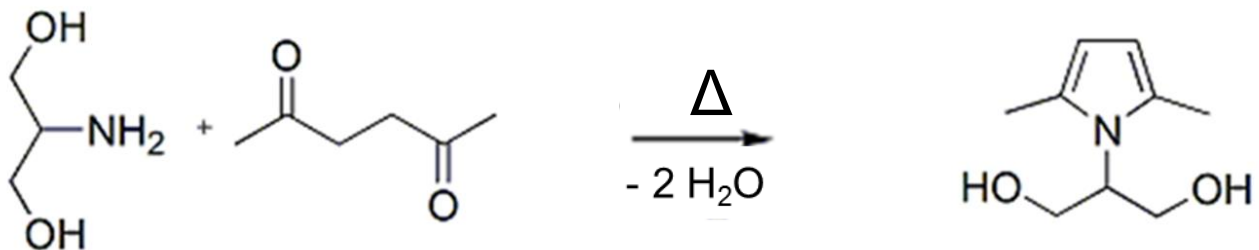
2-(2,5-dimethyl-1H-pyrrol-1-yl)-1,3-propanediol

# From serinol to serinol pyrrole



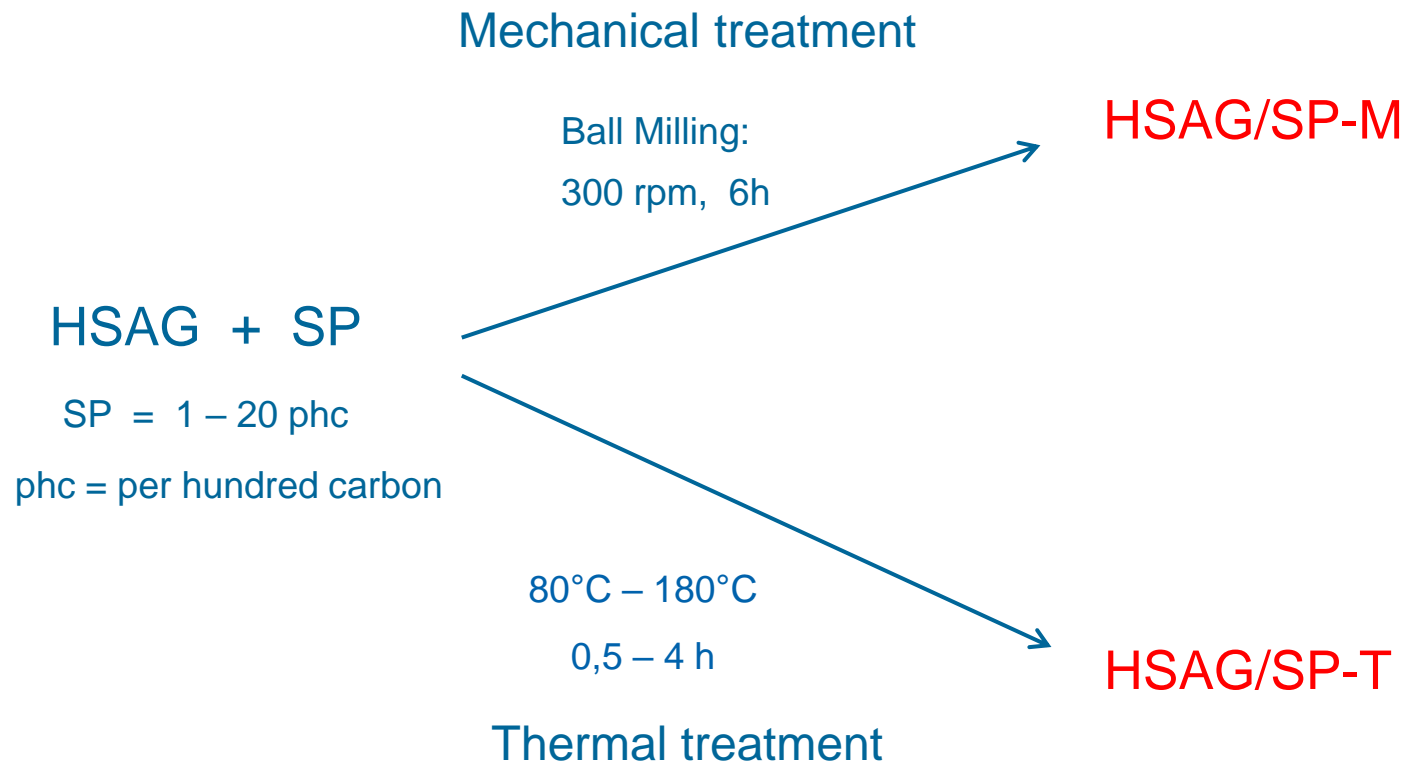
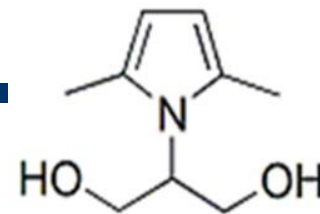
- ➡ Yield: at least **96%**
- ➡ Atom efficiency: **85%**
- ➡ Easy procedure
- ➡ **No solvent**
- ➡ By product: **H<sub>2</sub>O**

# From serinol to serinol pyrrole





# The functionalization of HSAG with SP

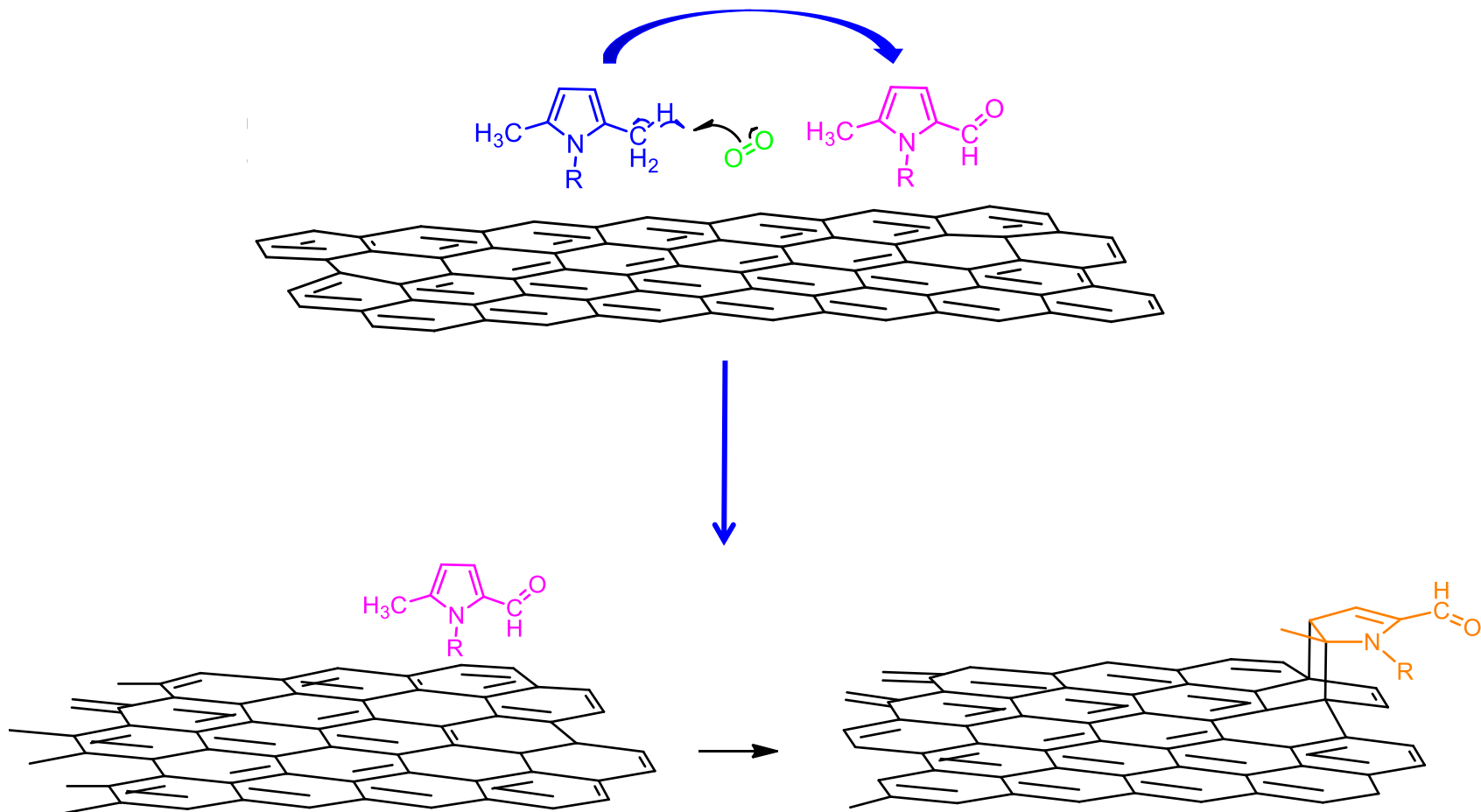


Galimberti, M., Barbera, V., Guerra, S., Conzatti, L., Castiglioni, C., Brambilla, L., A. Serafini, [RSC Advances, 5\(99\), \(2015\) 81142-81152](#)

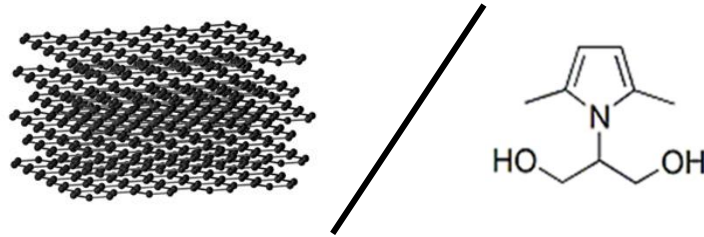
Galimberti, M., Barbera, V., Sebastiano, R., Valerio A.M. Leonardi, G., Citterio, [US 2017 0275169 A1](#)

Galimberti M., Barbera V., Guerra S., Bernardi A., [Rubber Chemistry and Technology, 2017, 90\(2\), 285-307.](#)

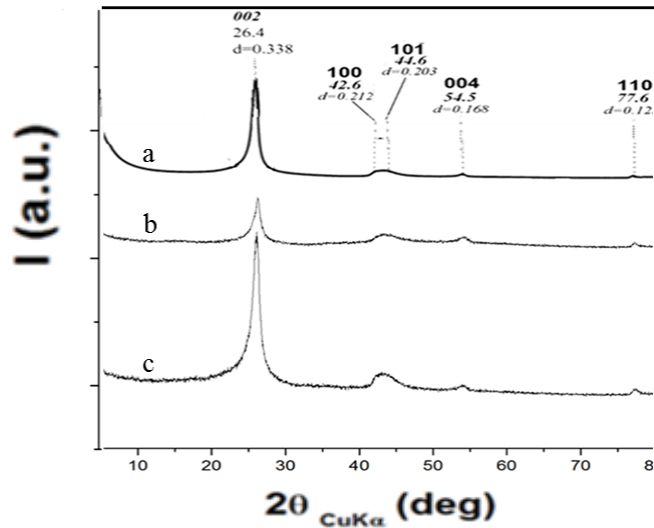
# The functionalization of an $sp^2$ carbon allotrope with a pyrrole molecule



# Adducts of HSAG with SP



WAXD

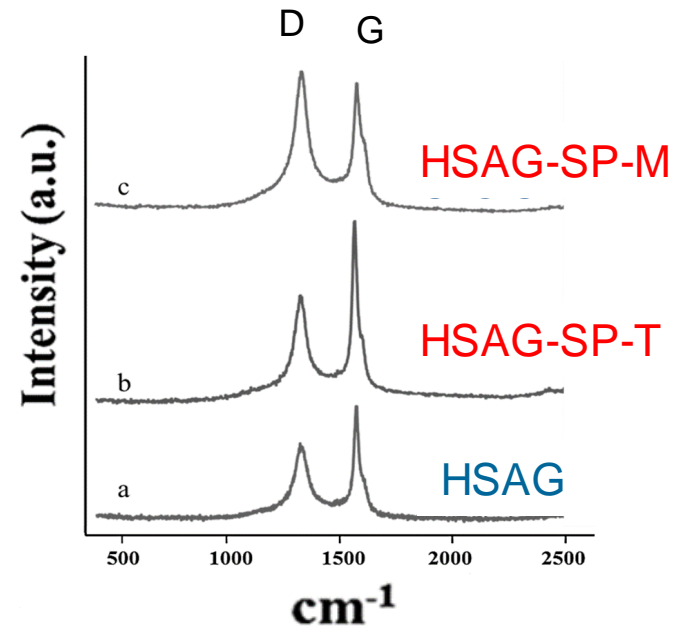


HSAG

HSAG-SP-M

HSAG-SP-T

Raman



HSAG-SP-M

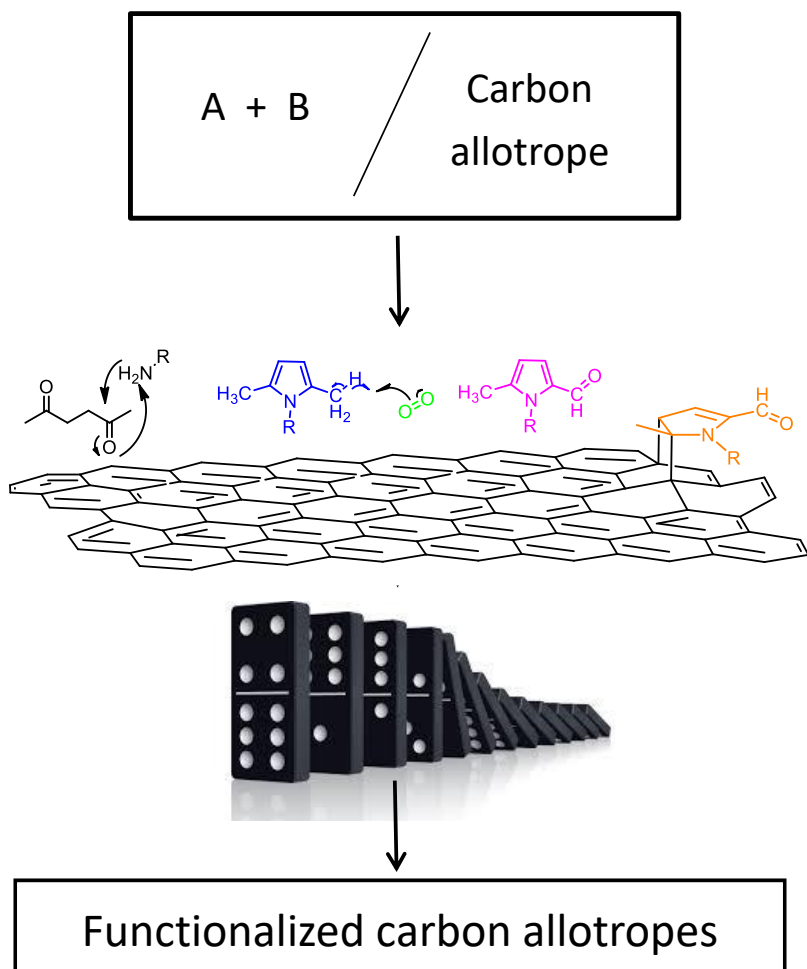
HSAG-SP-T

HSAG

Galimberti, M., Barbera, V., Guerra, S., Conzatti, L., Castiglioni, C., Brambilla, L., A. Serafini, *RSC Advances*, 5(99), (2015) 81142-81152

Galimberti M., Barbera V., Guerra S., Bernardi A., *Rubber Chemistry and Technology*, 2017, 90(2), 285-307.

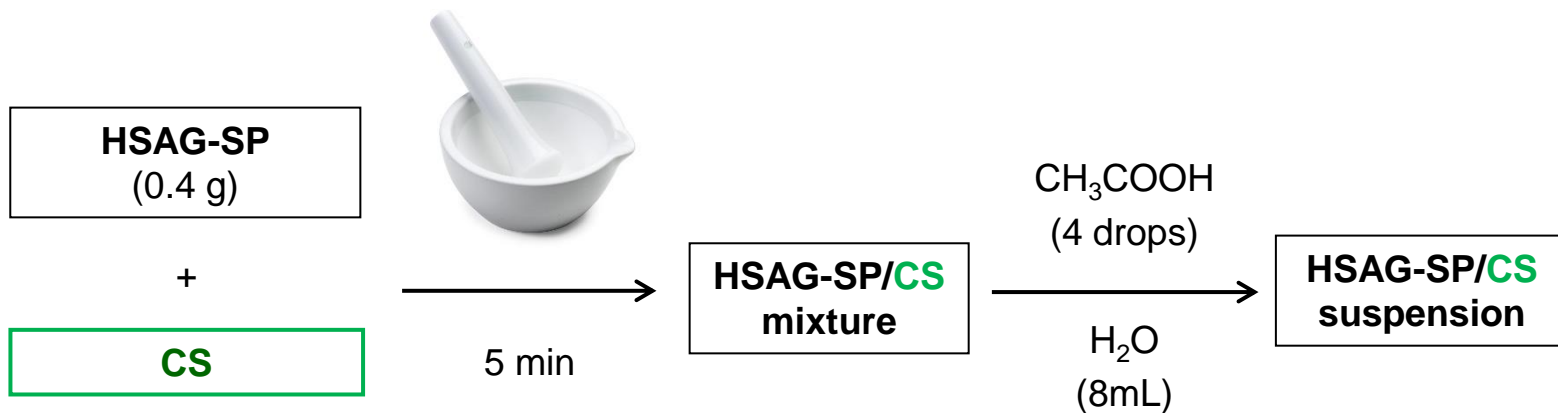
# Facile functionalization of carbon materials



- ➡ Functional group:  
from few % to 20%
- ➡ Functionalization yield:  
from 85% to quantitative
- ➡ Covalent bond  
between functional group  
and graphene layer
- ➡ Bulk structure of graphitic materials:  
substantially unaltered

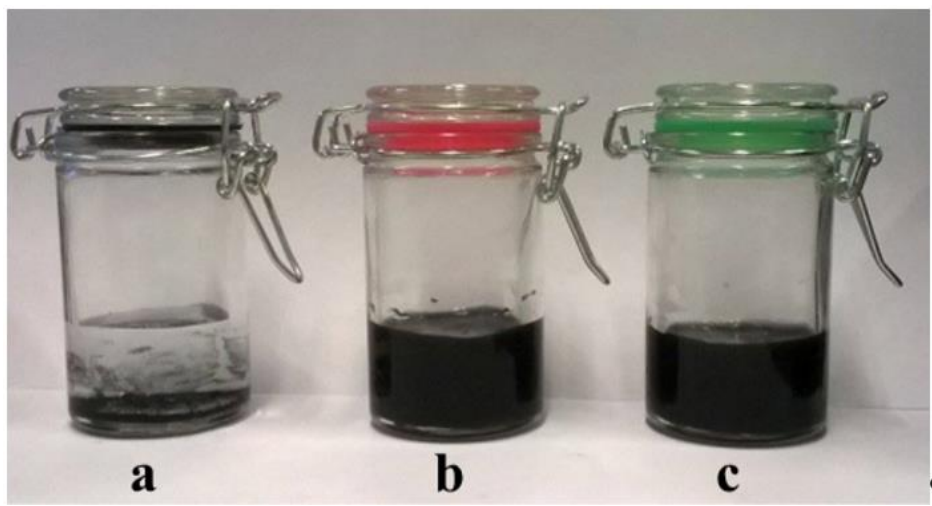
V. Barbera, A. Citterio, M. Galimberti, G. Leonardi, R. Sebastiano, S.U. Shisodia, A.M. Valerio. [WO/2015/189411 A1 \(2015\)](#)  
M. Galimberti, V. Barbera, R. Sebastiano, A. Citterio, G. Leonardi, A.M. Valerio. [WO/2016/050887 A1 \(2016\)](#)  
M. Galimberti, V. Barbera, R. Sebastiano, A. Truscillo, A.M. Valerio. [WO/2016/023915 A1 \(2016\)](#)  
M. Galimberti, V. Barbera, [Italian Patent 102016000113012 \(2016\)](#)  
M. Galimberti, V. Barbera, [Italian Patent 102016000113070 \(2016\)](#)

# Water suspensions of adducts of HSAG-SP with chitosan



HSAG-SP/CS = 1/1, 2/1, 4/1, 6/1

# stability of water dispersions of HSAG-SP/CS adducts



HSAG-SP/CS = 1/1

Concentration  
1 mg/mL

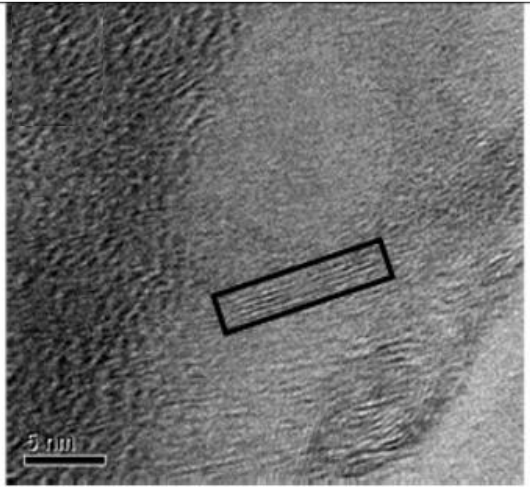
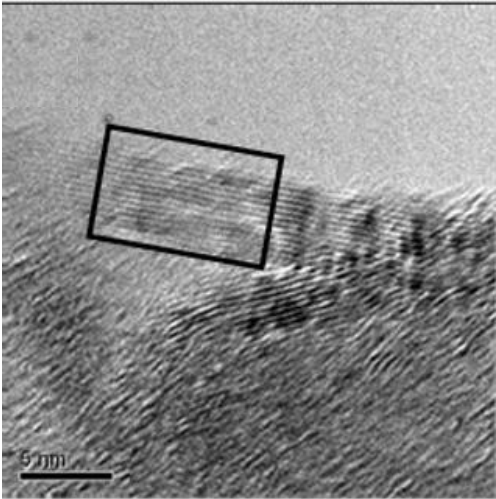
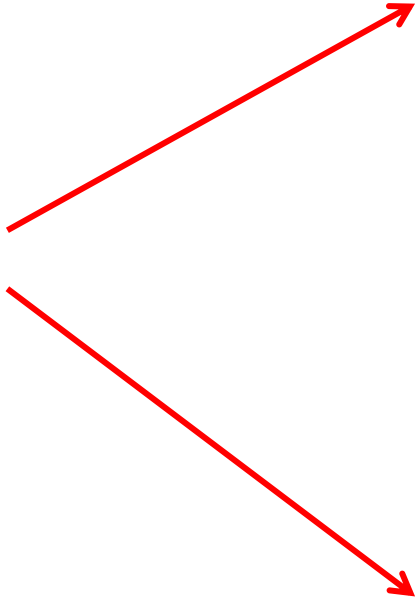
HSAG

HSAG-SP/CS  
after 1 month storage

HSAG-SP/CS  
after 30 min centrifugation at 9000 rpm

# Few layers graphene from HSAG-SP/CS adducts

HSAG-SP/CS = 1/1

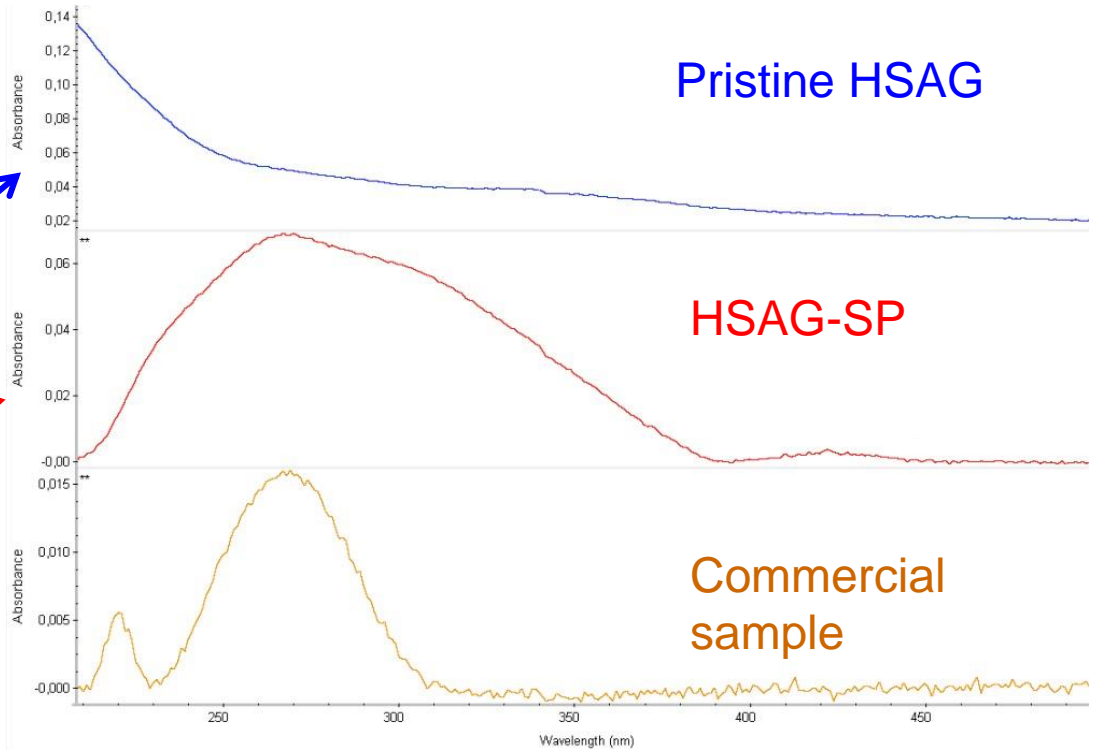
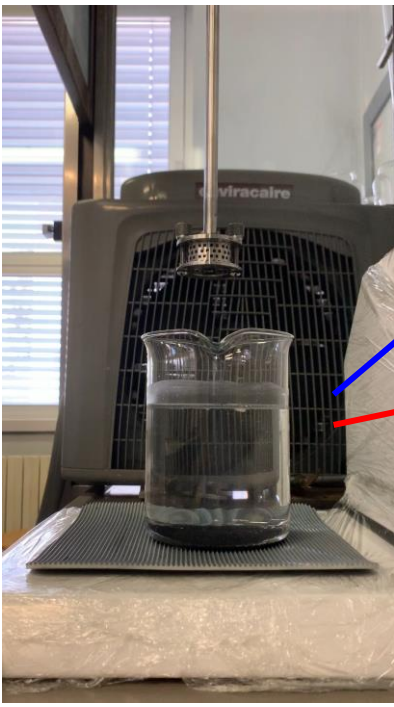


centrifugation allowed to isolate stacks made of few layers graphene

HRTEM analysis

# Exfoliation of HSAG-SP

## High shear exfoliation

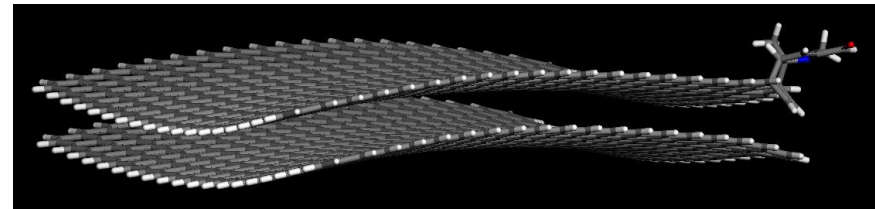




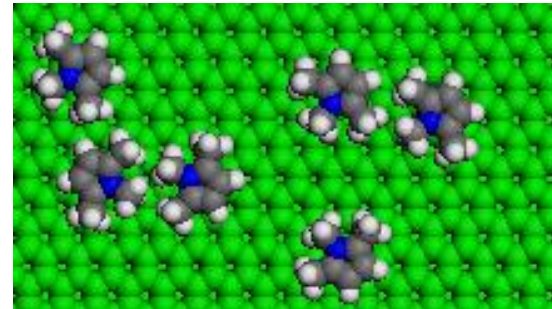
# The covalent and supramolecular interaction of PyC with graphene layers

Theoretical study based on Molecular Mechanics  
and Molecular Dynamics simulations of:

- Few layers of *nanographene*
- ☞ importance of covalent functionalization



- Adsorption of pyrrole compound
- ☞ role of  $\pi$ - $\pi$  interactions



Work in progress...

# Aerogels and carbon papers from HSAG-SP/CS adducts

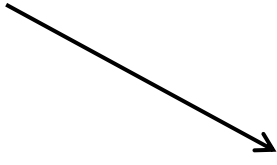
HSAG-SP/CS = 1/1



HSAG-SP/CS  
Hydrogel

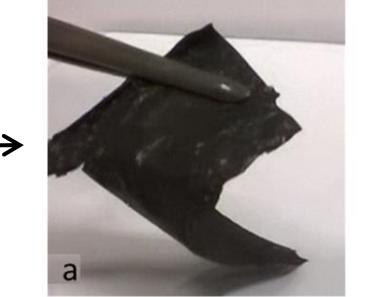
-50°C, 5mbar

HSAG-SP/CS  
Aerogel



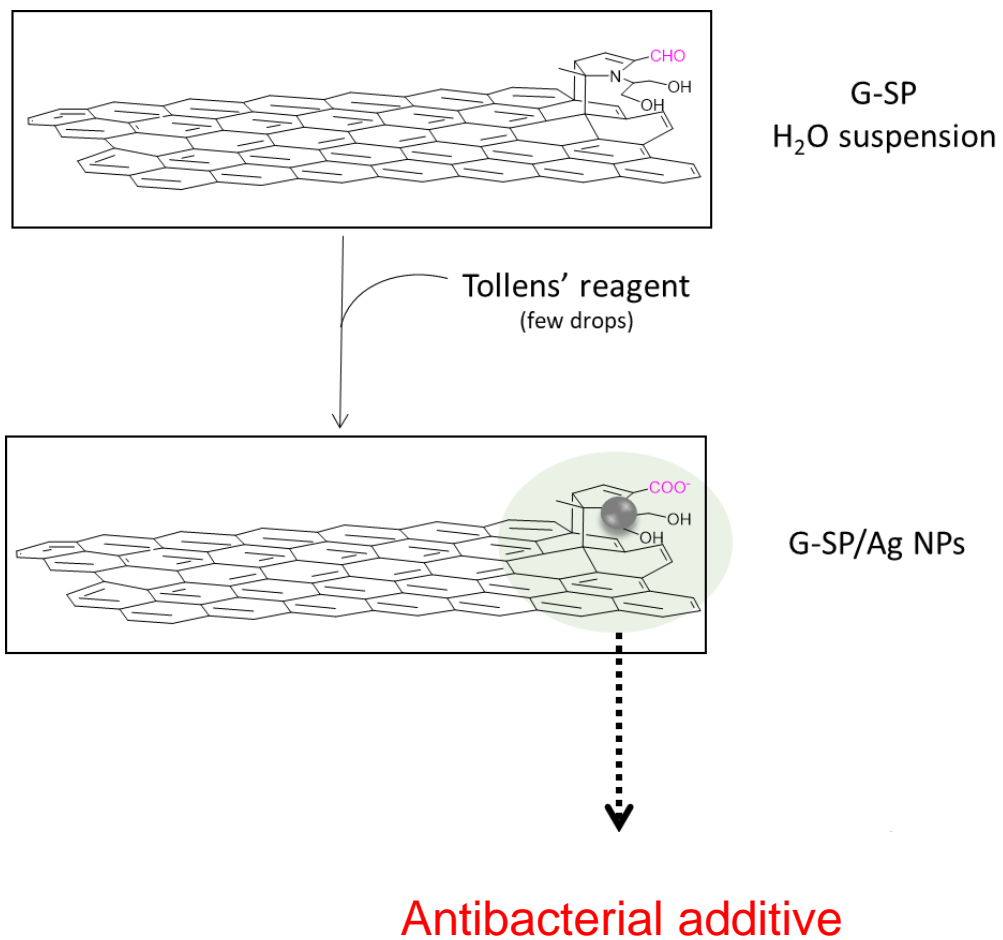
Casting  
on a glass plate

evaporation  
RT, 24 h



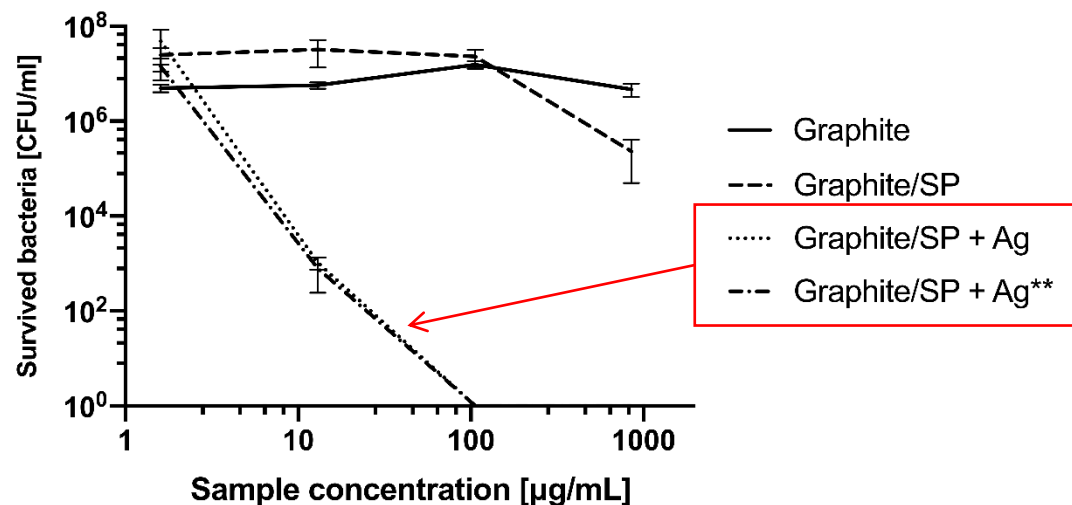
HSAG-SP/CS  
Carbon paper

# Antibacterial additives from HSAG-SP



## Antibacterial activity

Survived bacteria [CFU/ml] for Graphite samples



\*\*The sample has been functionalized with an almost double quantity of Tollens' reagent.

**Test:** ASTM Standard Guide E2315 – 16

**Bacteria:** *E. coli* JM109 – DSM3423

**Material state:** Dispersions of powders

**Inoculum concentration:** ~10<sup>6</sup> CFU/mL

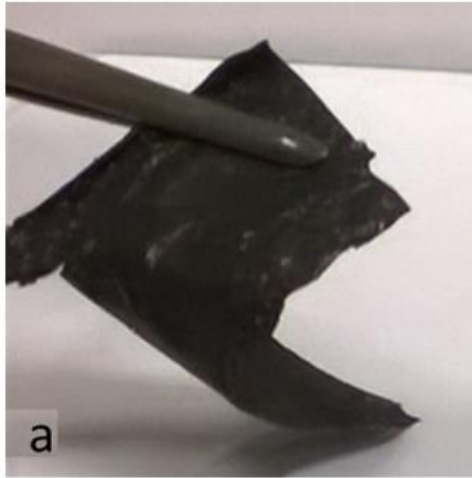
**Culture medium:** LB / PBS 1:100 (v/v)

**Culture conditions:** 24h, 37°C, 5% CO<sub>2</sub>, 90% R.H. Dynamic

conditions

# Carbon papers from HSAG-SP/CS adducts

HSAG-SP/CS = 1/1

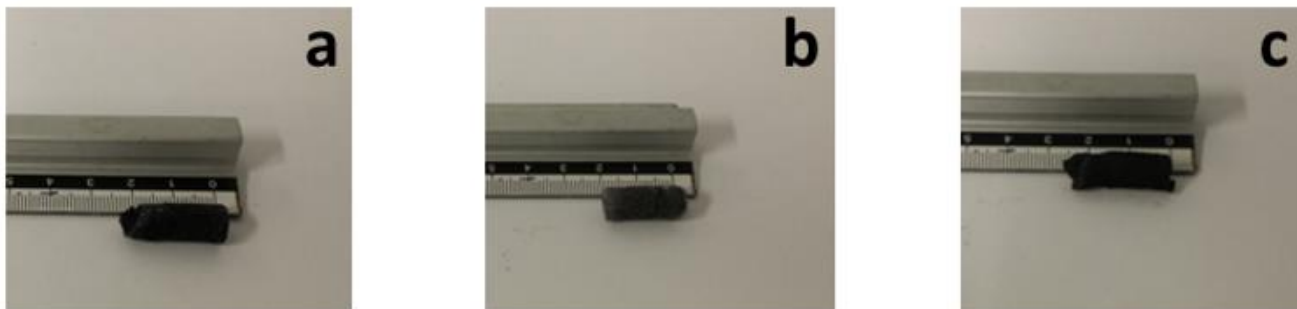


free-standing (thickness = 0.16 mm).

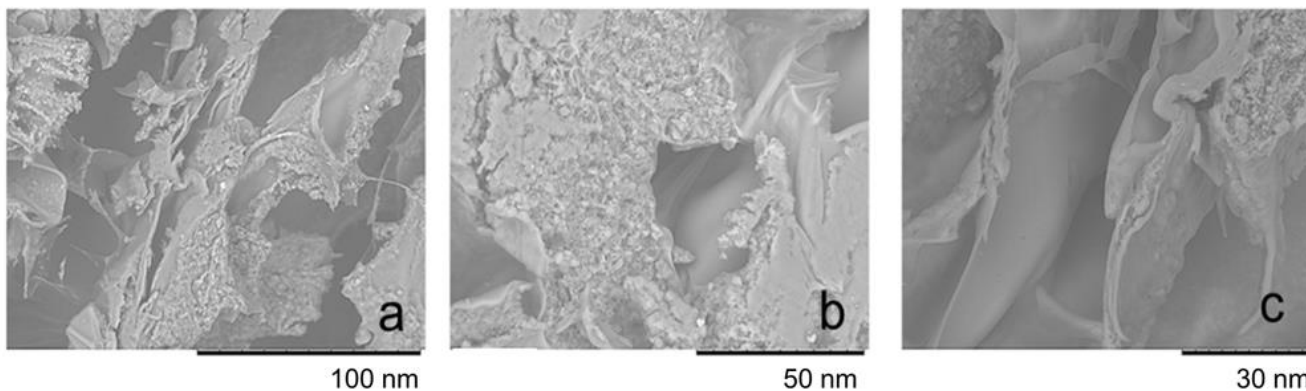
Very flexible and perfectly foldable

Curvature radius close to 180° without the appearance of cracks

# Aerogels from HSAG-SP/CS adducts



HSAG-SP/CS = 1:4, 1:1, 4:1



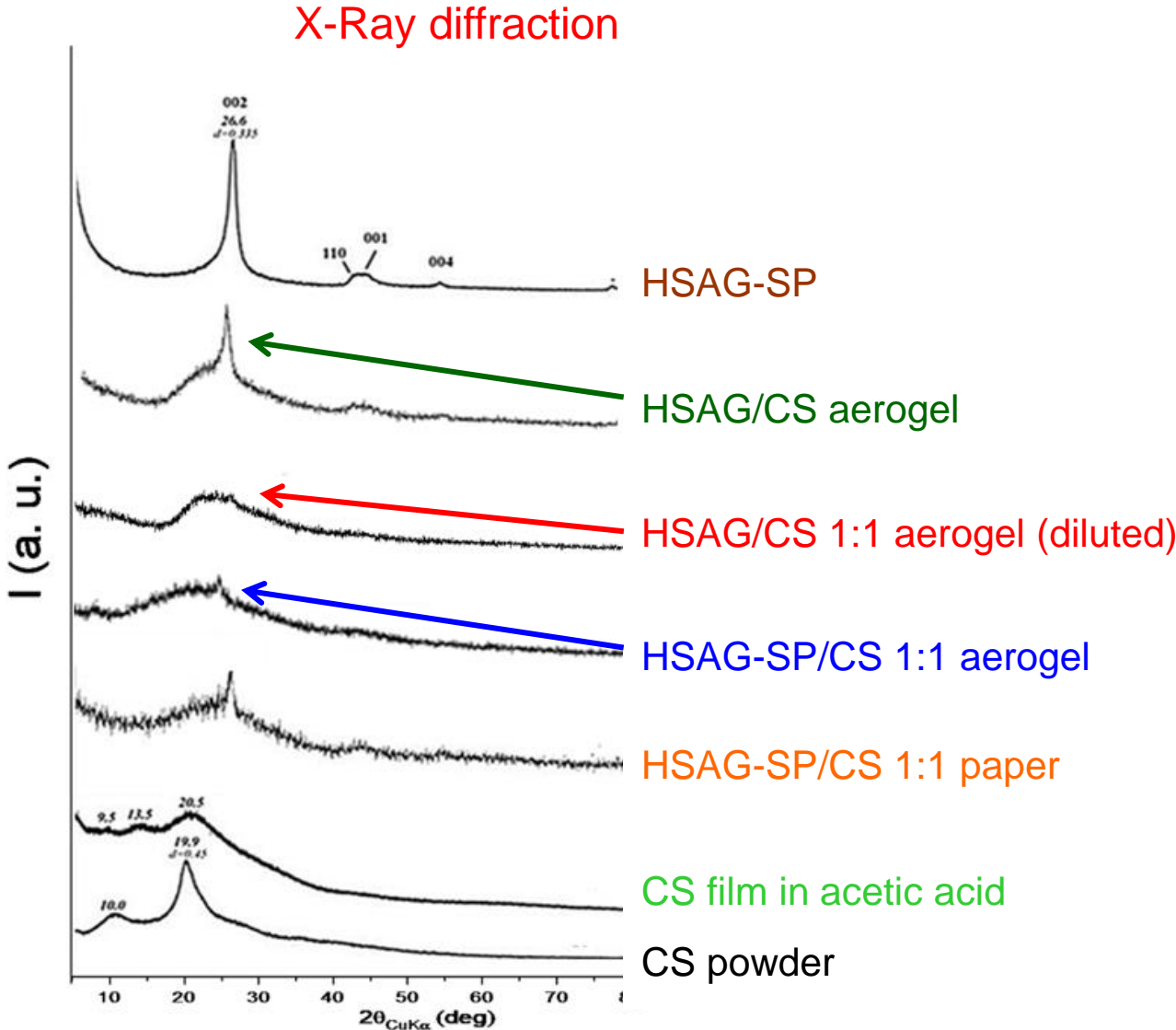
HSAG-SP/CS = 1:1

spongy like, highly porous structure. low density:  $0.026 \text{ g cm}^{-3}$ .

Walls of the cavity are made by chitosan, with or without HSAG-SP

Visible continuous HSAG network

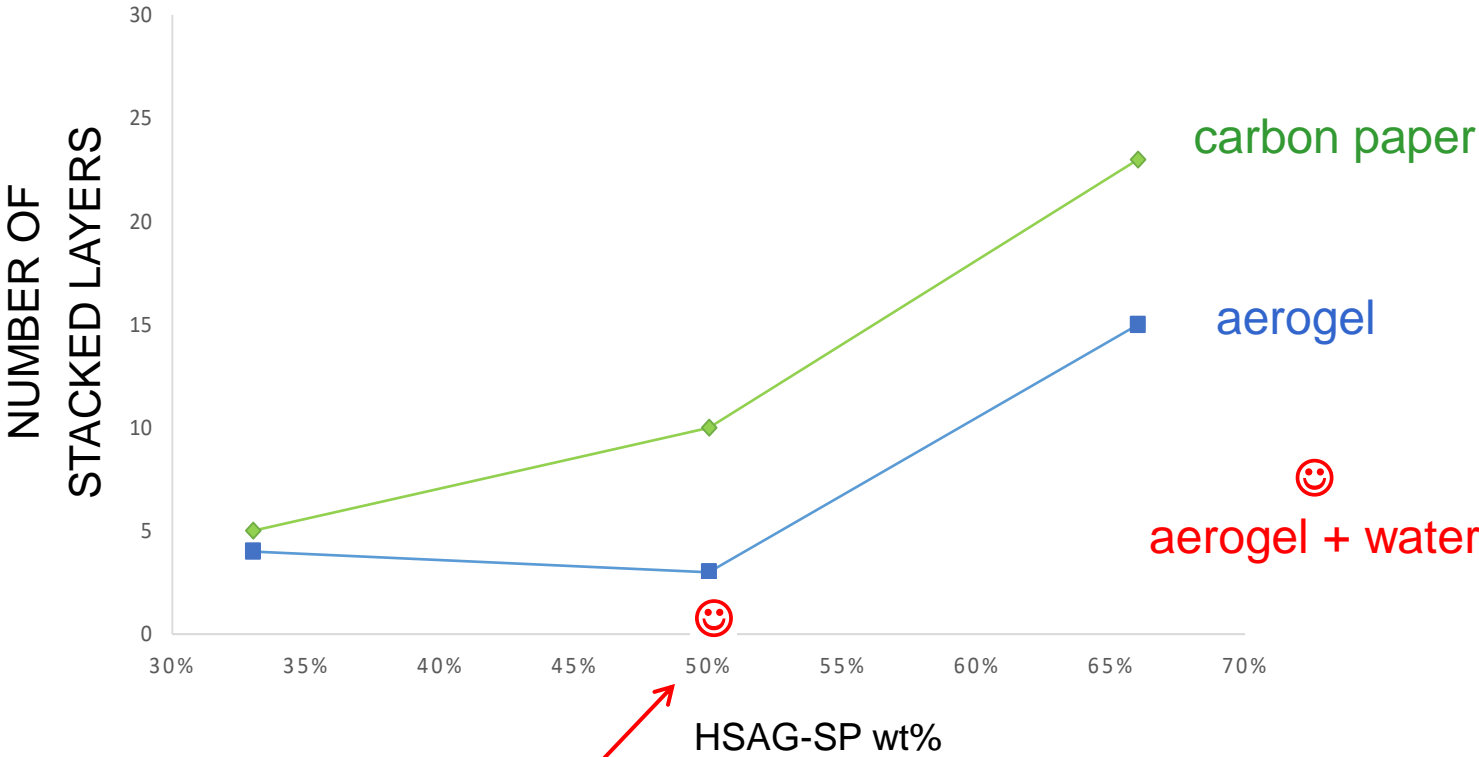
# Structure of HSAG/CS adducts



# Structure of HSAG/CS adducts

HSAG-SP/CS = 1/1

## Results from X-Ray diffraction



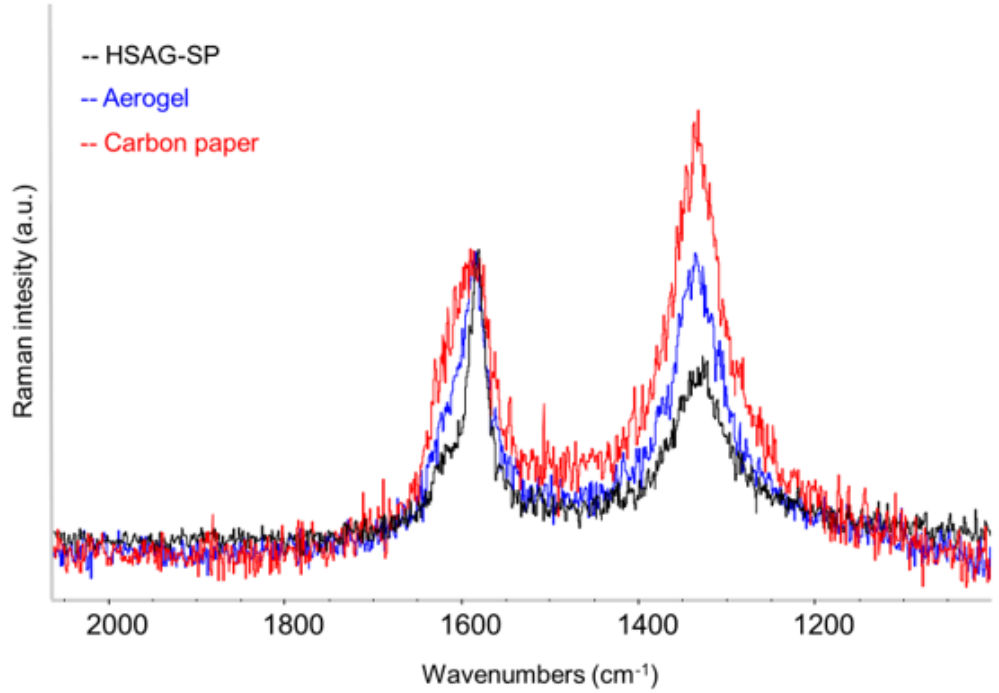
Undetectable stacked layers



# Structure of HSAG-SP/CS adducts

HSAG-SP/CS = 1/1

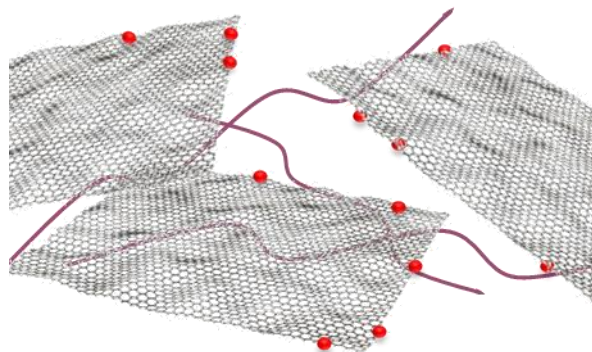
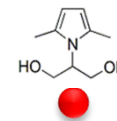
## Raman spectroscopy



Reduction of the size of the graphitic layers,  
and/or higher orientational disorder of the sp<sup>2</sup> graphitic flakes

# HSAG-SP/CS adducts. The interaction of CS with the graphene layers

No evidences of covalent bond between CS and functionalized graphene layers



Cation-  $\pi$  interaction

Protonated CS chains interact with graphene layers

Better:

- dispersion of graphene layers
- stability of the interaction with chitosan

thanks to SP

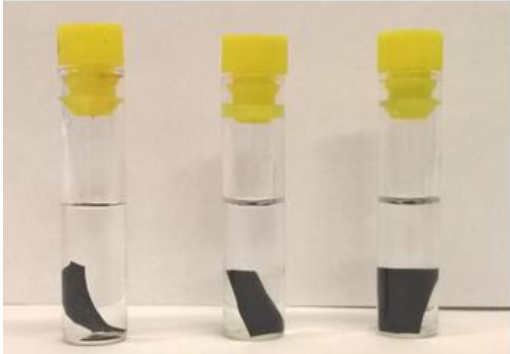
# Carbon papers and aerogels from HSAG-SP/CS adducts. Stability to solvents

HSAG-SP/CS = 1/1

stability in H<sub>2</sub>O and solvents

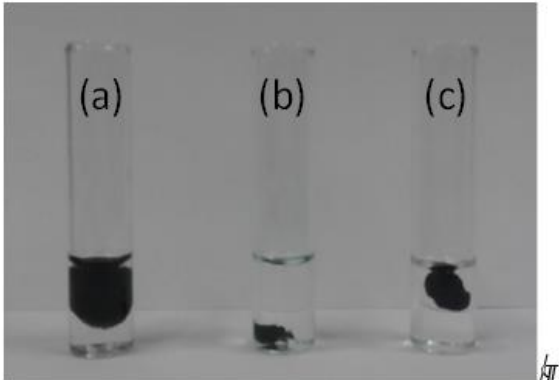
after 2 months storage

Carbon paper



H<sub>2</sub>O    Hexane    DMF

Aerogel



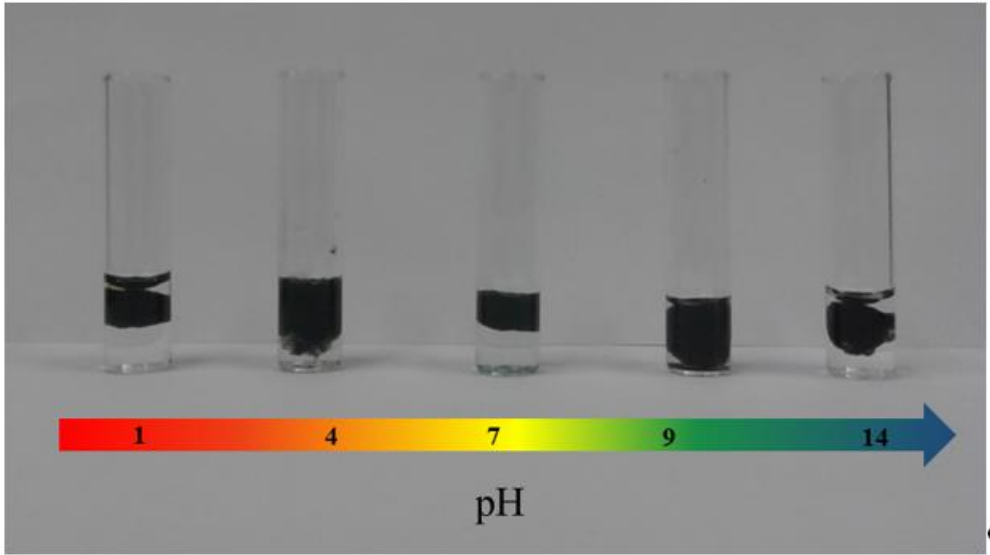
H<sub>2</sub>O    Hexane    DMF

TGA analysis did not reveal any mass loss. Swelling in water only for aerogel

# Aerogels from HSAG-SP/CS adducts. stability to pH

HSAG-SP/CS = 1/1

pH sensitive stability

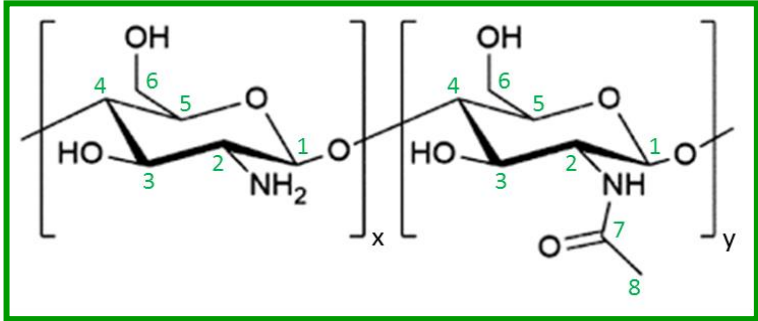
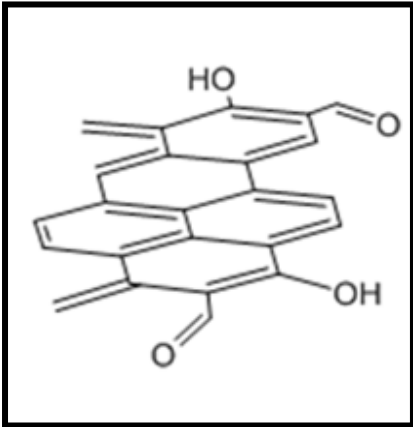


Swelling observed at every pH

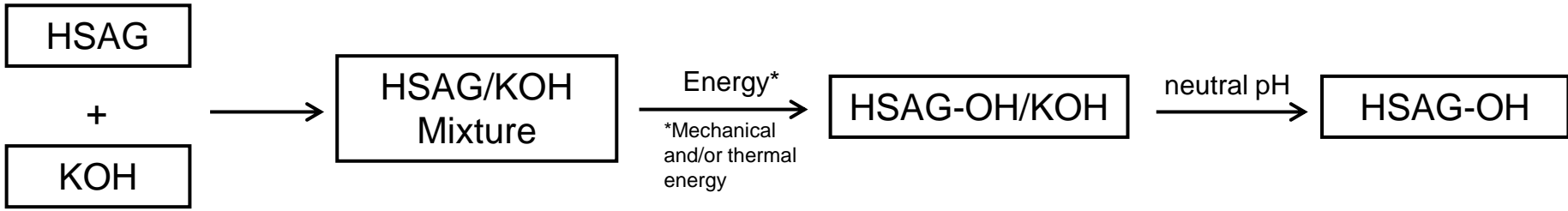
HSAG-SP/CS Ratio <sup>a</sup>	$\sigma$ ( $\mu\text{S/cm}$ )
CS powder	1 E <sup>-4</sup>
CS paper	1 E <sup>-4</sup>
1:1 paper	1 E <sup>1</sup>
1:1 aerogel	1.4 E <sup>1</sup>
<b>4:1 aerogel</b>	<b>1.1 E<sup>5</sup></b>

Aerogels with high HSAG content and good electrical conductivity

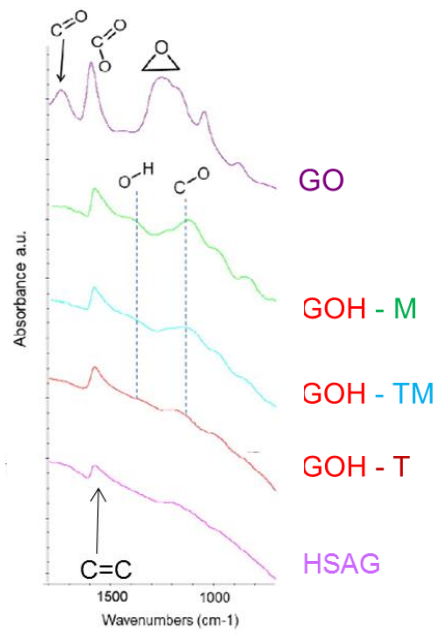
# Bionanocomposites based on graphene layers chemically crosslinked by chitosan



# Oxidation of HSAG with KOH: G-OH



# Oxidation of HSAG with KOH: G-OH



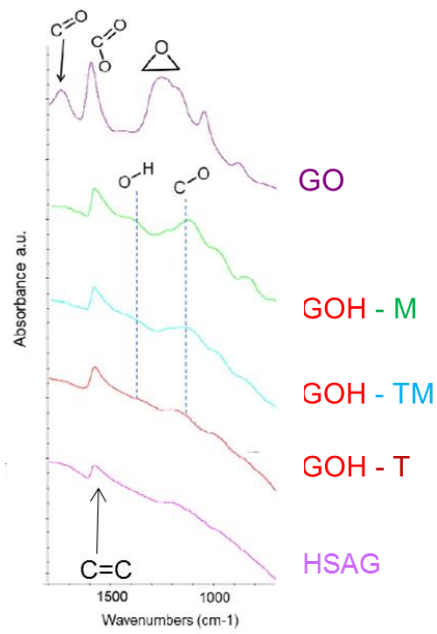
## XPS

☞ Increase of C-O / C=O ratio

	HSAG	GOH
<b>O1s / C1s atomic ratio</b>	0.04	0.07
<b>O atomic %</b>	4.2	6.4



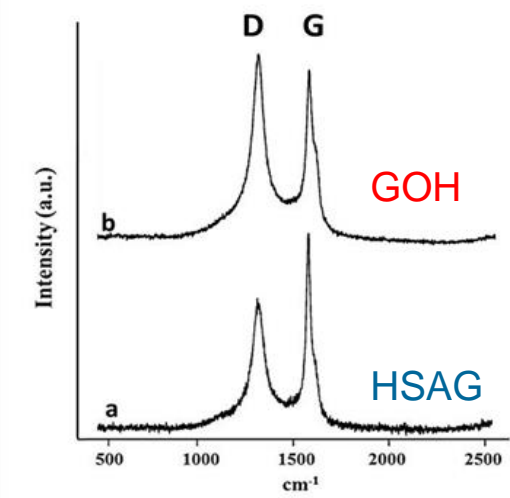
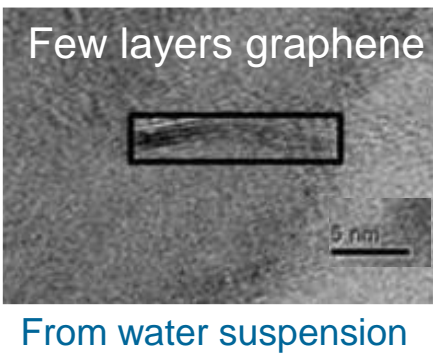
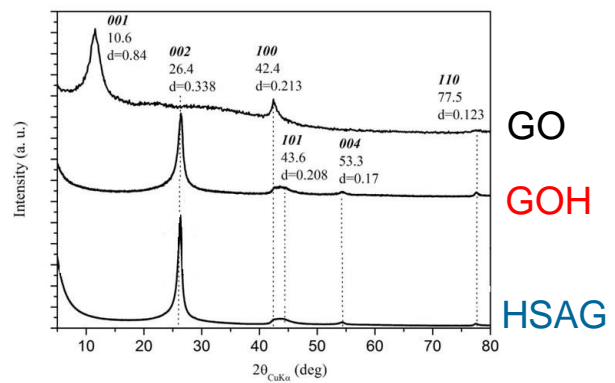
# Oxidation of HSAG with KOH: G-OH



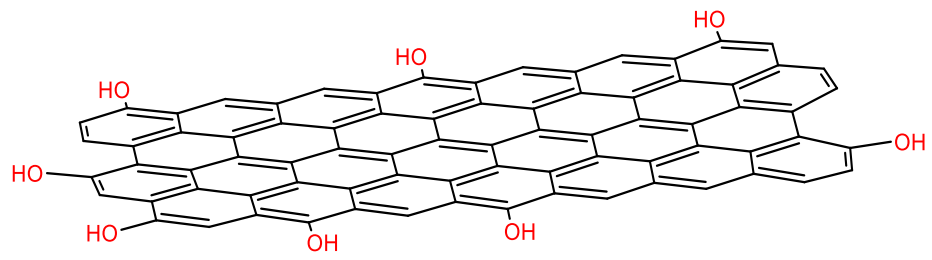
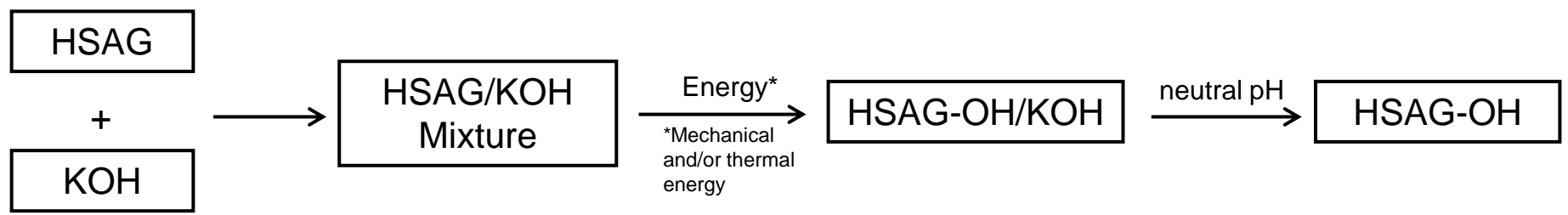
## XPS

☞ Increase of C-O / C=O ratio

	HSAG	GOH
<b>O1s / C1s atomic ratio</b>	0.04	0.07
<b>O atomic %</b>	4.2	6.4



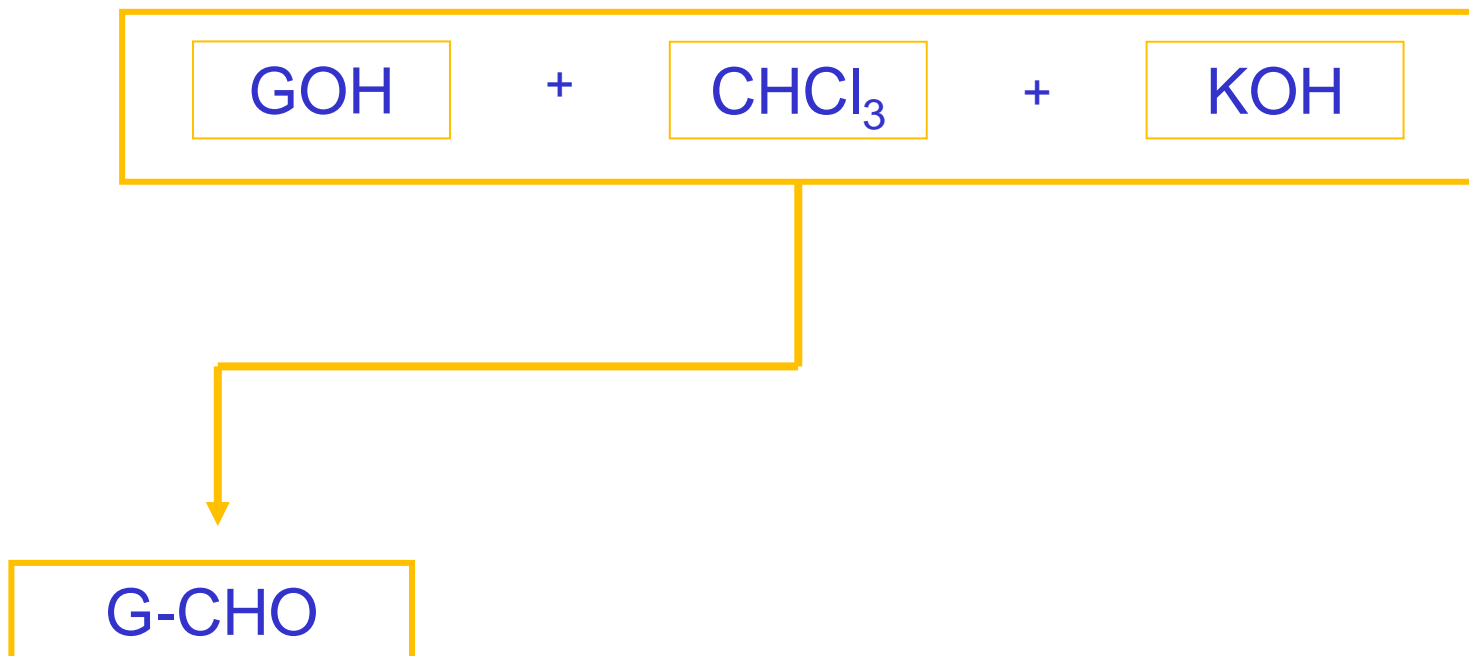
# Oxidation of HSAG with KOH to G-OH



Polyhydroxylated few layers graphene

- 👉 Selective introduction of OH groups up to 15 mass%
- 👉 In plane order substantially unaltered
- 👉 No expansion of interlayer distance

## From G-OH to G-CHO

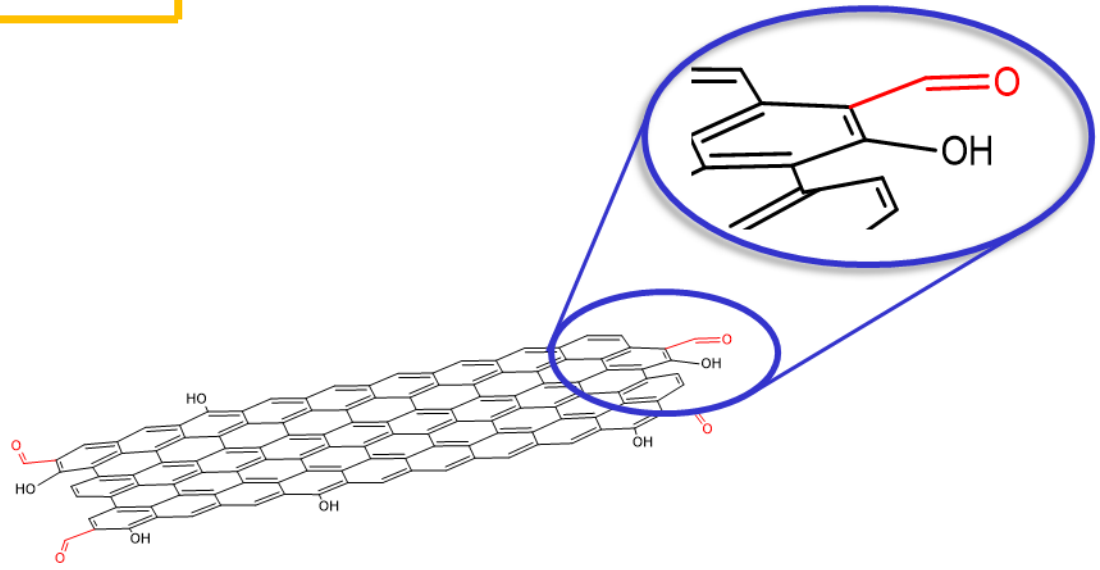


Selective ortho aldehyde

# From G-OH to G-CHO

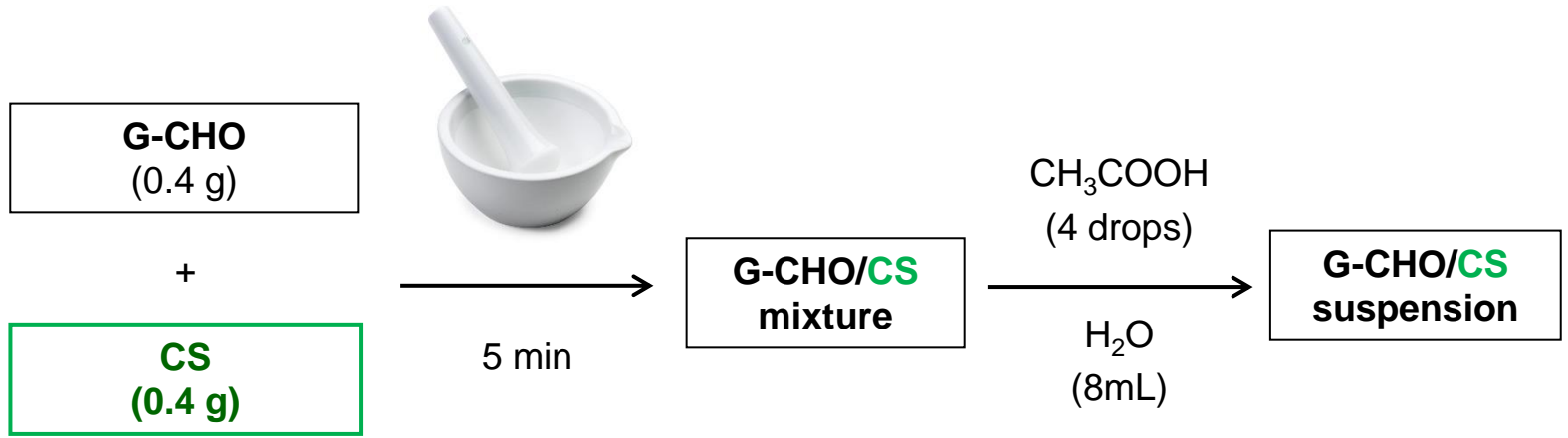


Selective ortho aldehyde



Reimer-Tiemann reaction

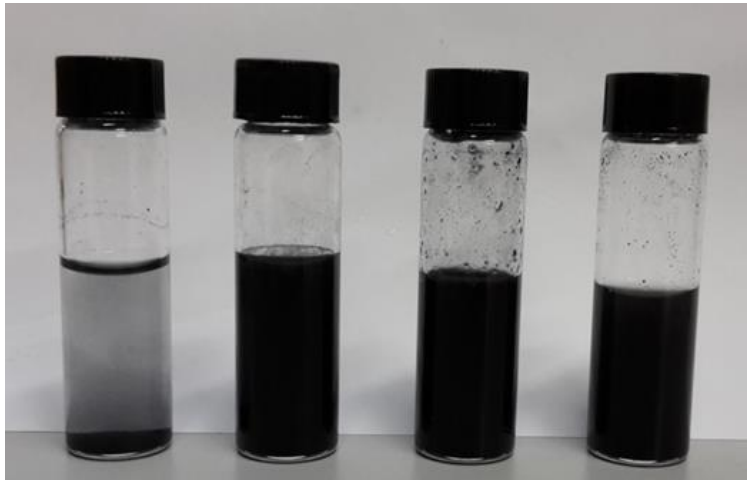
# Water suspensions of adducts of G-CHO with chitosan



**G-CHO/CS = 1/1**

# stability of water dispersions of G-CHO

G-CHO/CS = 1/1



G-CHO/CS = 1/1

Concentration  
1 mg/mL

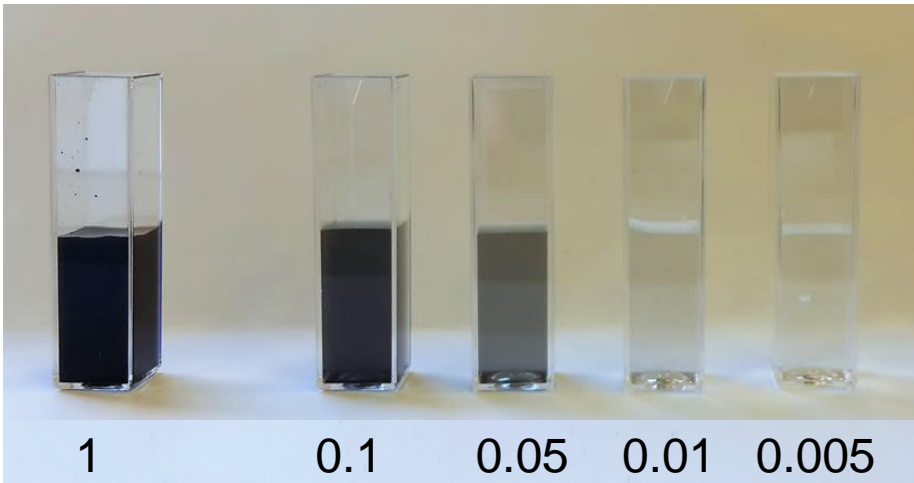
HSAG

G-CHO

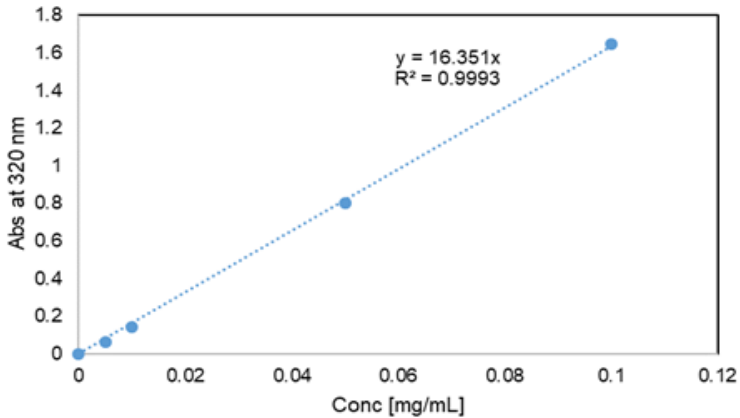
G-CHO/CS  
after 1 month storage

G-CHO/CS  
after 30 min centrifugation at 6000 rpm

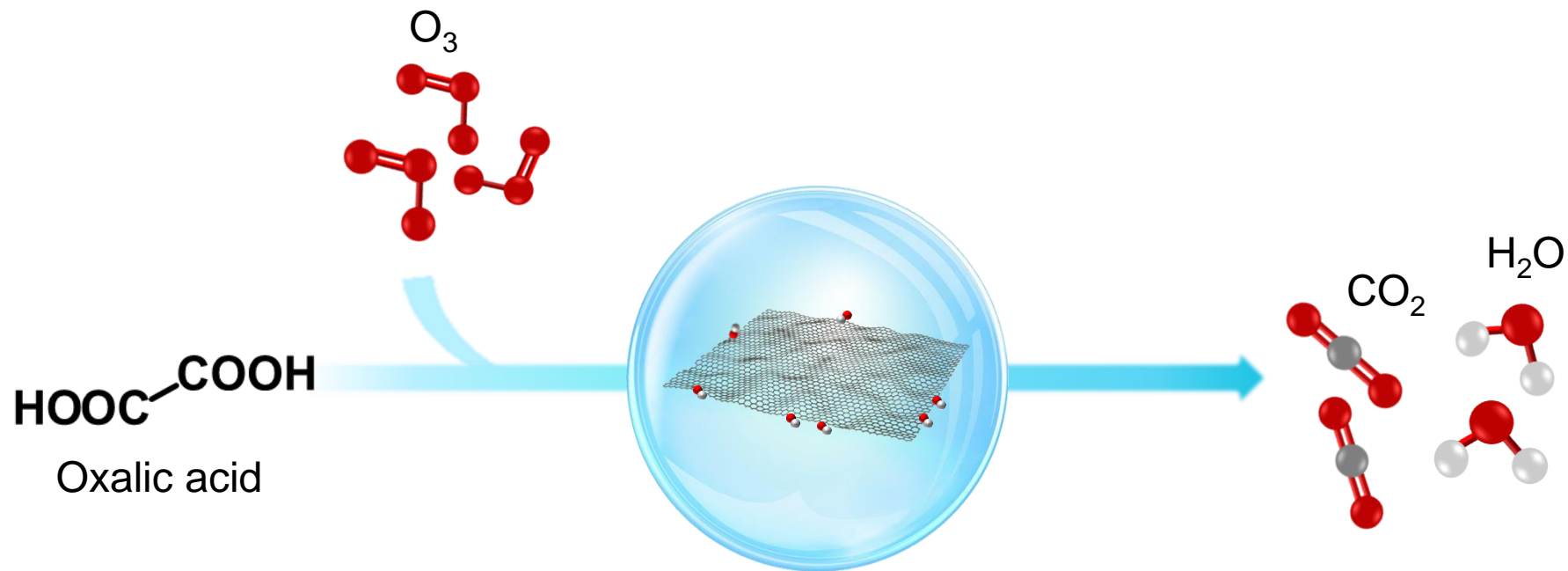
# stability of water dispersions of G-CHO



Concentration (mg/mL)

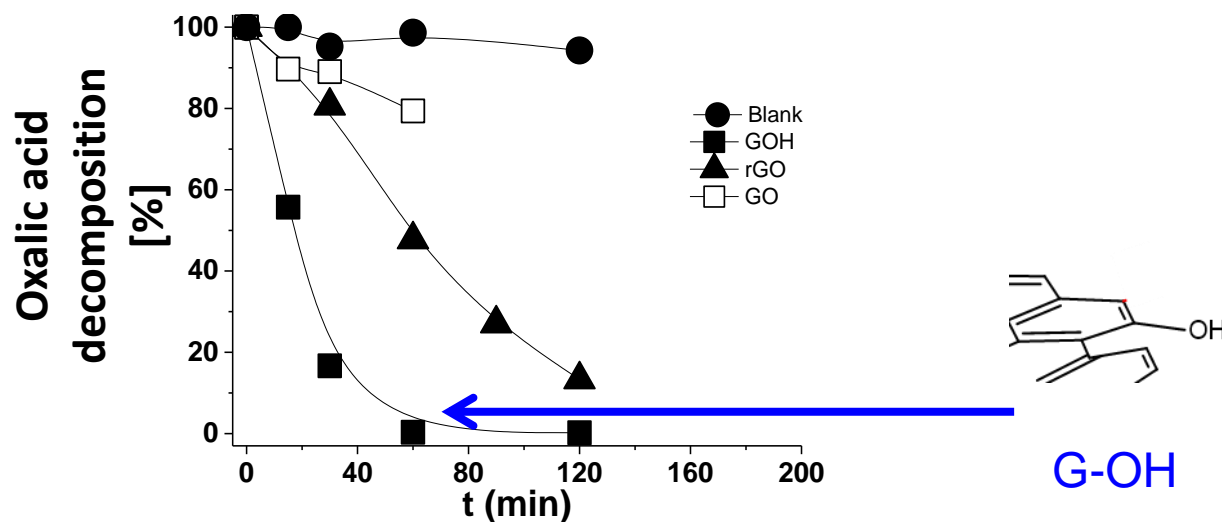
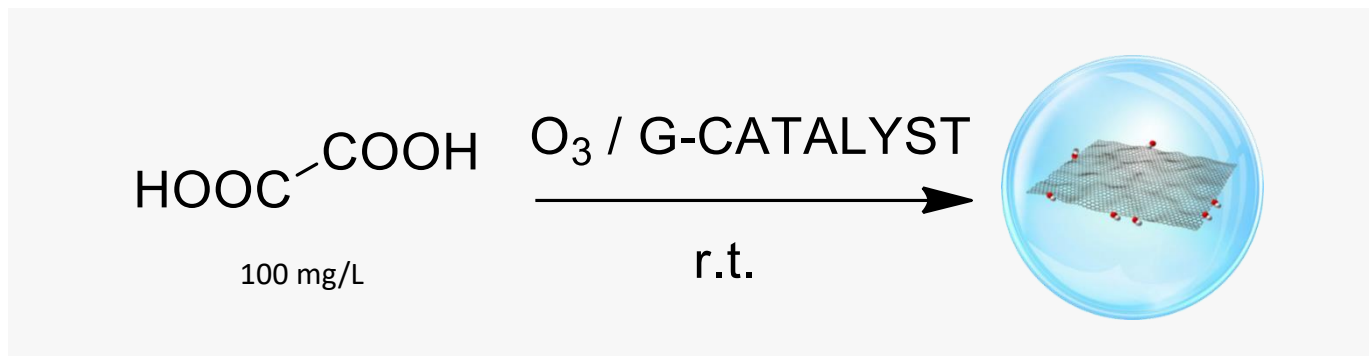


# G-OH and derivatives as catalyst for Ozonation

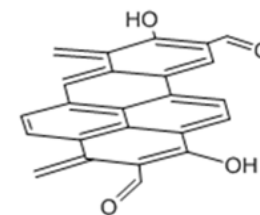
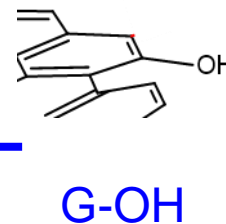
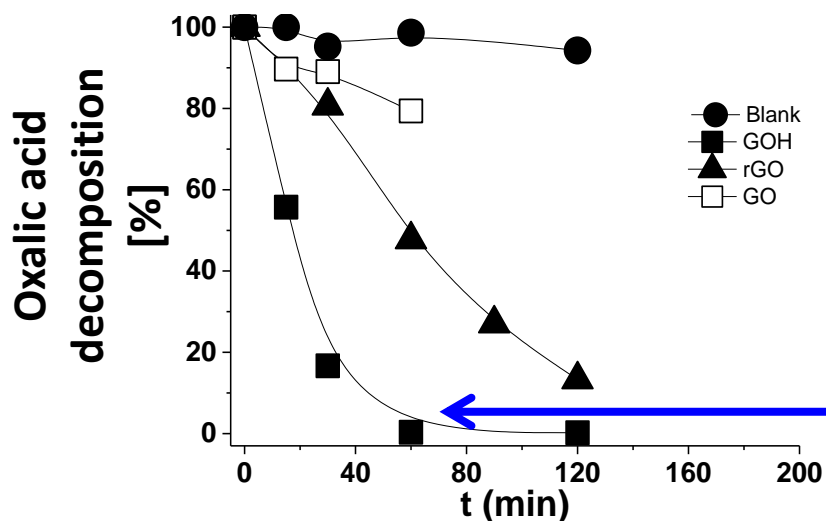
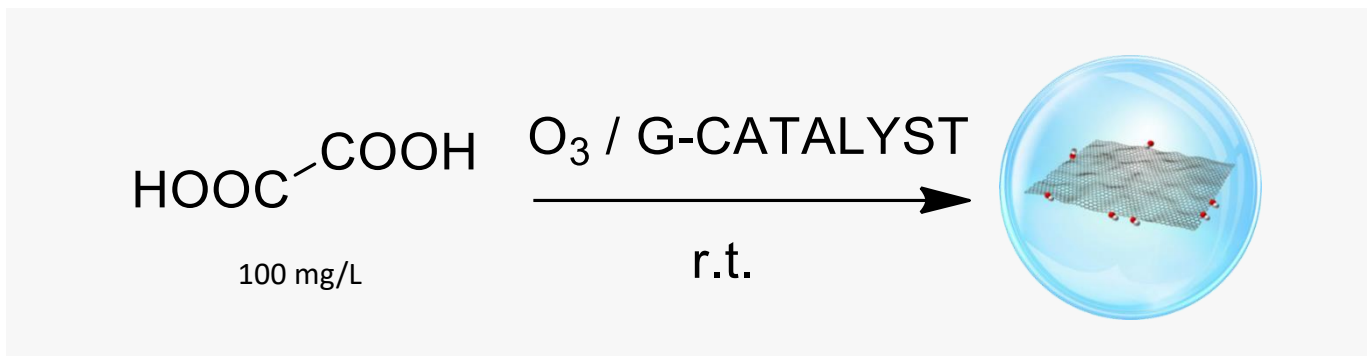




# G-OH, G-CHO as catalysts for Ozonation

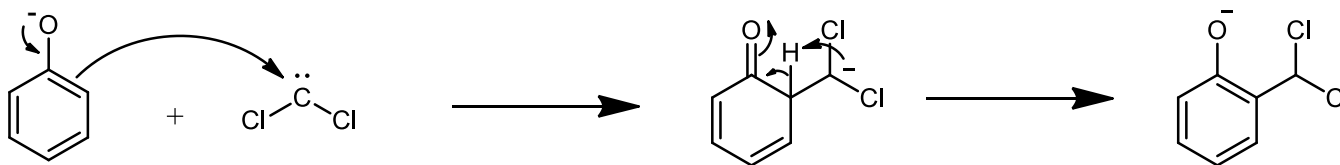


# G-OH, G-CHO as catalysts for Ozonation

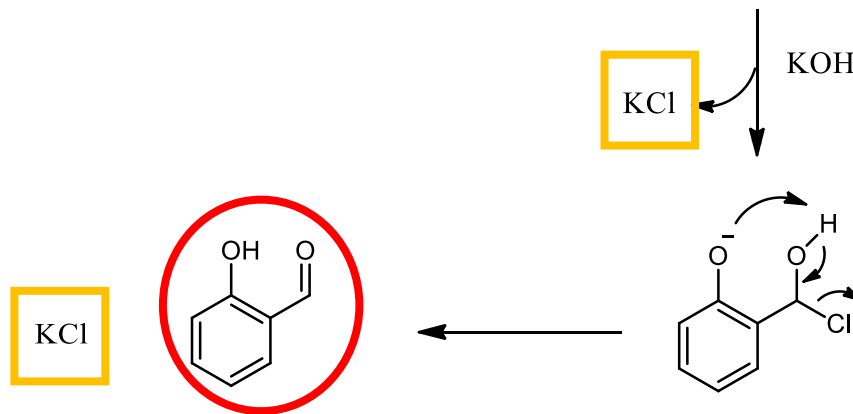


G-CHO  
even better

# Mechanistic pathway of the Reimer-Tiemann reaction

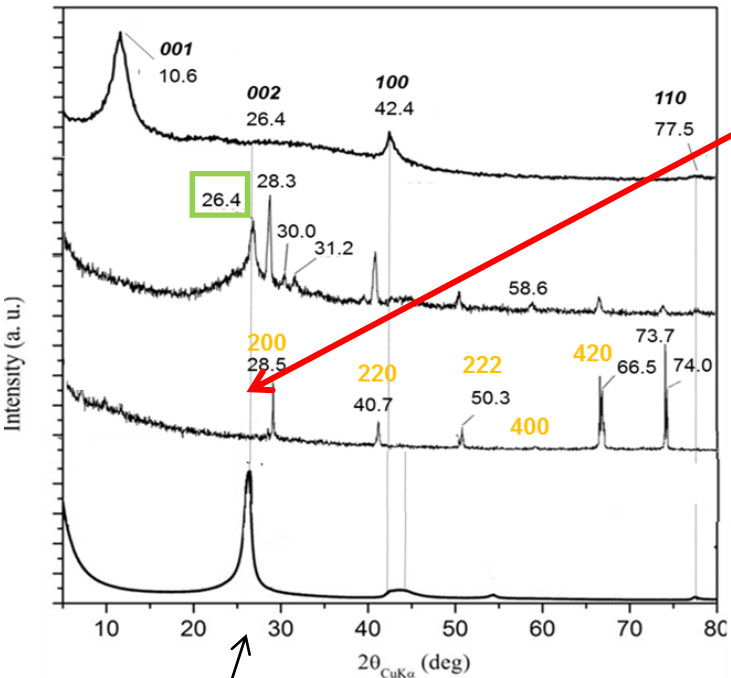


**KCl is the  
by-product of reaction**



For each Aldehyde formed  
there are also 3 KCl molecules

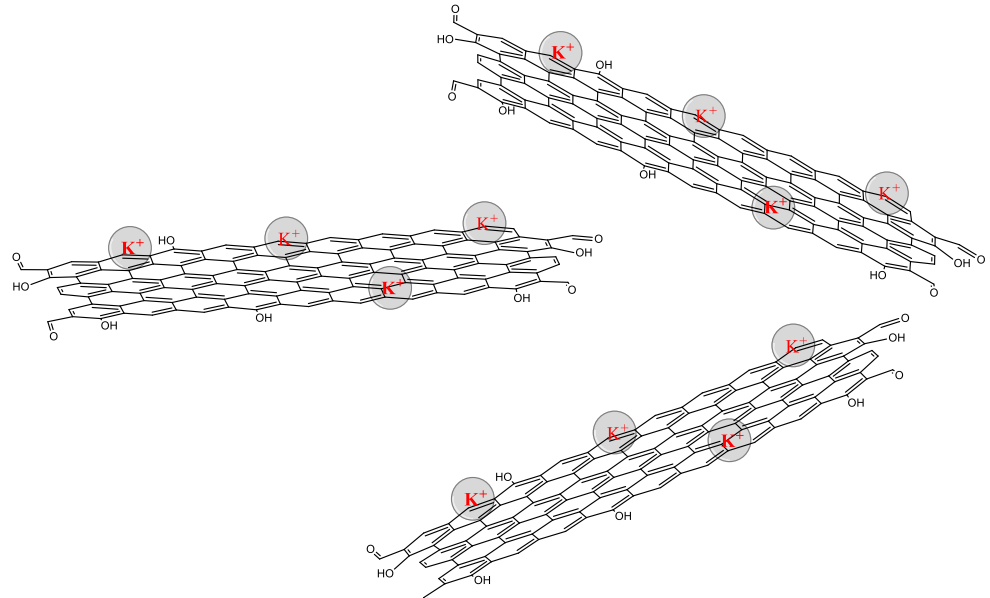
# Exfoliation of nanographite



G-CHO after KCl removal

G-CHO in the presence of KCl

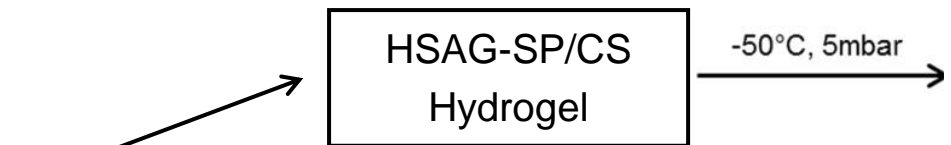
(002) reflection of graphite



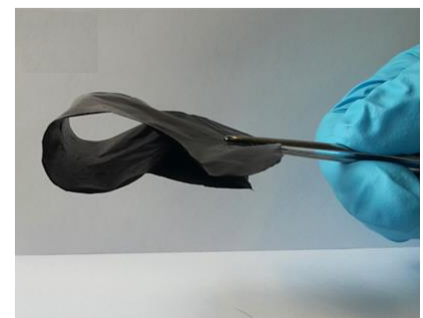
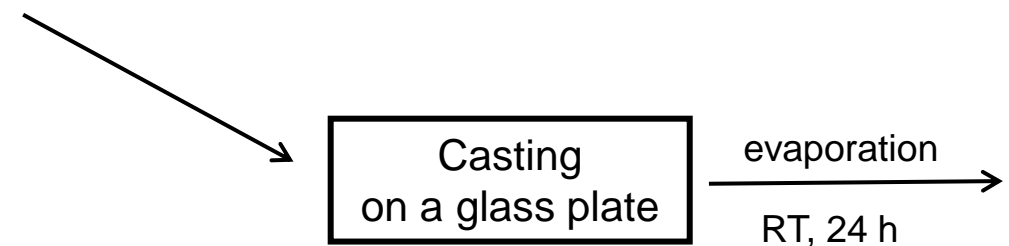
Barbera V., Brambilla L., Porta A., Bongiovanni R., Vitale A., Torrisi G., Galimberti M., *Journal of Materials Chemistry A*, (2018) 6, 7749-7761.

# Aerogels and carbon papers from G-CHO/CS

G-CHO/CS = 1/1



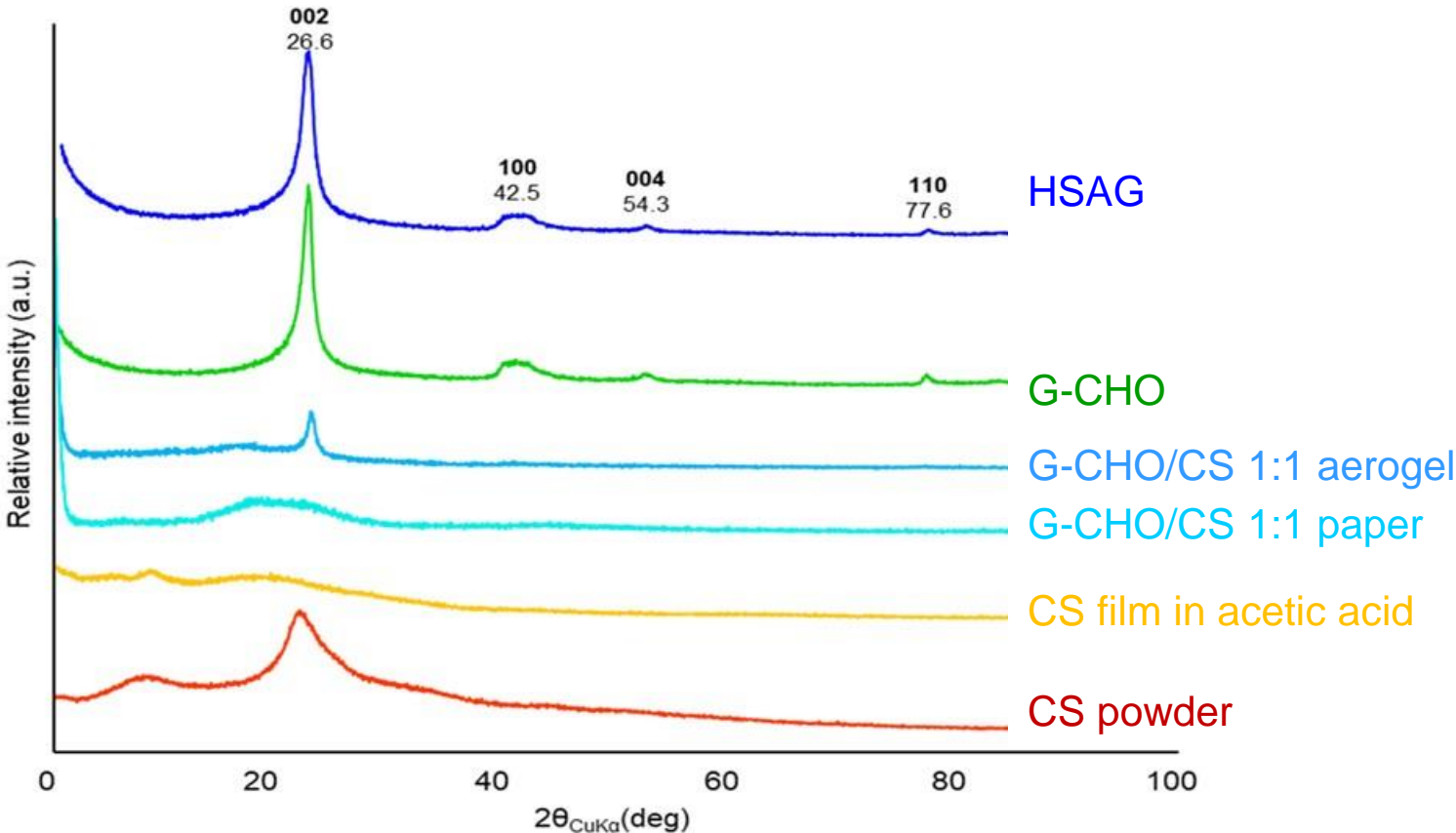
G-CHO/CS Aerogel



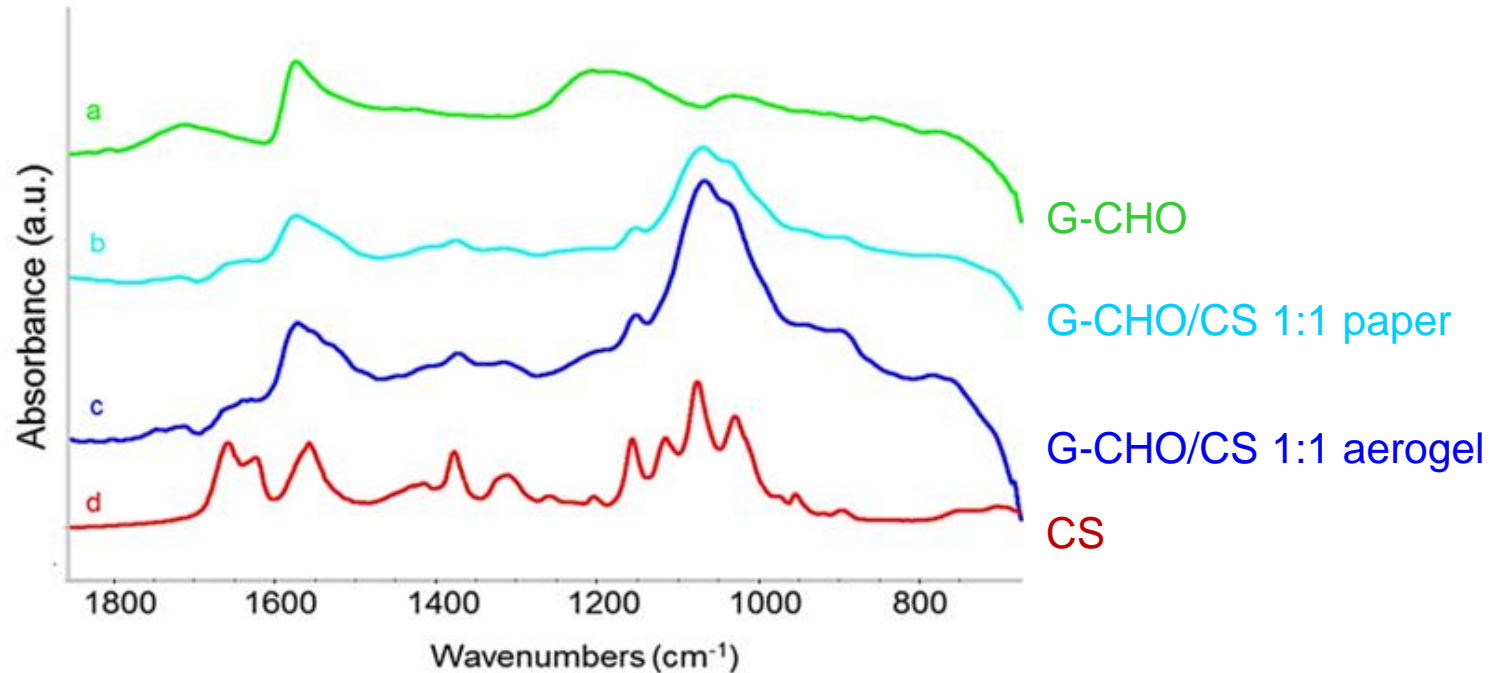
G-CHO/CS Carbon paper

# Aerogels and carbon papers from G-CHO/CS

## X-Ray diffraction



# Aerogels and carbon papers from G-CHO/CS

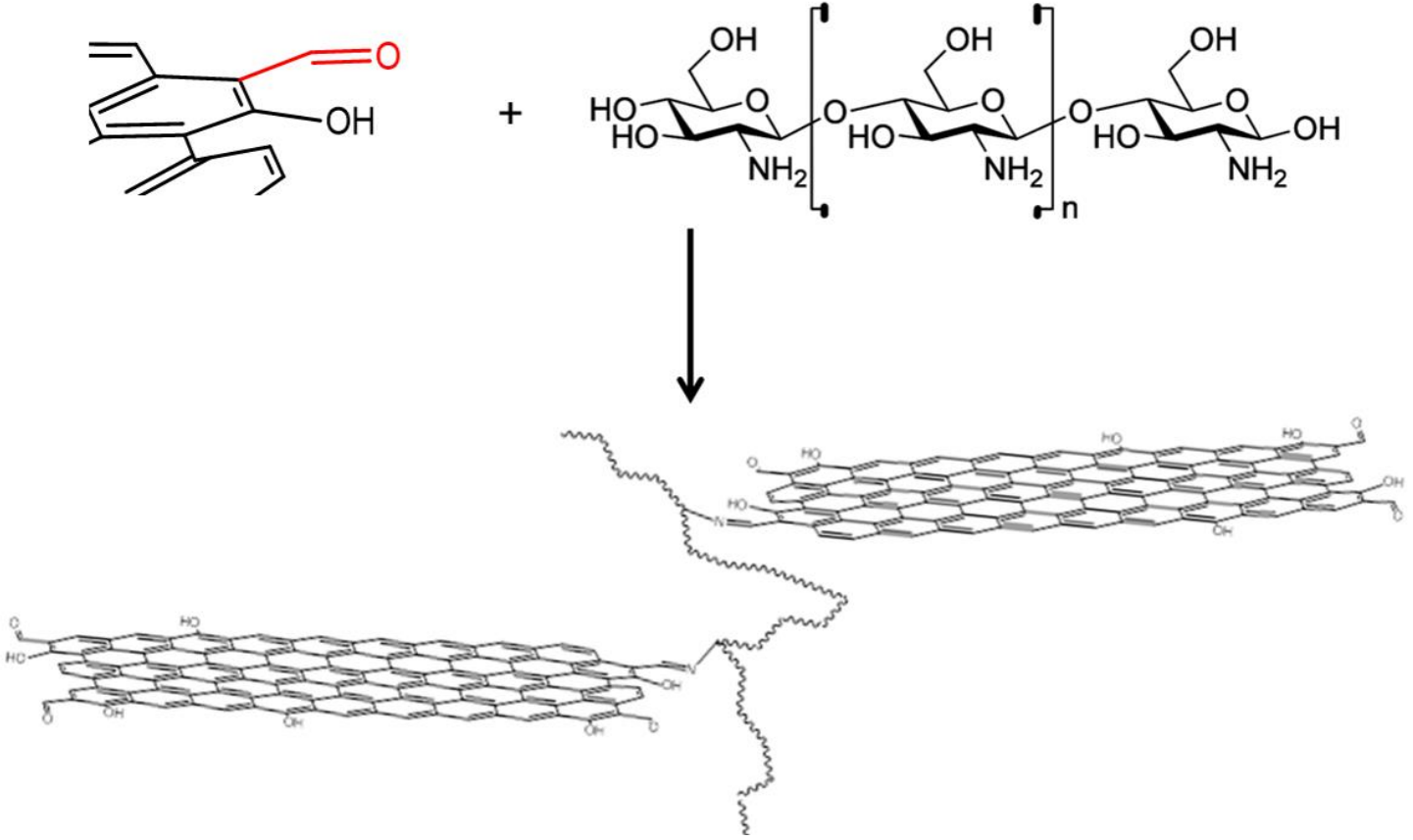


G-CHO/CS 1:1 paper, G-CHO/CS 1:1 aerogel

1715 cm<sup>-1</sup> (assigned to -C=O stretching vibration) is reduced

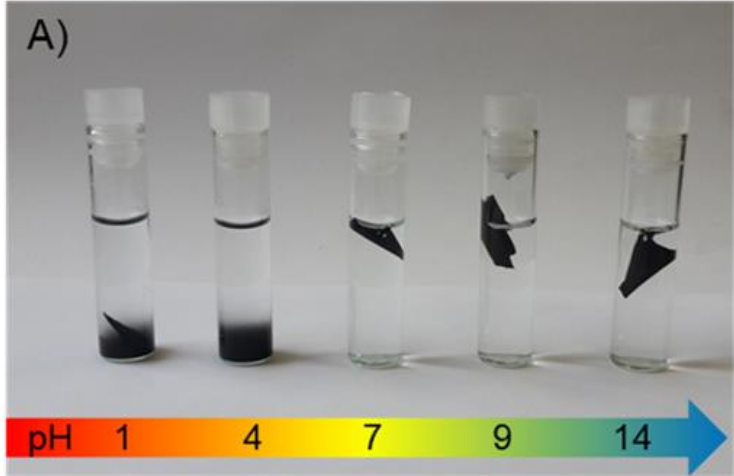
New feature at 1656 cm<sup>-1</sup> appears: imine functionalities

# The structure of G-CHO/CS bionanocomposites

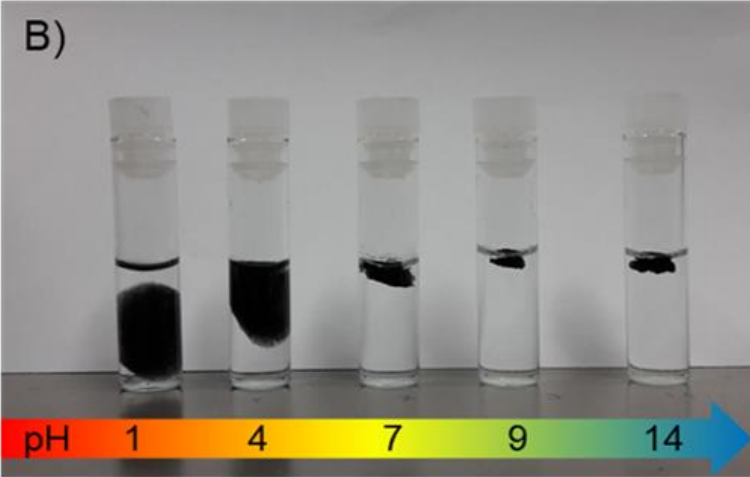




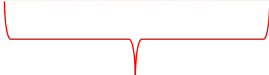
# Carbon papers and aerogels from HSAG/CS adducts. stability to pH



Carbon papers



Aerogels

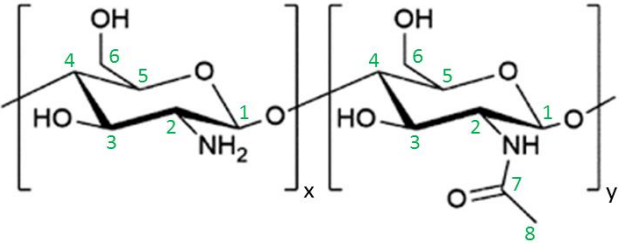
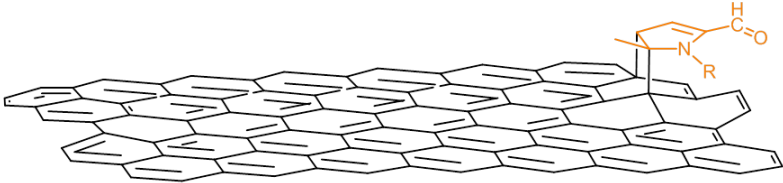
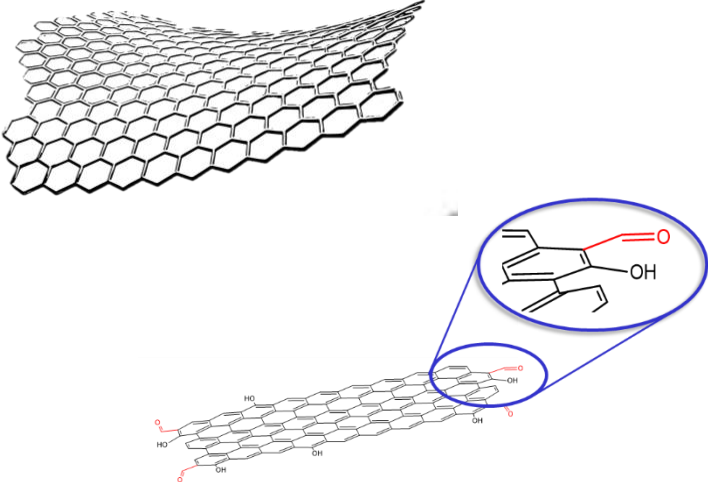


swelling



stability

# Conclusions



## Applications

- ☞ pH sensitive sensors
- ☞ filters: antimicrobial
- ☞ Catalysis



***Thanks  
for your attention!***

2<sup>ND</sup> GLOBAL  
VIRTUAL SUMMIT ON  
**CARBON, GRAPHENE, 0D,  
1D, AND 2D MATERIALS**

Theme: A stronger and greener future with graphene

**November 15-16, 2021**



instagram: @ismaterials.polimi