Bionanocomposites based on a covalent network of chitosan and edge functionalized graphene layers

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ISCaMaP

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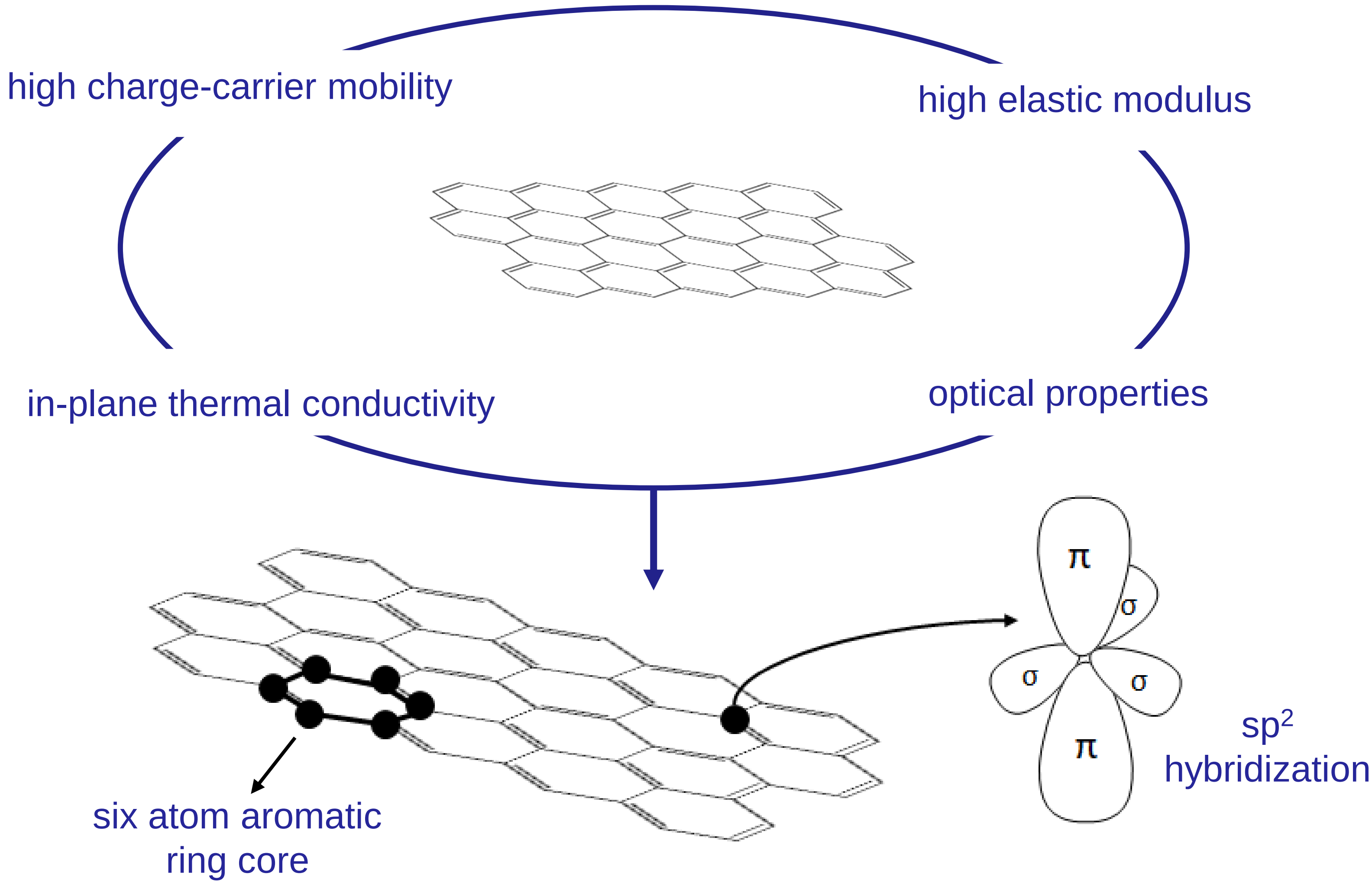
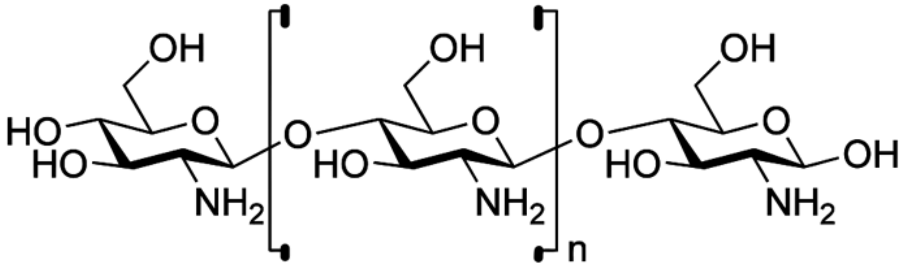
Politecnico di Milano, Department of Chemistry, Materials and Chemical Engineering "G. Natta"

Why graphene?



KS. Novoselov, SV. Morozov, TMG. Mohinddin, et al. *Electronic properties of graphene*, Phys Status Solidi (b), 2007; 244(11): 4106–4111.
C. Soldano, A. Mahmood and E. Dujardin. *Production, properties and potential of graphene*, Carbon, 2010; 48: 2127–2150.
Kumar, K. Sharma and AR. Dixit. *A review of the mechanical and thermal properties of graphene and its hybrid polymer nanocomposites for structural applications*, J Mater Sci, 2019; 54(8): 5992–6026.

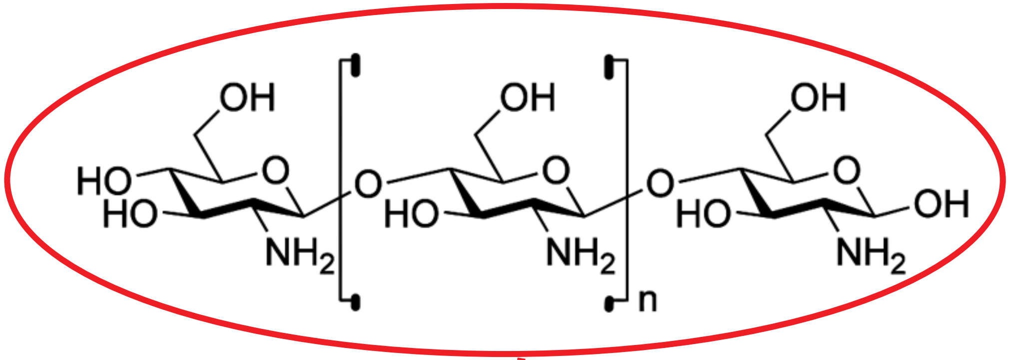
Why Chitosan?



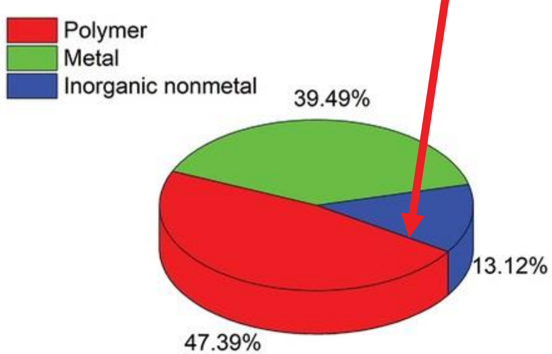
- ✓ non-toxicity
- ✓ biodegradability
- ✓ antimicrobial effect
- ✓ biocompatibility

X. Sun, C. Huang, L. Wang, L. Liang, Y. Cheng, W. Fei, Y. Li. *Recent Progress in Graphene/Polymer Nanocomposites*, Adv. Mater., 2021; 33(6): e2001105C.
M. Rinaudo. *Chitin and chitosan: properties and applications*, Prog. Polym. Sci., 2006; 31(7): 603−632.

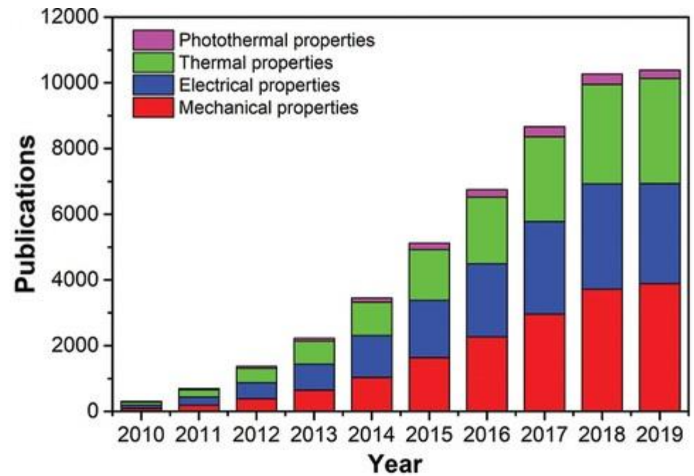
Why Chitosan?



- non-toxicity
- biodegradability
- antimicrobial effects
- biocompatibility



Biopolymers



Graphene/Biopolymer nanocomposites

M. Rinaudo. *Chitin and chitosan: properties and applications*, Prog. Polym. Sci., 2006; 31(7): 603−632.
L. Jianguo, L. Yanqun, L. Haiyan, et al. *Preparation, bioactivity and mechanism of nano-hydroxyapatite/sodium alginate/ chitosan bone repair material*, J. Appl. Biomater. Funct. Mater., 2018; 16(1): 28–35
X. Sun, C. Huang, L. Wang, L. Liang, Y. Cheng, W. Fei, Y. Li. *Recent Progress in Graphene/Polymer Nanocomposites*, Adv. Mater., 2021; 33(6): e2001105C.

Chitosan/Graphene (CS/G) nanocomposites

CS/G nanocomposites

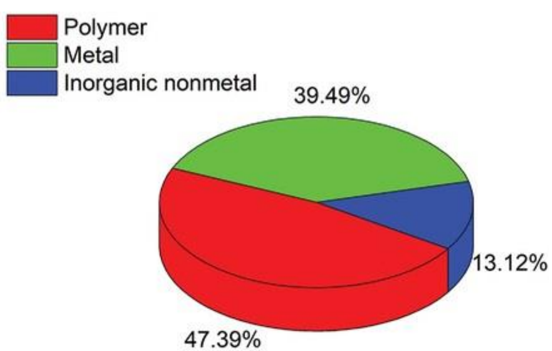
Field of applications

biotechnology

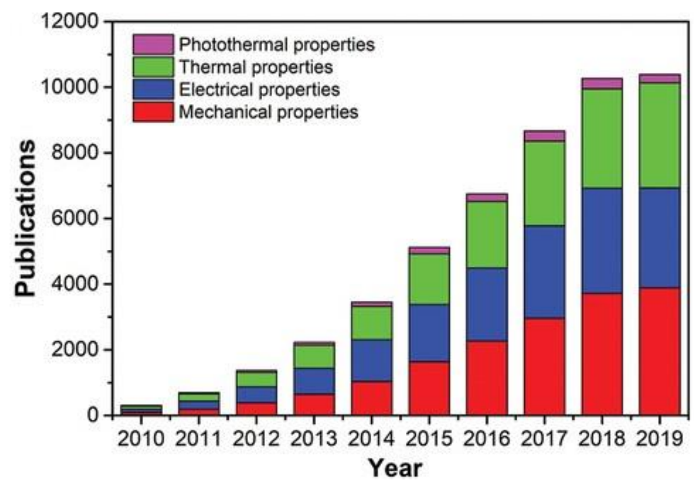
catalysis

pollutants remotion

supercapacitors



Biopolymers



Graphene/Biopolymer nanocomposites

H. Bao, Y. Pan, Y. Ping, et al. *Chitosan-functionalized graphene oxide as a nanocarrier for drug and gene delivery*, Small, 2011; 7(11): 1569–1578.
B. Aghabarari, et al. *Effect of molybdophosphoric acid in iron and cobalt graphene/chitosan composites for oxygen reduction reaction*, Int. J. Hydrog. Energy., 2017; 42(46): 28093–28101.
ASK Kumar and SJ Jiang. *Chitosan-functionalized graphene oxide: a novel adsorbent an efficient adsorption of arsenic from aqueous solution*, J. Environ. Chem. Eng., 2016; 4(2): 1698–1713.
G. Sun, et al. *Three- dimensional hierarchical porous carbon/graphene composites derived from graphene oxide-chitosan hydrogels for high performance supercapacitors*, Electrochim. Acta, 2015; 171: 13–22.

Key aspects for Chitosan/Graphene (CS/G) nanocomposites

- Dispersion of graphene
- Interaction of graphene with chitosan

Key aspects for Chitosan/Graphene (CS/G) nanocomposites

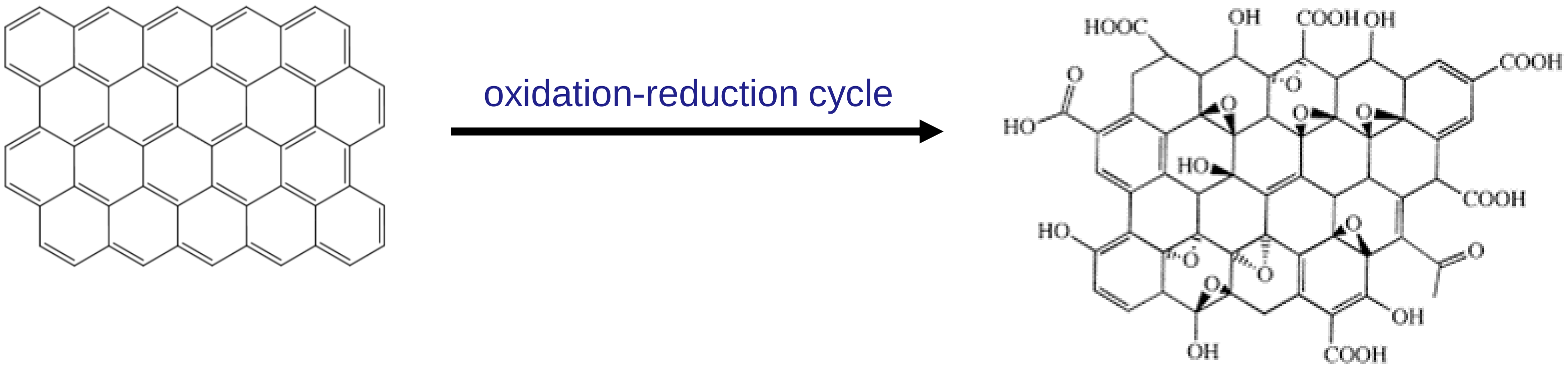
- Dispersion of graphene
- Interaction of graphene with chitosan

Prior Art

graphene (G)

oxidation-reduction cycle

graphene oxide (GO)



- use of dangerous and toxic chemicals
- harsh reaction conditions
- defective GO layers

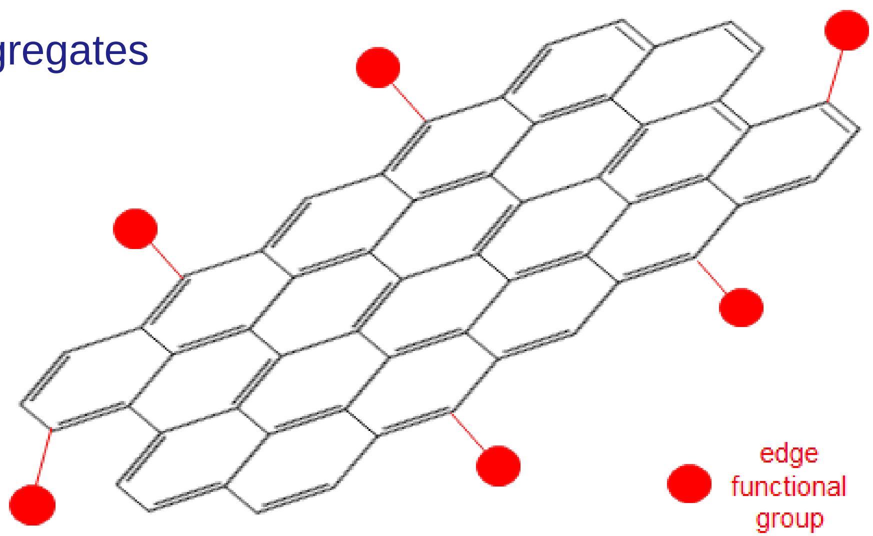
Edge functionalizzation of graphene

no alteration of sp^2 hybridization

preservation of bulk crystalline structure

separation of graphene aggregates

tailor made functional groups are able to chemically react with matrix in CS/G nanocomposites



V. Barbera, A. Bernardi, A. Palazzolo, A. Rosengart, L. Brambilla and M. Galimberti. *Facile and sustainable functionalization of graphene layers with pyrrole compounds*, Pure Appl. Chem., 2018; 90(2): 253–270.
V. Barbera, L. Brambilla, A. Milani, et al. *Domino reaction for the sustainable functionalization of few-layer graphene*, Nanomaterials, 2019; 9(1): 44.
M. Galimberti, V. Barbera, S. Guerra and A. Bernardi. *Facile functionalization of sp2 carbon allotropes with a biobased Janus molecule*, Rubber Chem. Technol. 2017; 90(2): 285–307.

Objective of the research activity

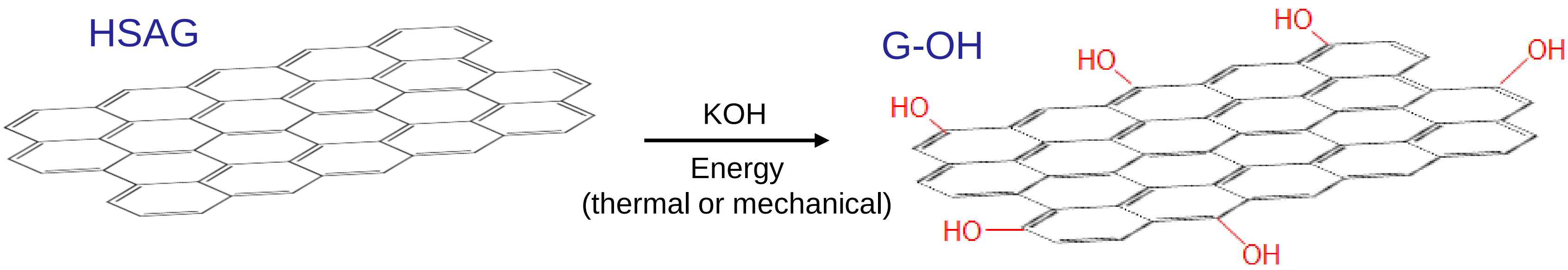
- To prepare an innovative network using graphene layers with edge aldehydic functional groups **(G-CHO)** able to chemically react with the amino groups of chitosan **(C)**

- To obtain bionanocomposite based on graphene layers and chitosan **(G-CHO/CS)**

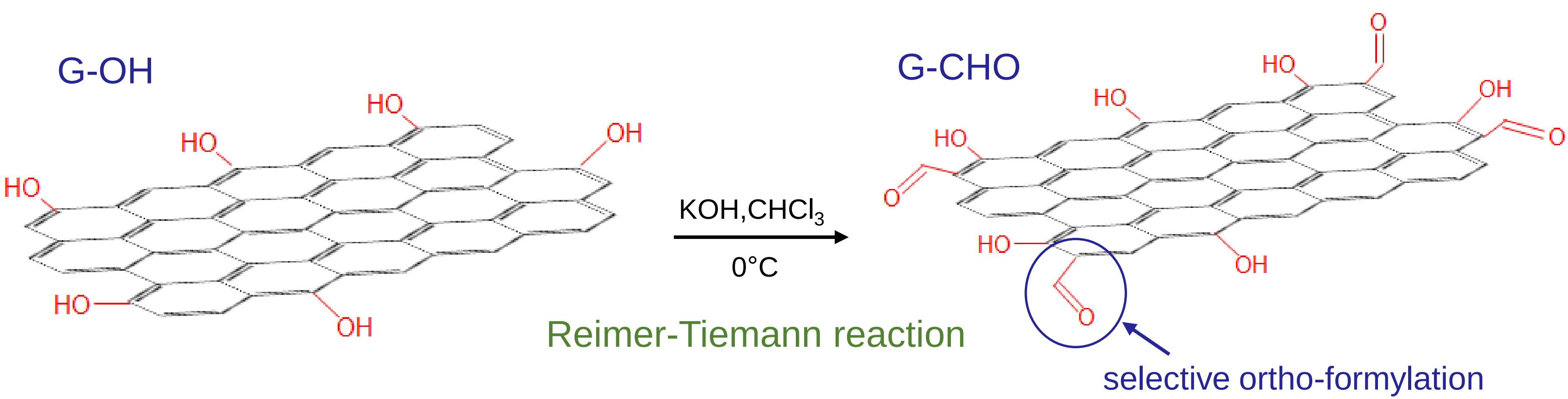
V. Barbera, G. Torrisi, M. Galimberti. *Bionanocomposites based on a covalent network of chitosan and edge functionalized graphene layers*, Journal of Applied Biomaterials & Functional Materials, 2021; 19: 22808000211017431.

Preparation of edge functionalized graphene layers

1st step: G-OH preparation

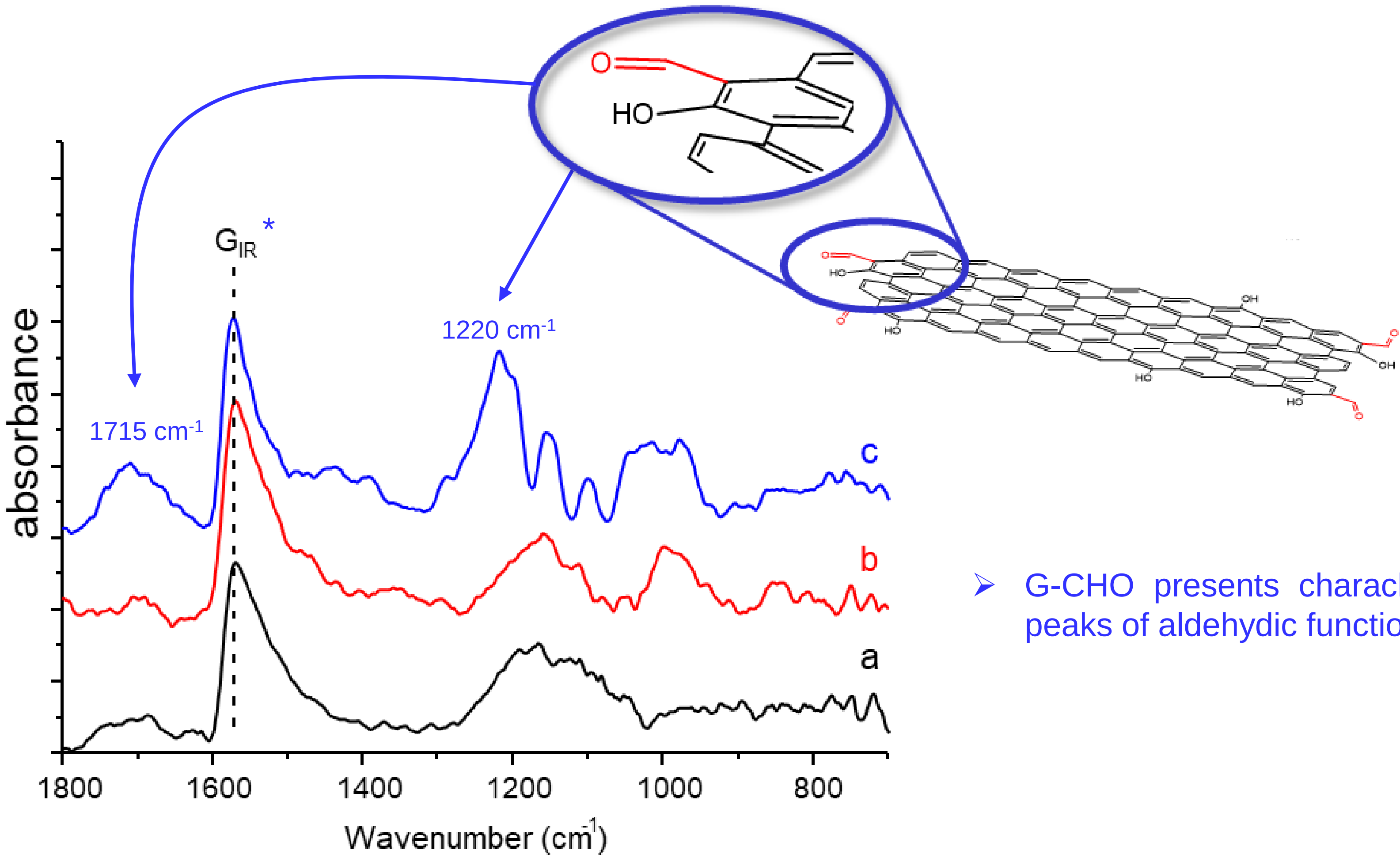


2nd step: G-CHO preparation



V. Barbera, L. Brambilla, A. Porta, et al. *Selective edge functionalization of graphene layers with oxygenated groups by means of Reimer-Tiemann and domino Reimer-Tiemann/Cannizzaro reactions,* J. Mater. Chem. A., 2018; 6(17): 7749–7761.

Characterization of edge functionalized graphene layers



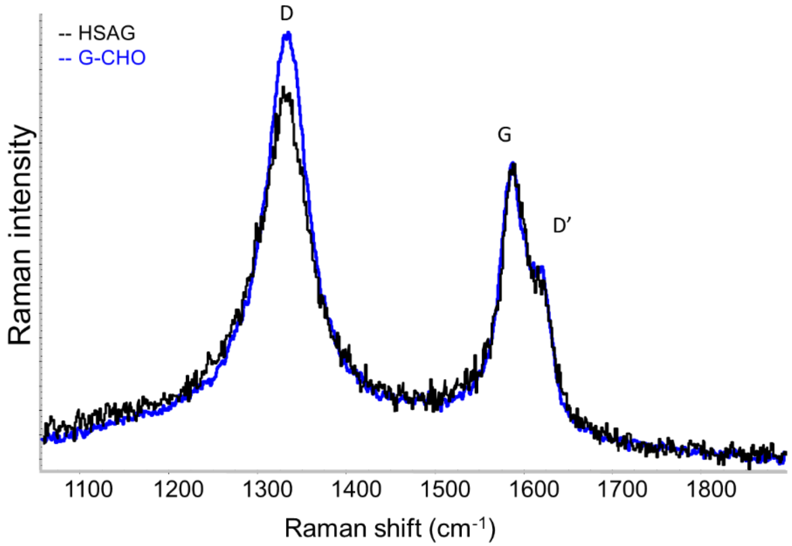
- G-CHO presents charachteristic peaks of aldehydic functionalities

FT-IR spectra of HSAG (a), G-OH (b) and G-CHO (c)

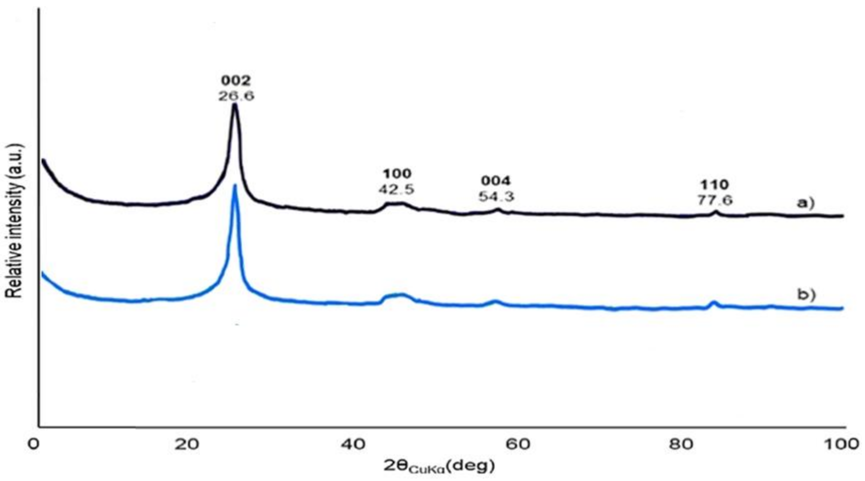
* reflection of the graphitic plane

Characterization of edge functionalized graphene layers

Raman spectra of HSAG and G-CHO



WAXD of HSAG (a) and G-CHO (b)

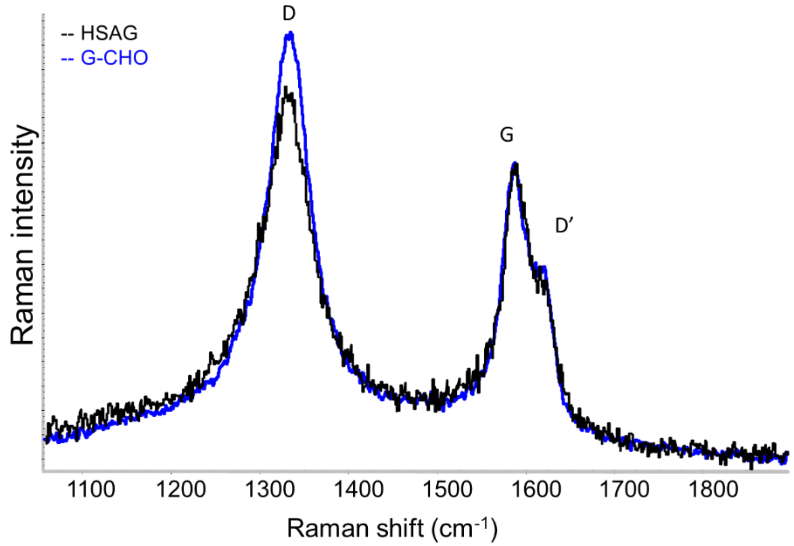


- no appreciable Raman component between D and G peaks
- enhancement of D peak is in line with the introduction of a further functional groups

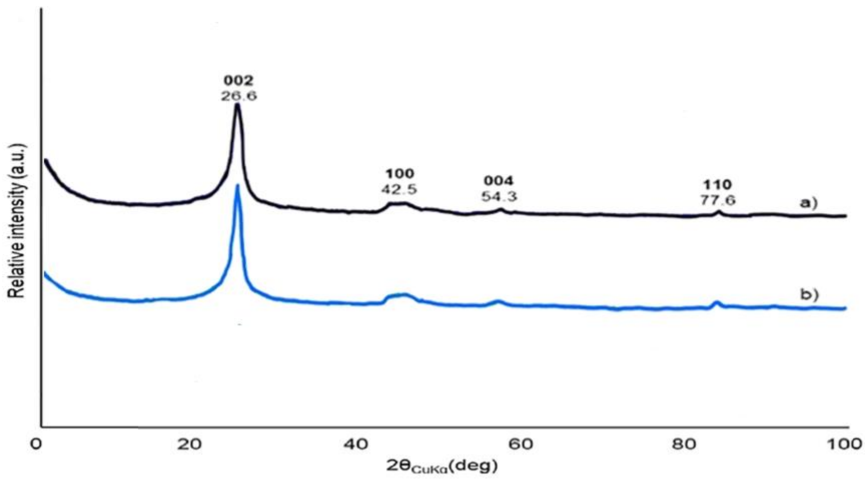
- HSAG and G-CHO present the same profile and Miller indexes
- In plane order is not substantially altered passing from HSAG to G-CHO

Characterization of edge functionalized graphene layers

Raman spectra of HSAG and G-CHO

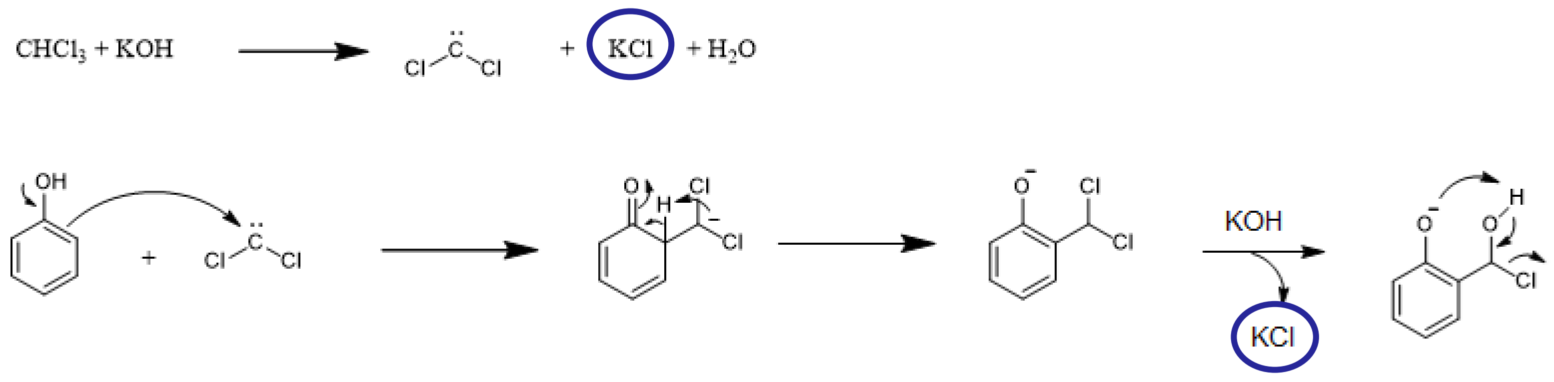


WAXD of HSAG (a) and G-CHO (b)

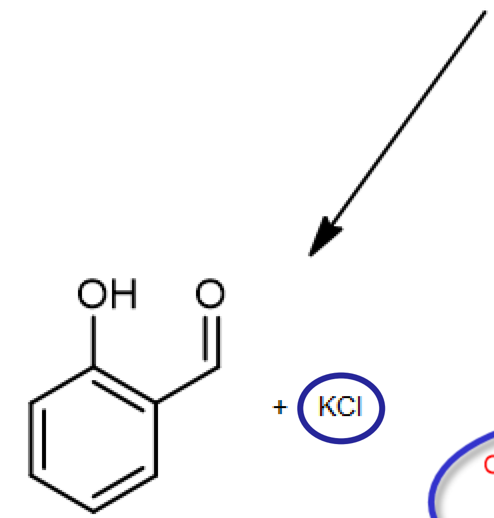


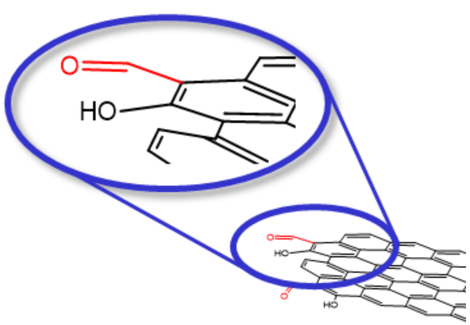
Reimer-Tiemann reaction
do not alter significantly the bulk structure of graphene layers

Mechanistic pathway: the Reimer-Tiemann reaction



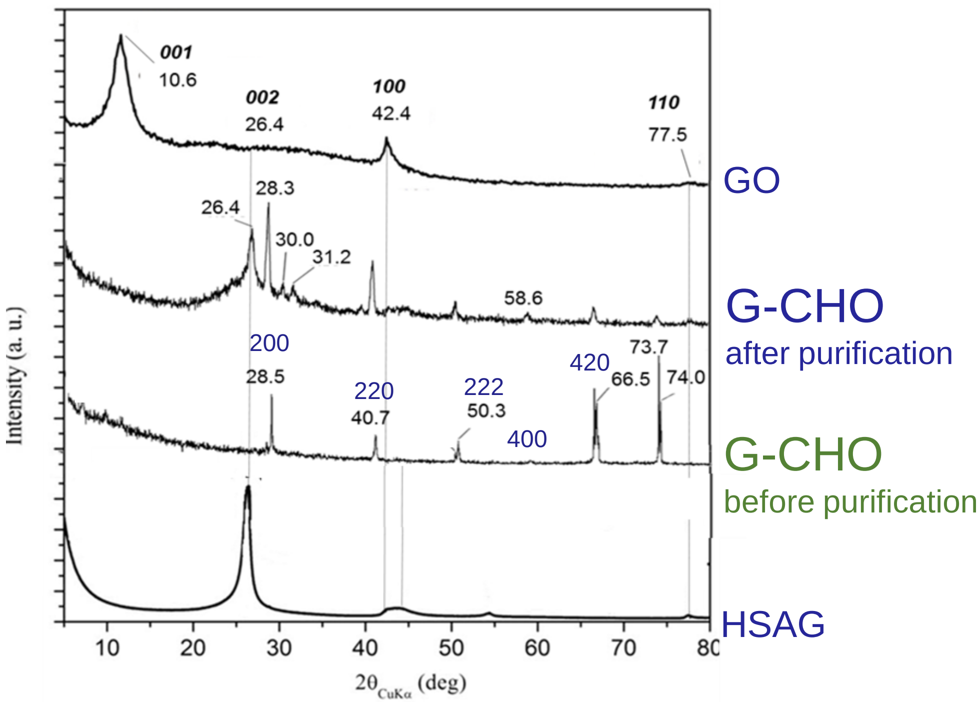
- each –OH mol leads to the formation of 1 mol of –CHO and 3 mol of KCl
- KCl is the only by-product of reaction

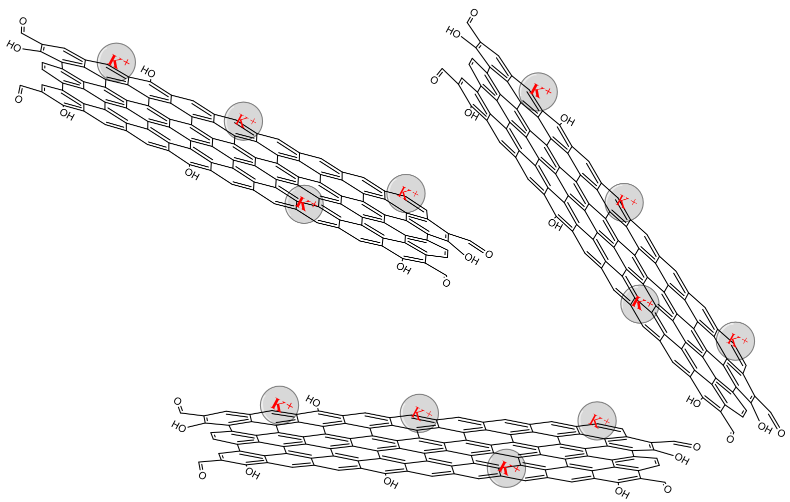




Mechanistic pathway: the Reimer-Tiemann reaction

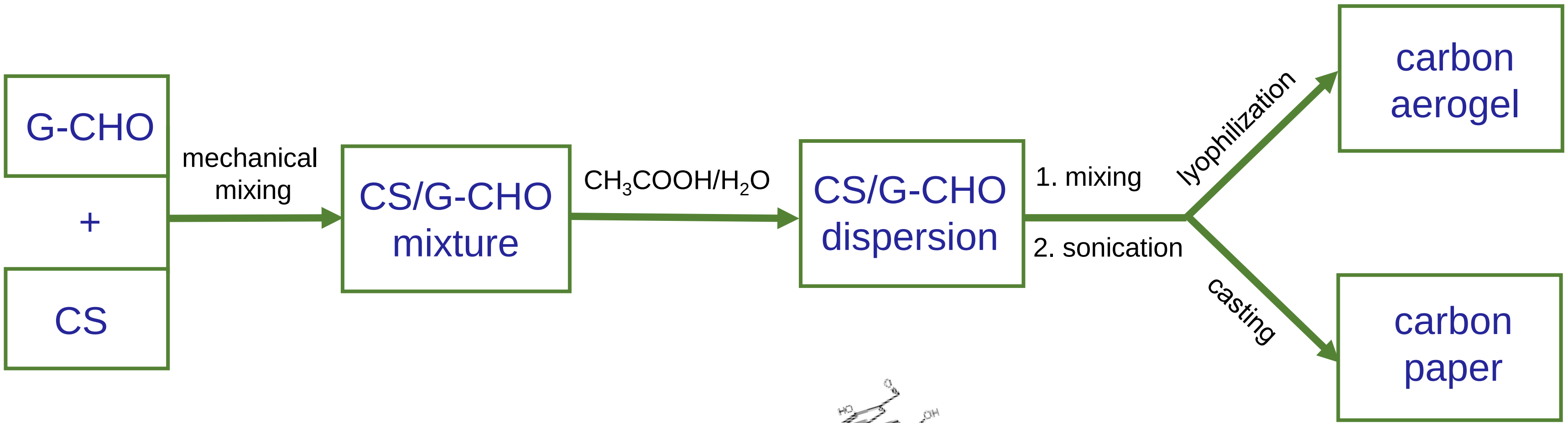
WAXD patterns

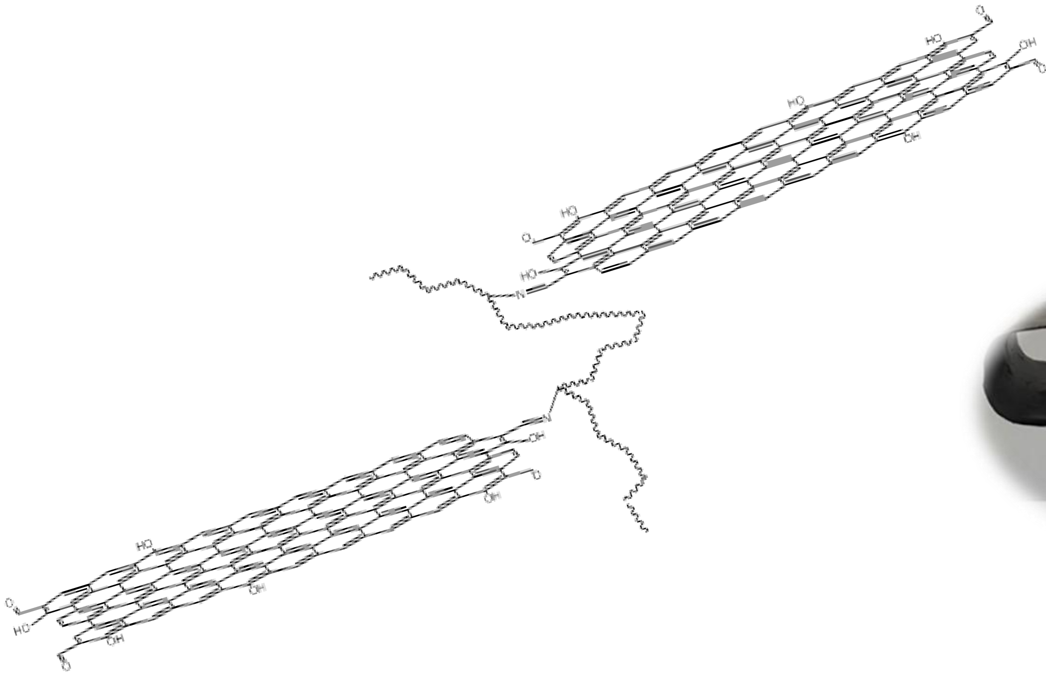


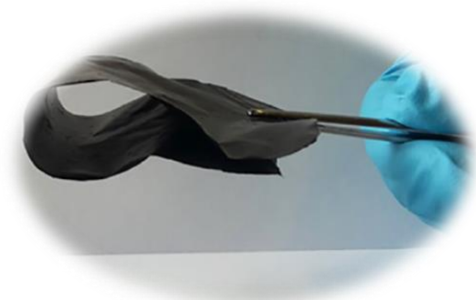


KCl
has the ability to interact
with graphene layers!

Simple preparation of CS/G-CHO nanocomposites



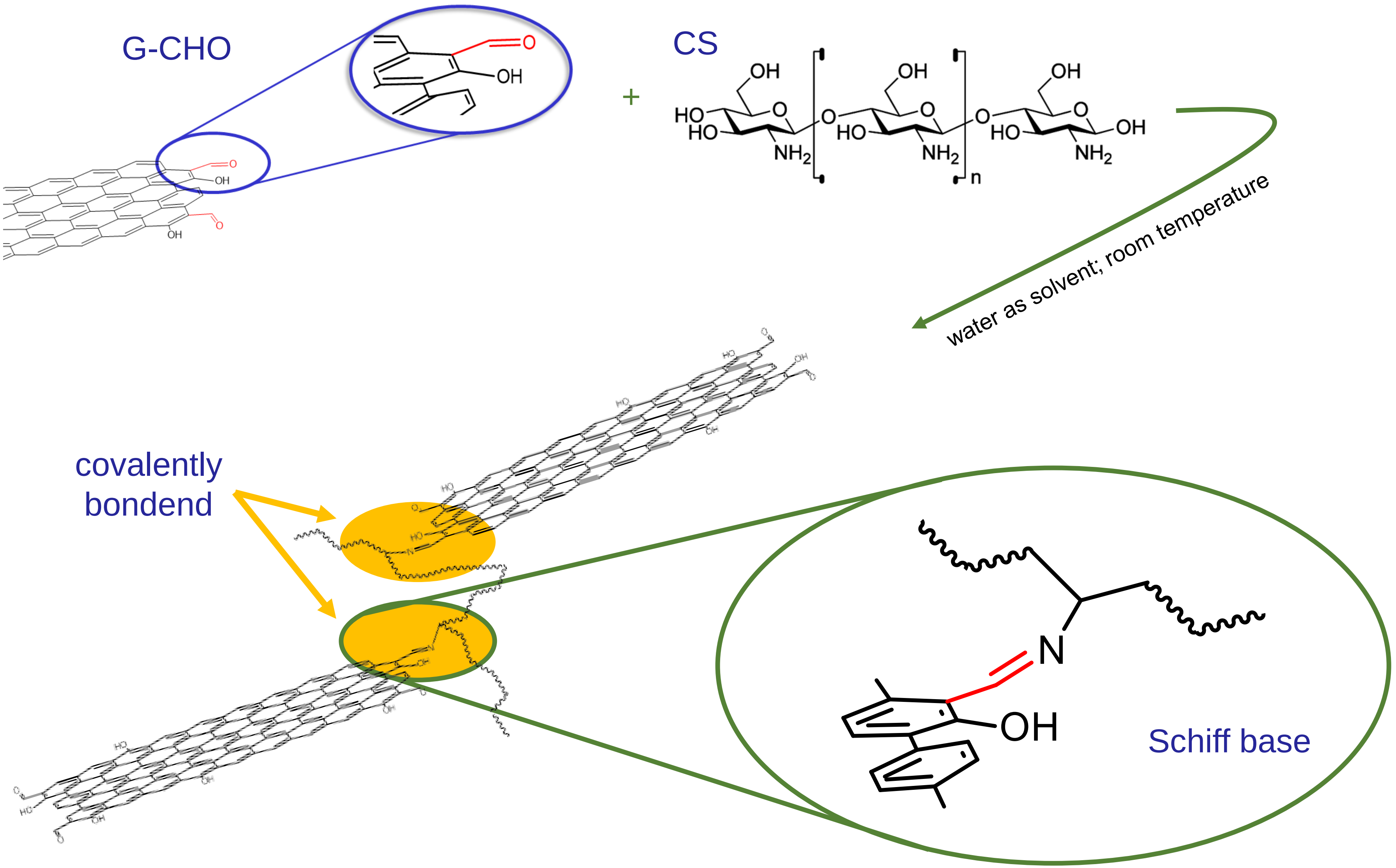




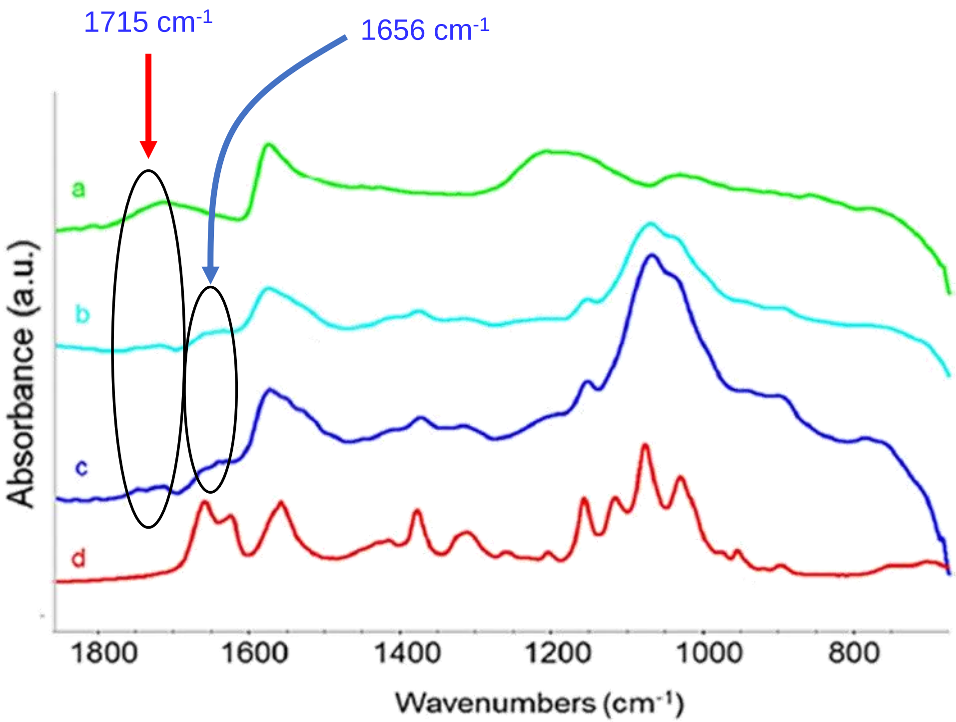
carbon paper

carbon aerogel

CS/G-CHO – composite materials

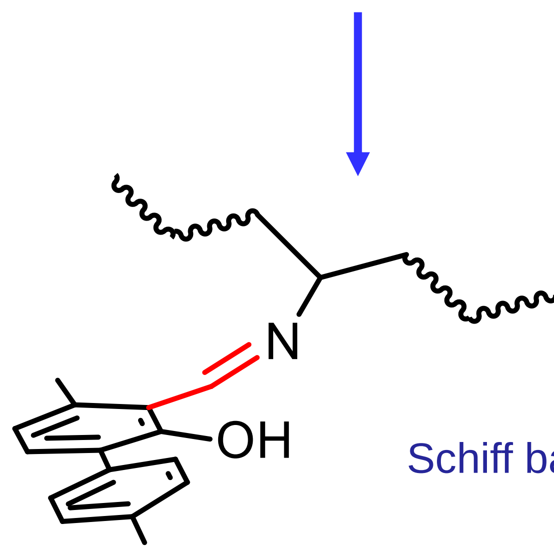


CS/G-CHO – composite materials



FT-IR spectra of G-CHO (a), CS/G-CHO paper (b), CS/G-CHO aerogel (c) and chitosan (d)

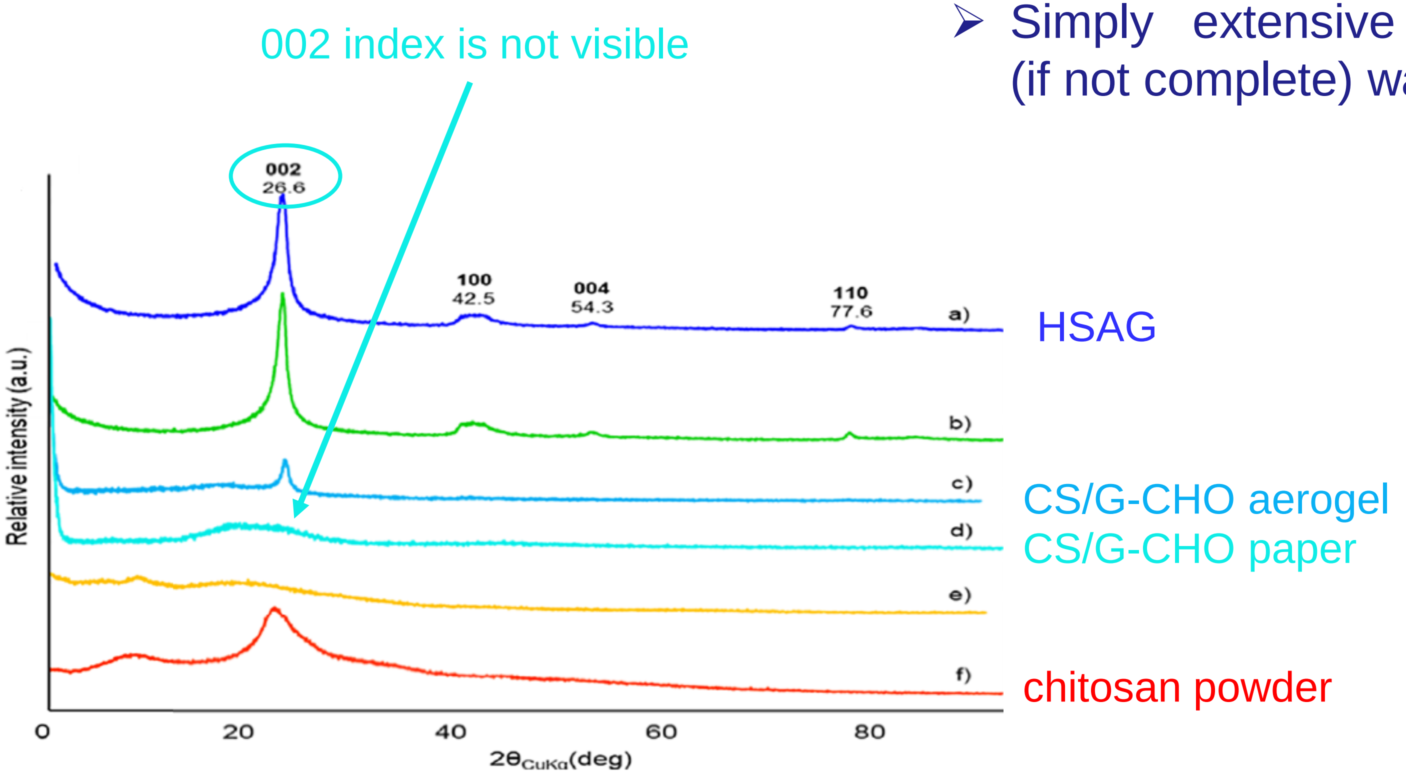
- 1715 cm^{-1} → reduction of band intensity (-C=O stretching vibration)
- 1656 cm^{-1} → iminic group stretching vibration



Schiff base

CS/G-CHO – composite materials

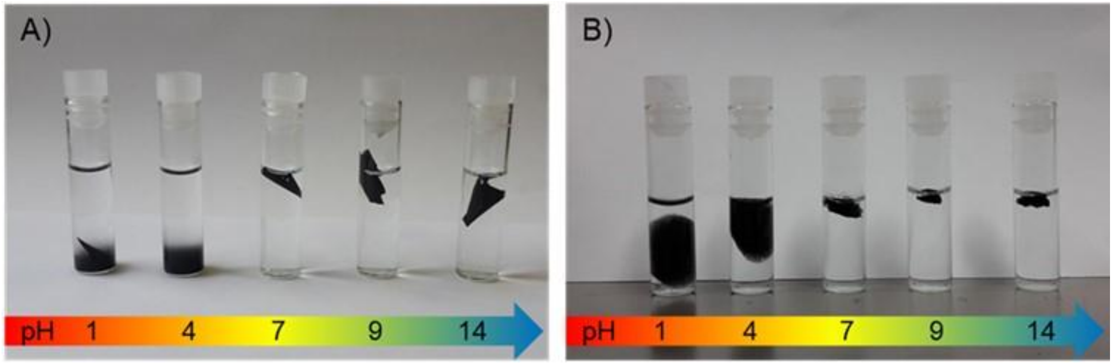
➢ Simply extensive exfoliation (if not complete) was obtained



WAXD of HSAG (a), G-CHO (b), CS/G-CHO aerogel (c), CS/G-CHO paper (d), CS film in acetic acid (e) and chitosan powder (f)

CS/G-CHO – composite materials

pH stability of carbon parer (A) and carbon aerogel (B)



➢ Both paper and aerogel show stability at pH from 7 to 14

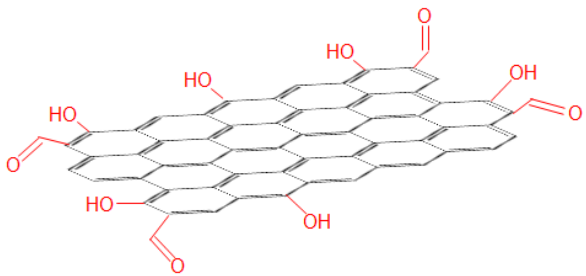
DC conductivity of carbon paper with different G-COH content

CS/G-CHO ratio[a]	σ (S/m)
Chitosan	$1E^{-8}$
1:1	0.013
1:2	0.10
2:1	0.012

[a]Content respect to 100 mg of chitosan.

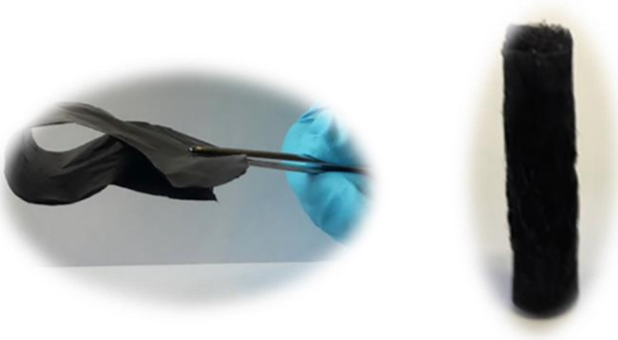
➢ Good electrical conductivity for many electrical applications

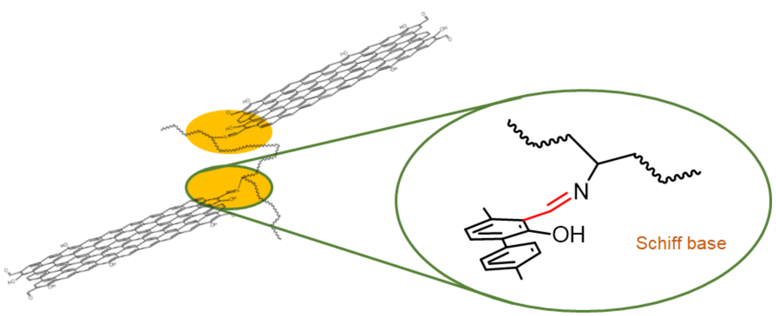
Conclusion



- Edge functionalized graphene layers with aldehydic groups **(G-CHO)** were succesful achieved *via* Reimer-Tiemann reaction

- Innovative nanobiocomposite based on chitosan and graphene layers **(G-CHO/CS)** were prepared by simply mixing G-CHO and CS





- A covalent network using graphene layers with edge aldehydic functional groups (G-CHO) and chitosan (C) was obtained

Thanks for your attention!

*ISM*aterials group
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