Playing with chemistry on sp^2 carbon allotropes: domino reactions for tailor made functionalization

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ISCaMaP

Innovative Sustainable Chemistry and Materials and Proteomics Group

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

Playing with chemistry on sp^2 carbon allotropes

Carbon fillers from a layer of sp^2-bonded carbon atoms

graphene

stacked

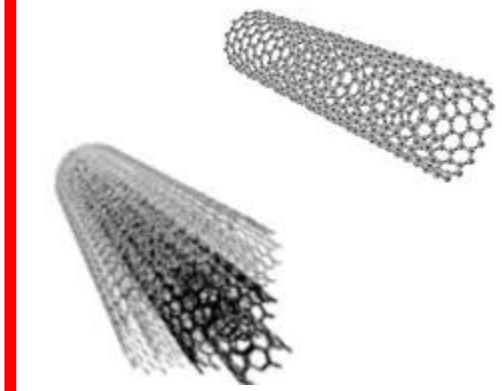
wrapped

stacked graphene layers

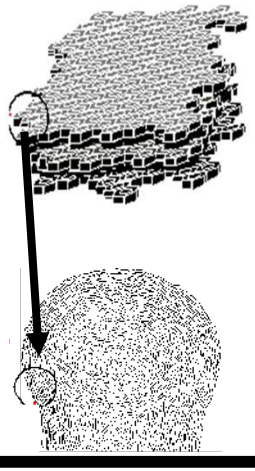
randomly arranged

with different shape anisotropy

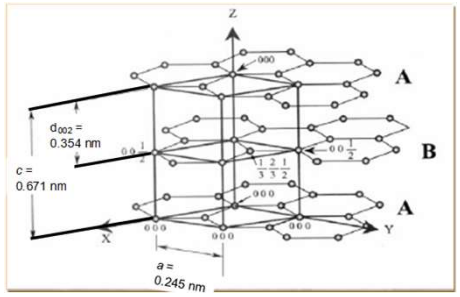
CNT



carbon black

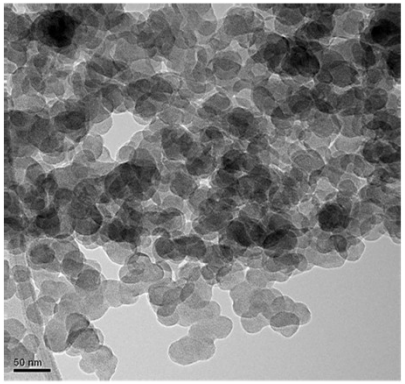


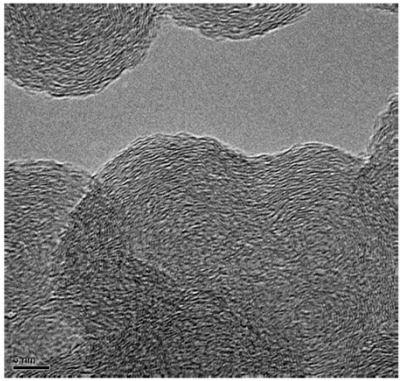
graphite,
nano-graphite,
graphene



Carbon allotropes (CA)

CB





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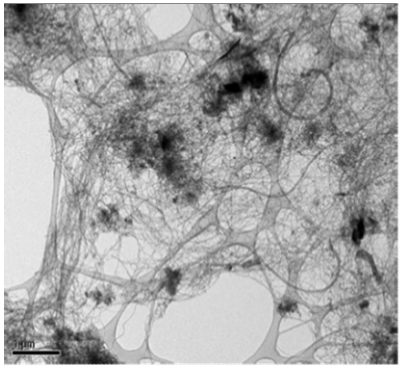
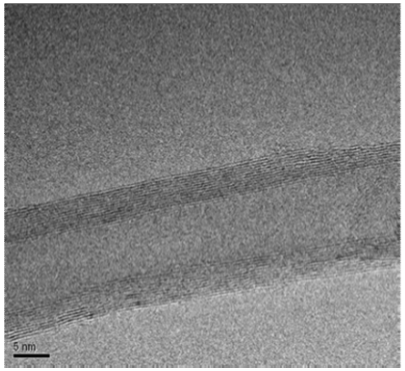
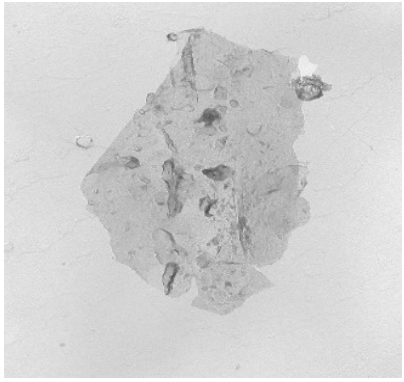
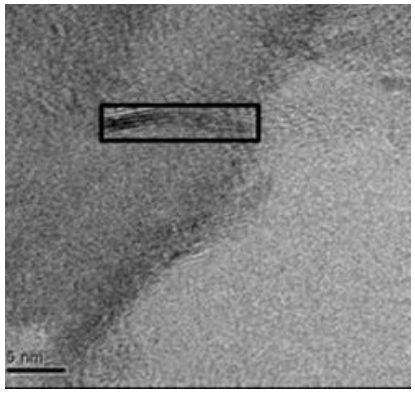




FEW LAYERS GRAPHENE





Objectives of the research activity

- To functionalize various carbon allotropes
  with a sustainable, facile, versatile method,
  preserving the sp^2 hybridization

- To reduce the synthetic footprint in carbon allotropes functionalization

- To prepare tailor made materials,
  in view of the final application

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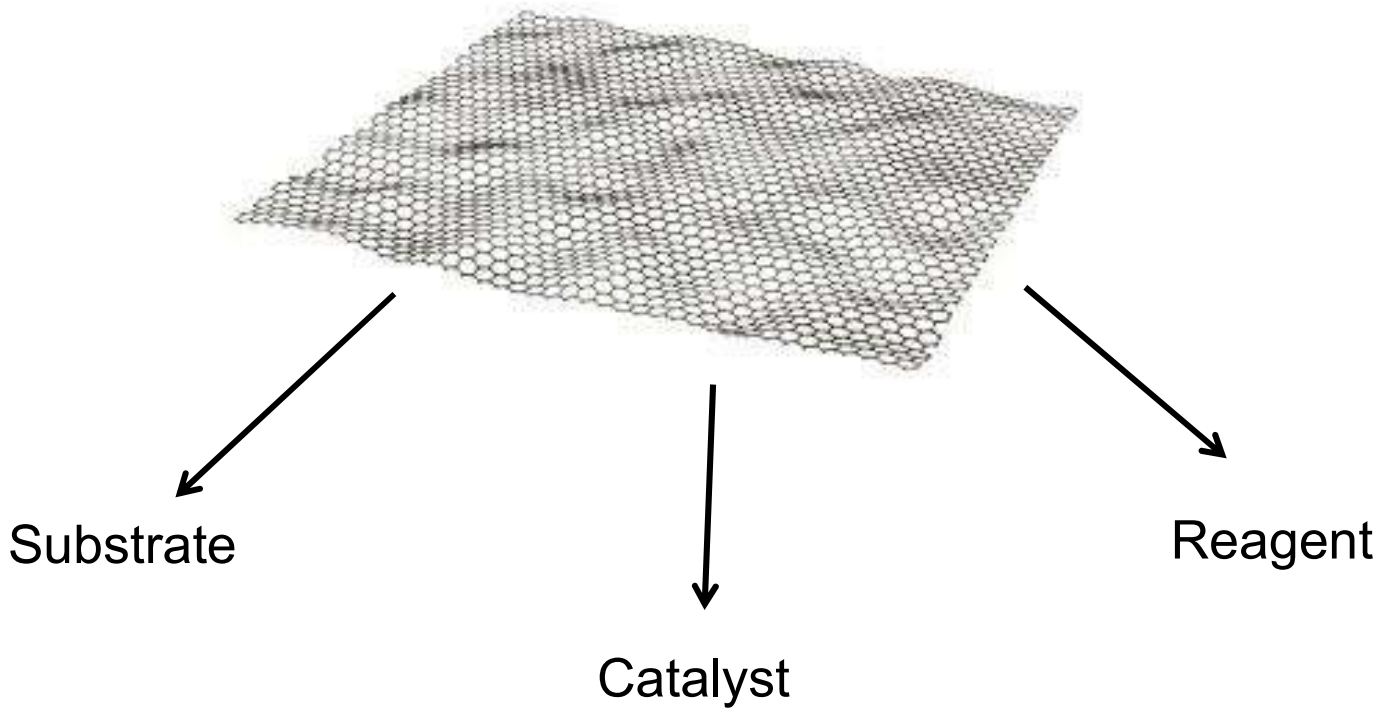
Playing with chemistry on sp^2 carbon allotropes

Manifold role for the carbon allotrope



Playing with chemistry on sp^2 carbon allotropes

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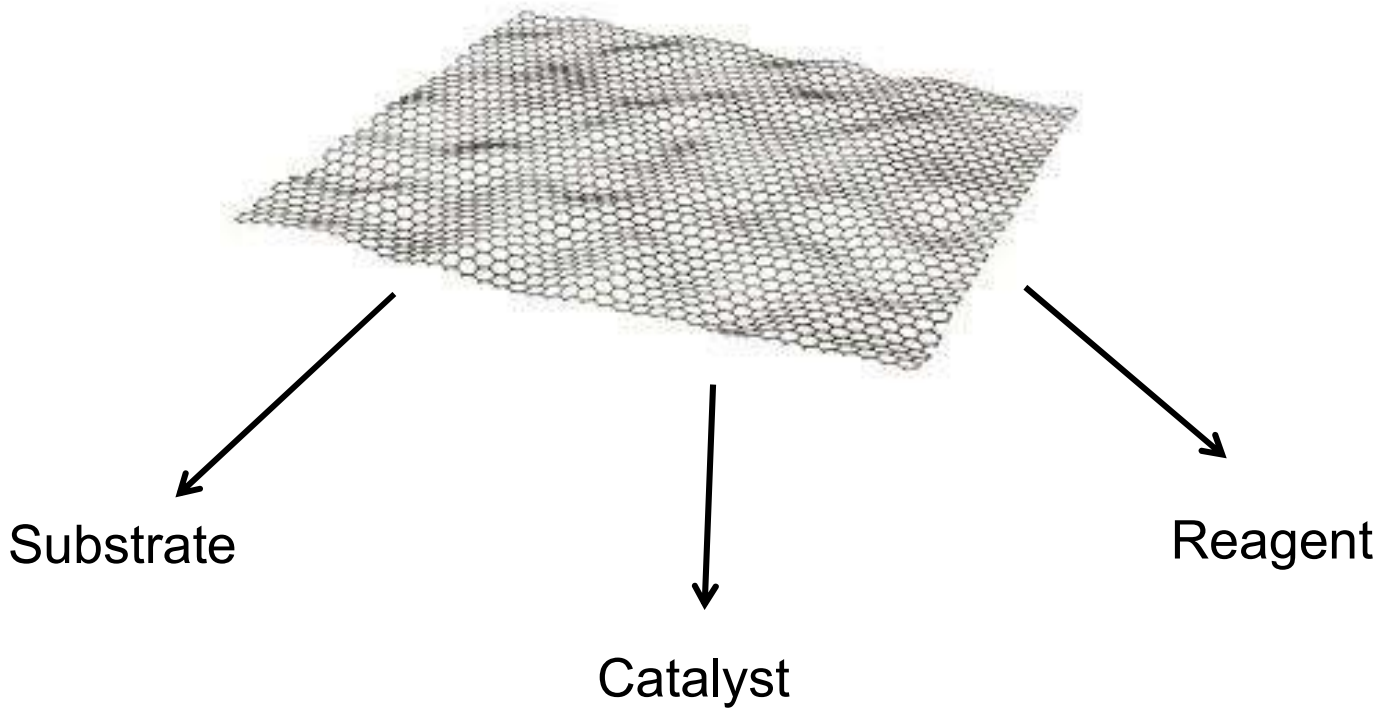


Investigation of mechanisms

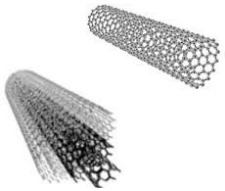
Playing with chemistry on sp^2 carbon allotropes

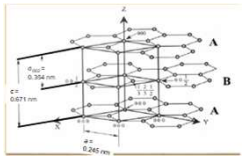
Technical problems

- Difficult analytical investigations
- Reactivity or simple absorption of chemicals?
- Graphite: intercalation?

Facile functionalization

sp^2 carbon allotropes (CA)

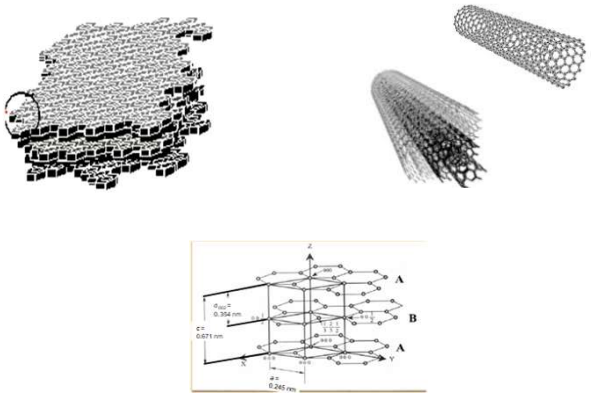




Galimberti, M., Barbera, V., Guerra, S., Conzatti, L., Castiglioni, C., Brambilla, L., A. Serafini, RSC Advances, 5(99), (2015) 81142-81152
Barbera, V., Porta, A., Brambilla, L., Guerra, S., Serafini, A., Valerio, M.A., Vitale, A., Galimberti, M. RSC Adv., 2016, 6, 87767-87777
V. Barbera, A. Bernardi, G. Torrisi, A. Porta, M. Galimberti, Elastomery, 2017, 21(4), 235-251

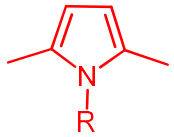
Facile functionalization

sp^2 carbon allotropes (CA)



+

- Pyrrole derivatives



- KOH

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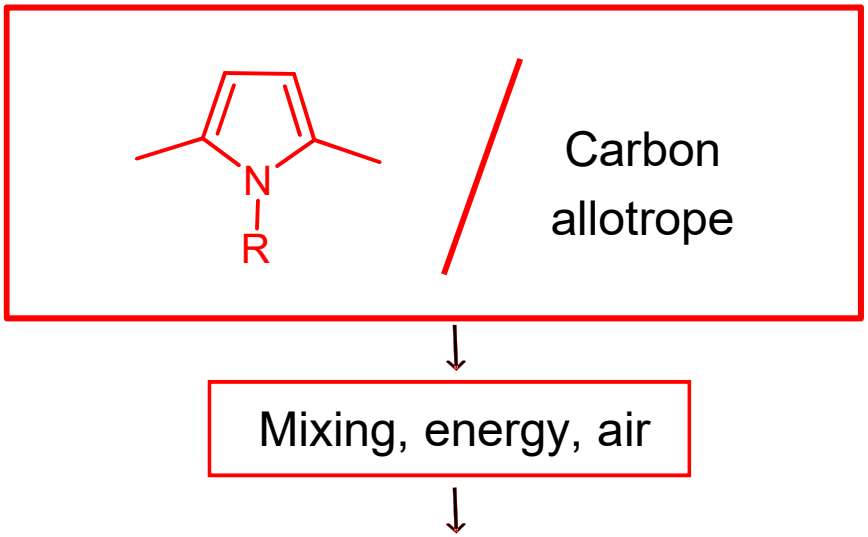
Functionalization of carbon materials

with pyrrole derivative

Facile functionalization of carbon materials



carbon allotrope

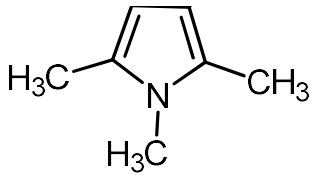
functional groups on surface

bulk structure substantially unaltered

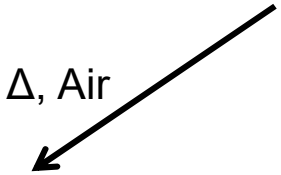
M. Galimberti, V. Barbera, R. Sebastiano, A. Citterio, G. Leonardi, A.M. Valerio. WO/2016/050887 A1 (2016)

Mechanism of the functionalization reaction

Investigation with a model compound



1,2,5-Trimethylpyrrole
(TMP)



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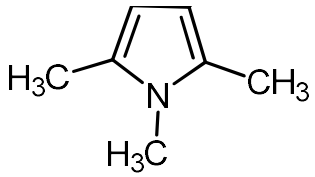

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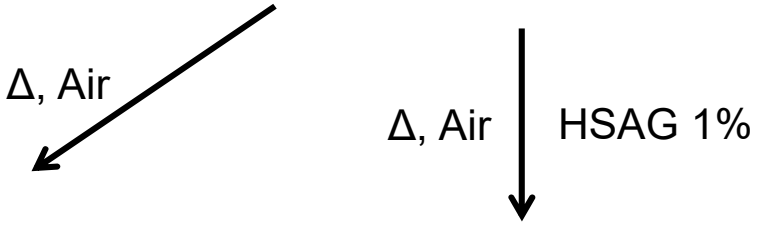

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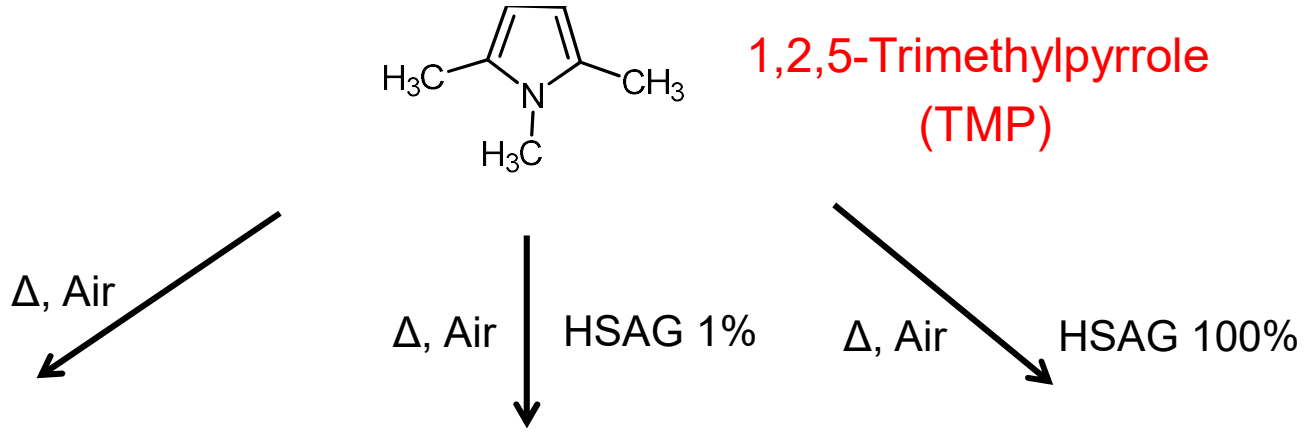

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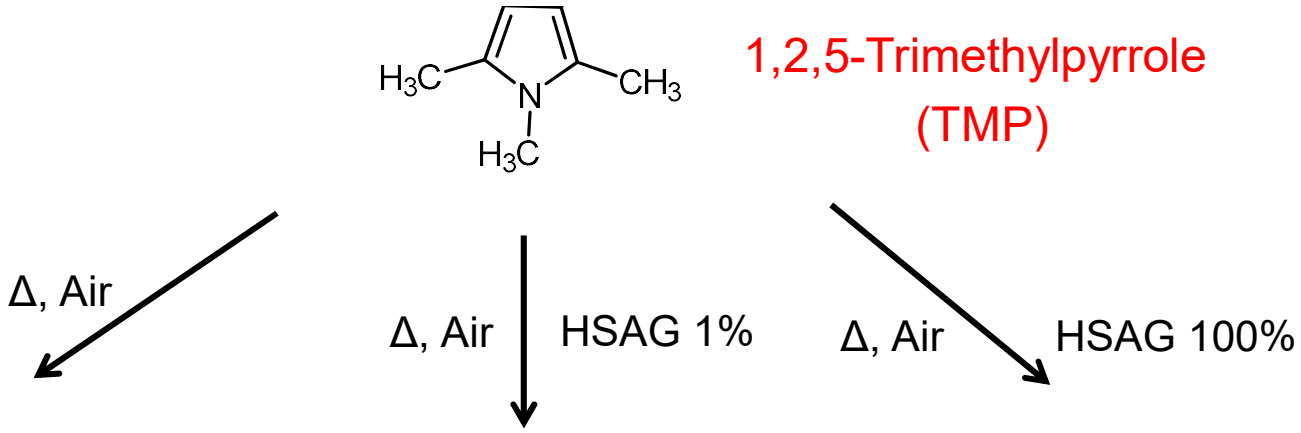
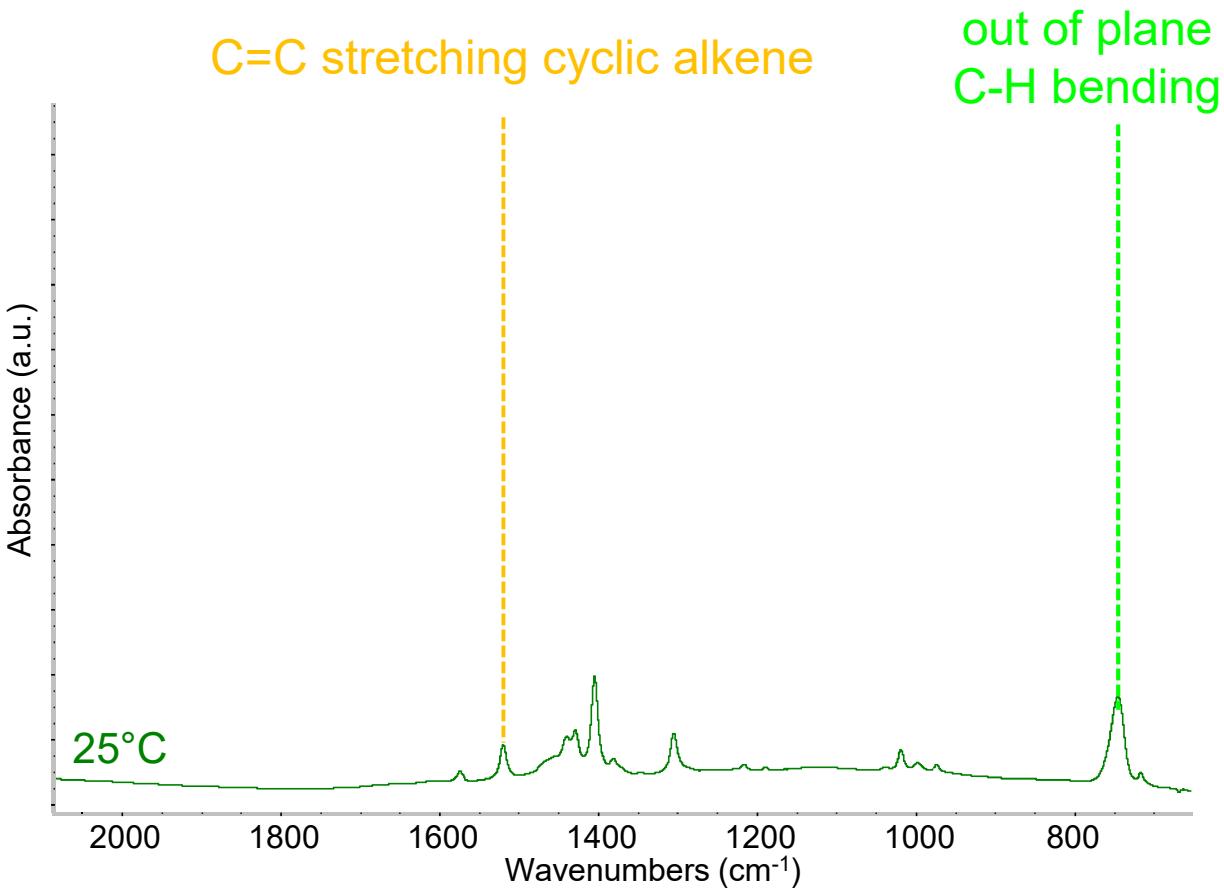
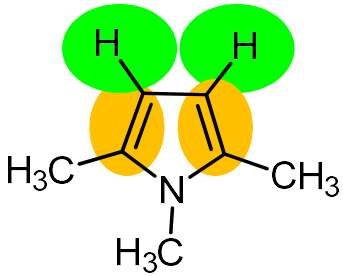


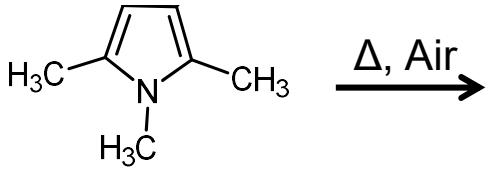
- Analysis of: liquids, HSAG/TMP adducts
- FT-IR and ^{1}H-NMR spectroscopies
- FT-IR spectra generation with Density Functional Theory (DFT) quantum chemical modelling.

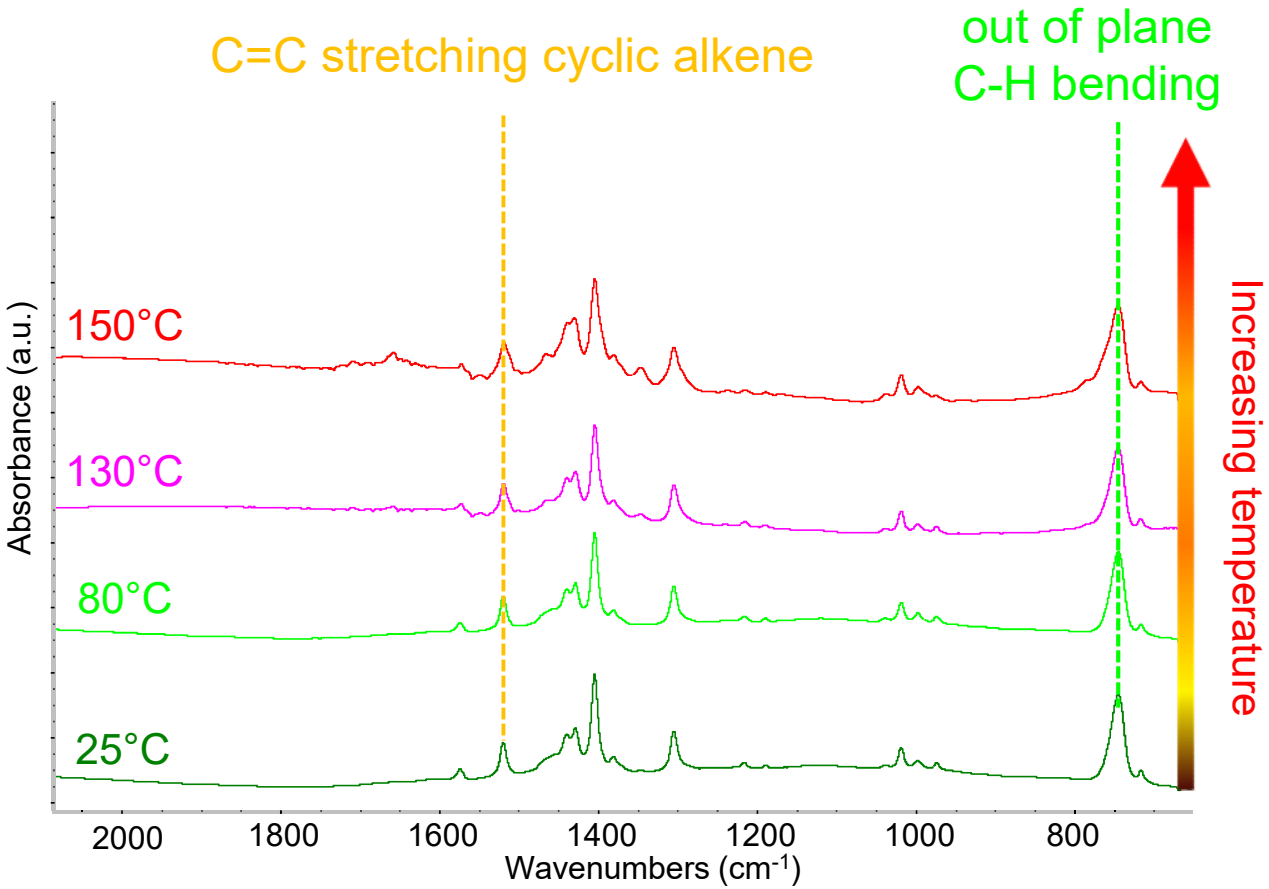
1,2,5-Trimethylpyrrole (TMP)

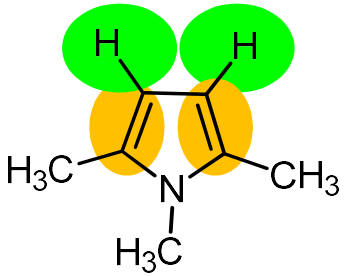




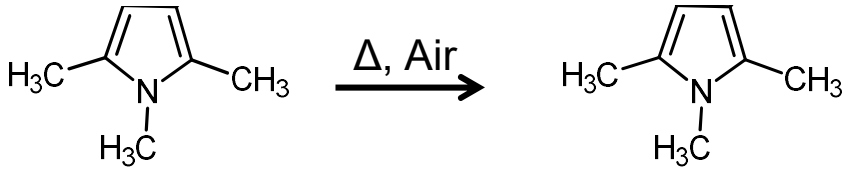
TMP + Air - From 25°C to 150°C

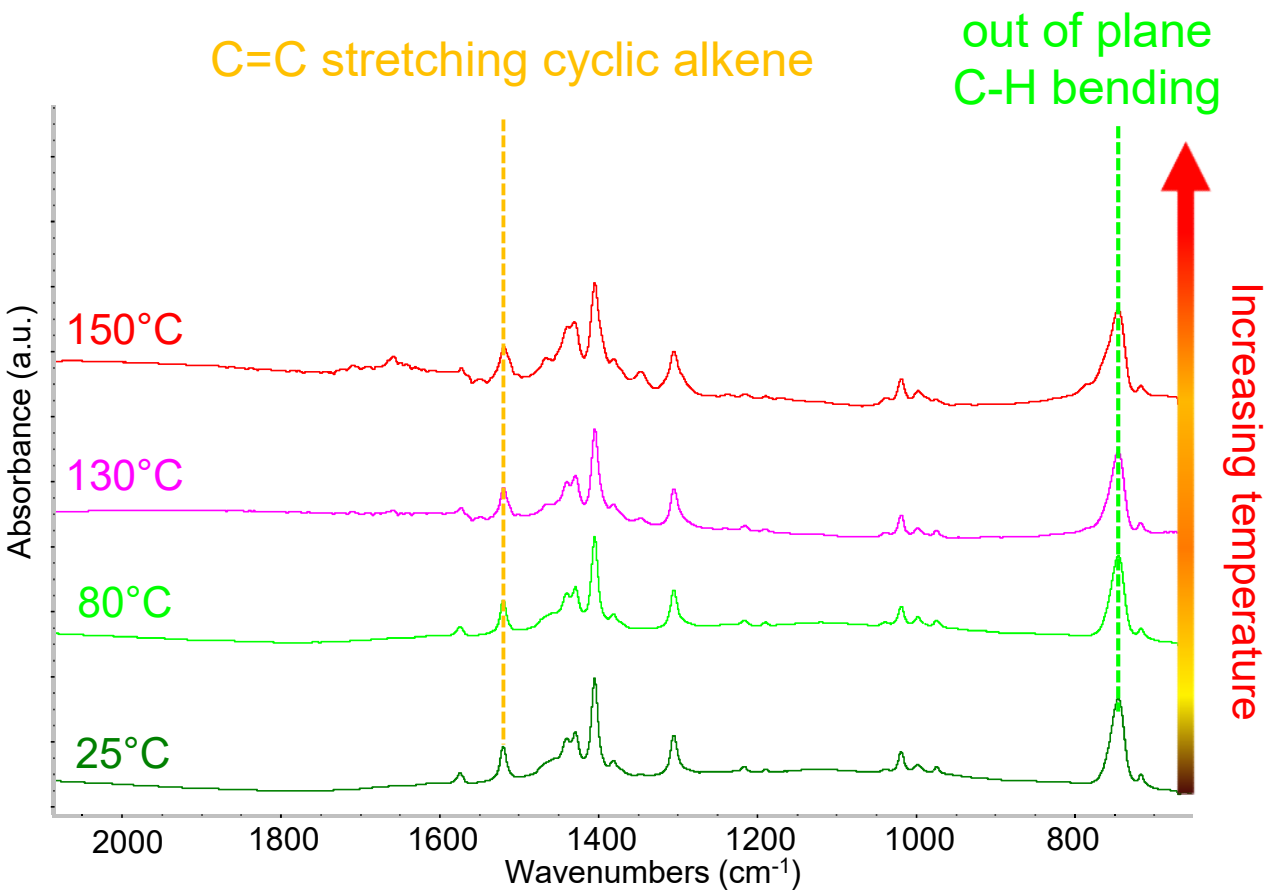


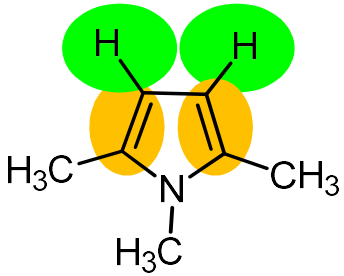




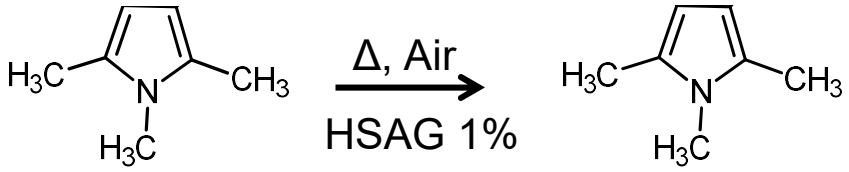
TMP + Air - From 25°C to 150°C

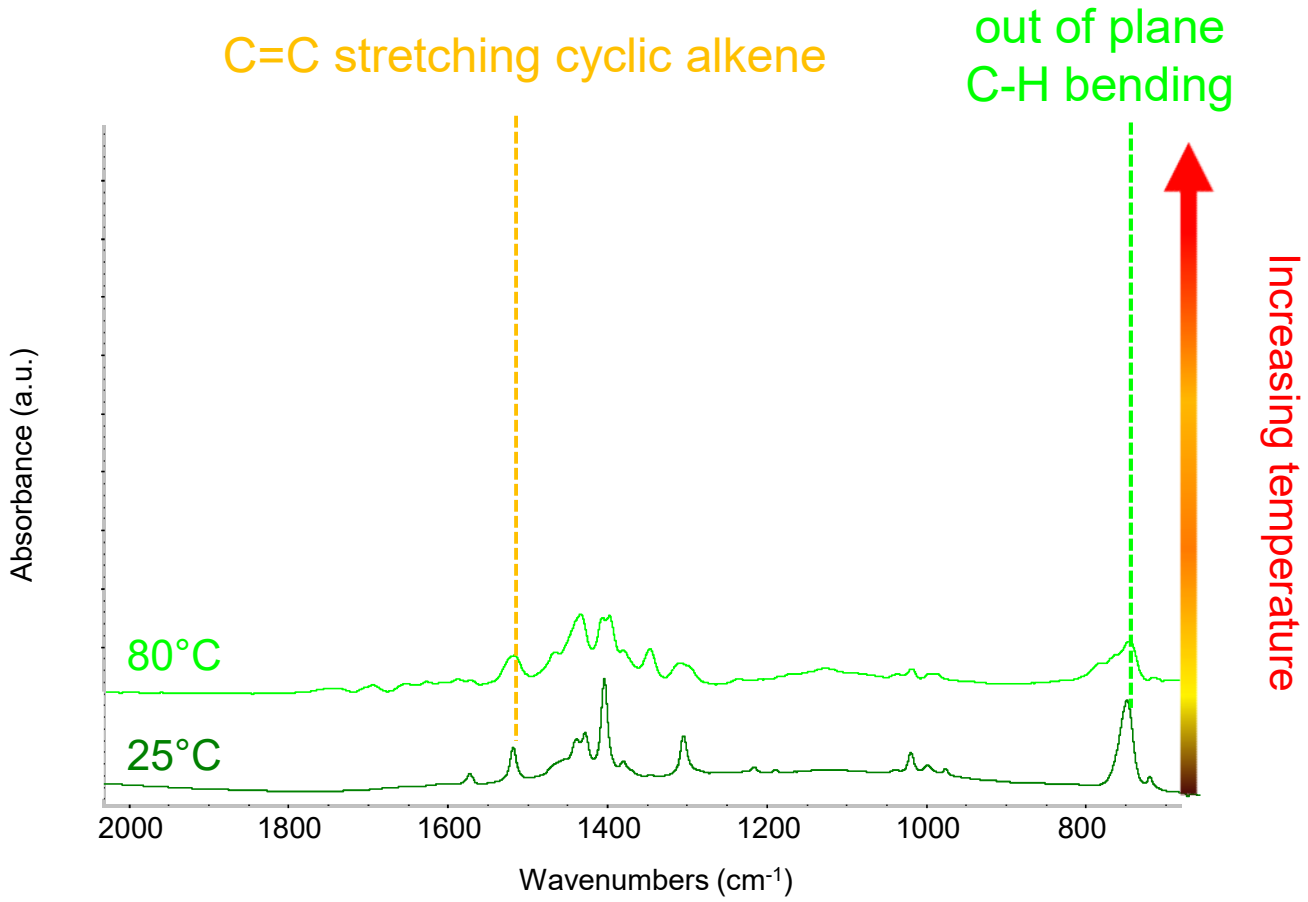


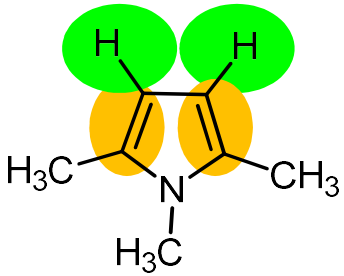




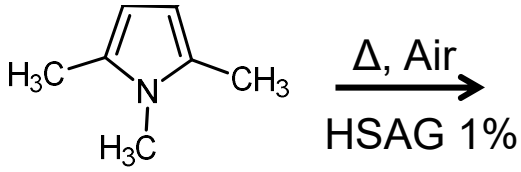
TMP + HSAG 1% / Air - From 25°C to 80°C





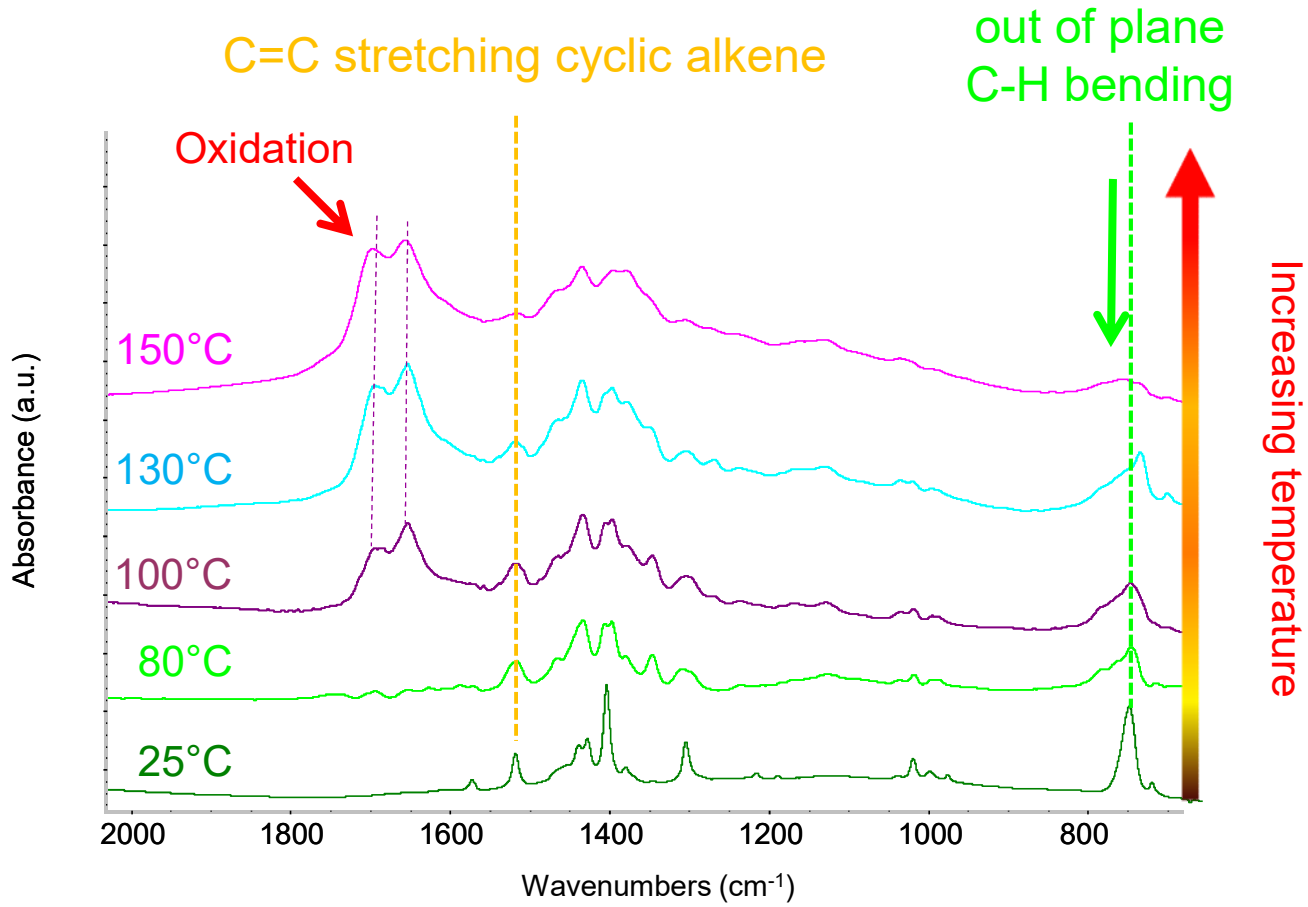


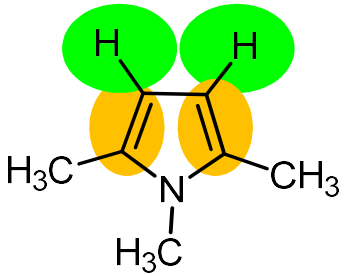
TMP + HSAG 1% - from 100°C to 150°C



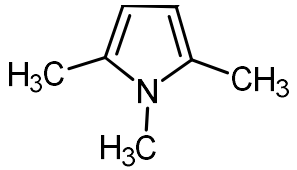
Δ, Air
HSAG 1%

Oxidation products



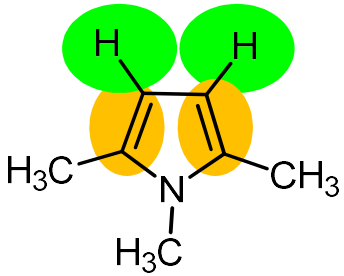


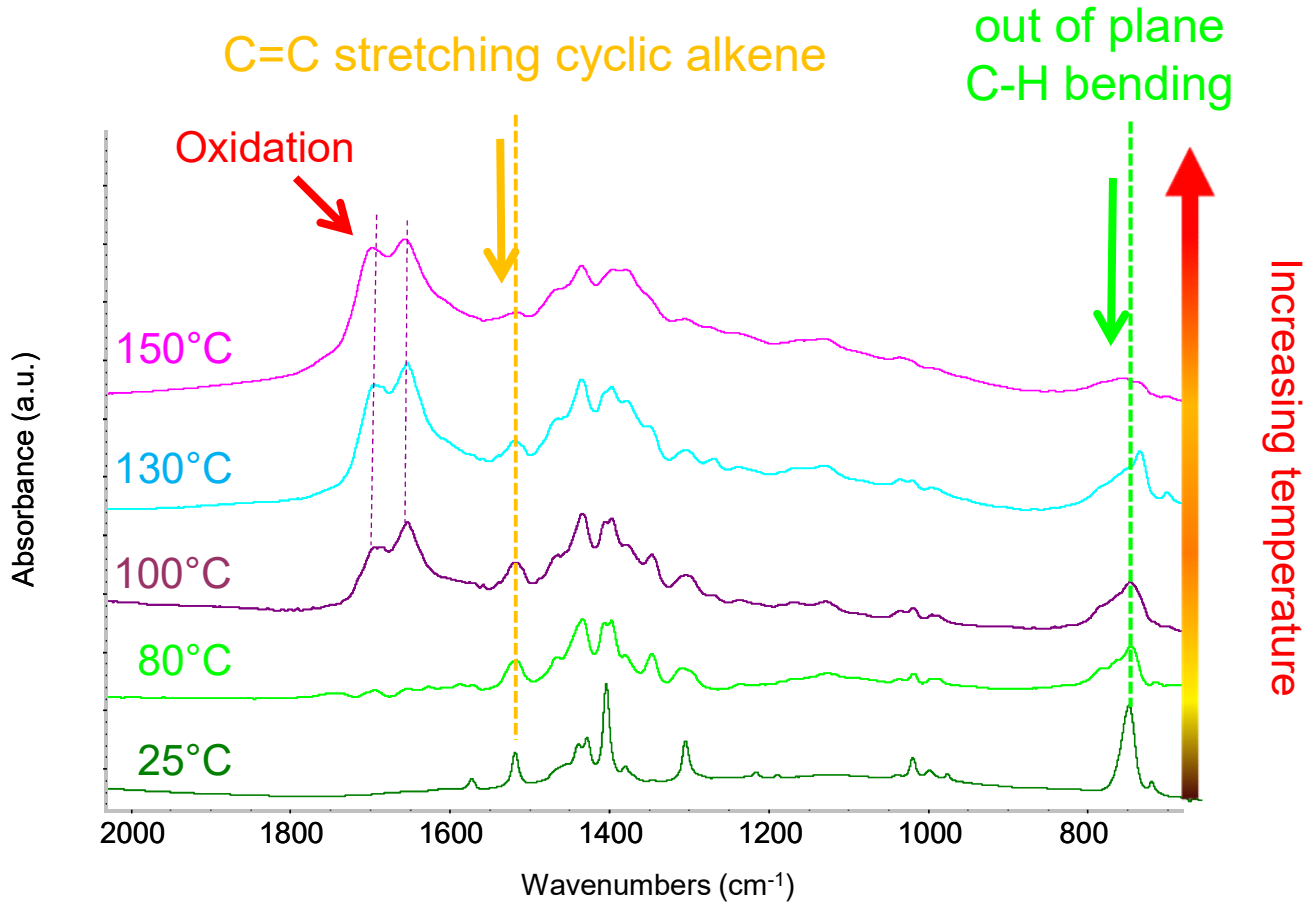
TMP + HSAG 1% - @ 150°C



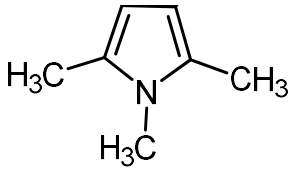
Δ, Air
HSAG 1%

Reaction products of intra-annular double bonds





TMP + HSAG 1/1 - from 25 to 150°C



1

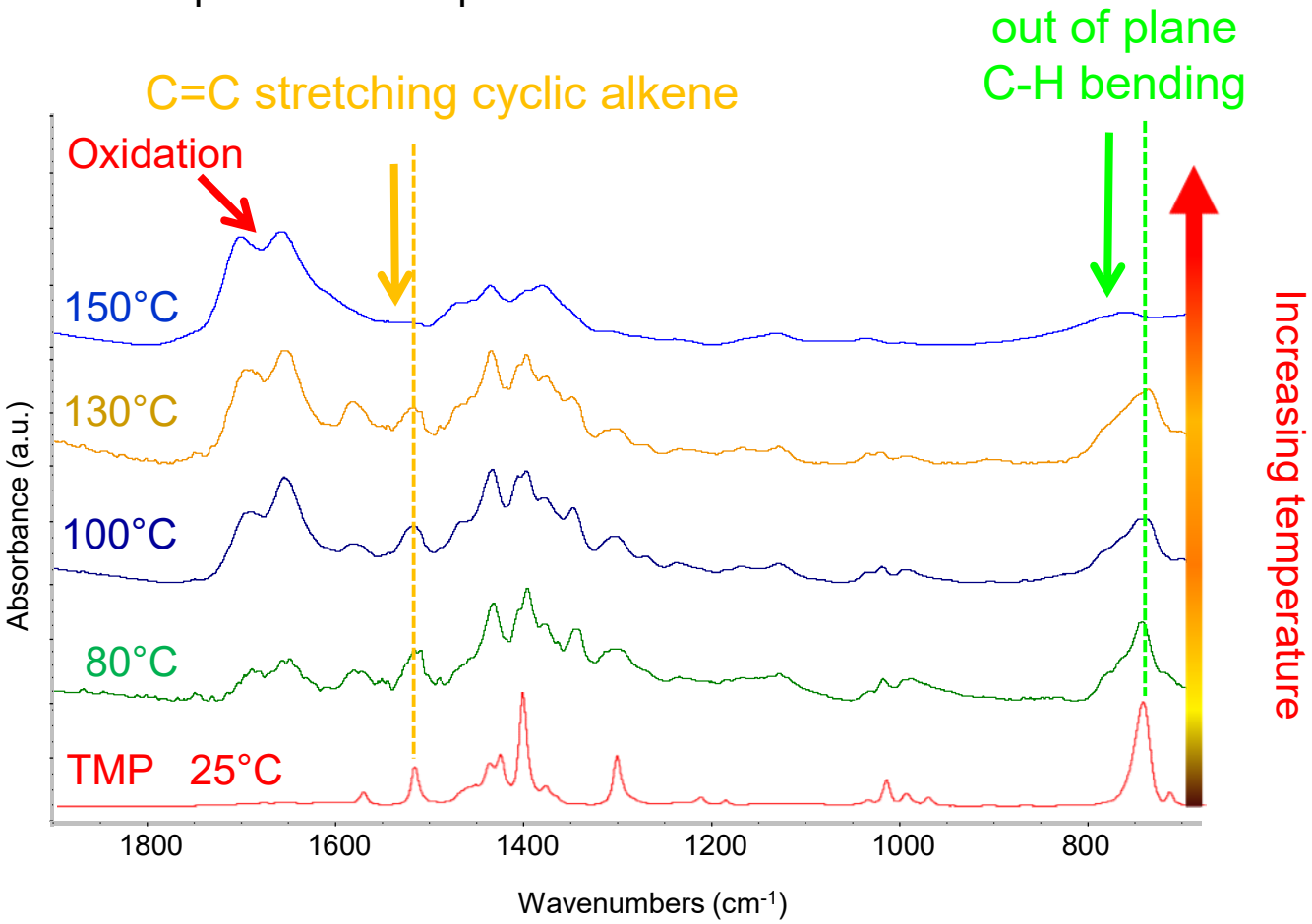
+ HSAG

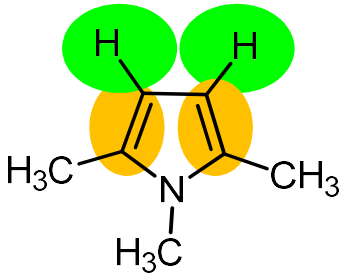
1

Δ, Air

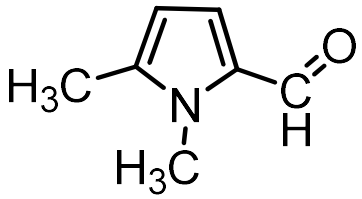
Oxidation products

Reaction products of intra-annular double bonds



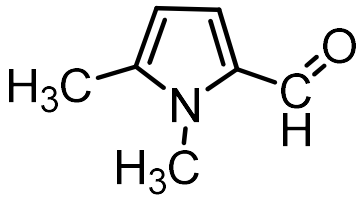


TMP oxidation product



1,5-dimethyl-1*H*-pyrrole-2-carbaldehyde

TMP oxidation product



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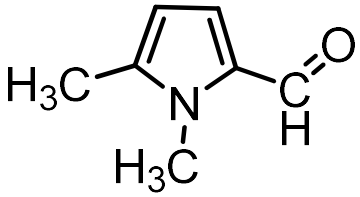

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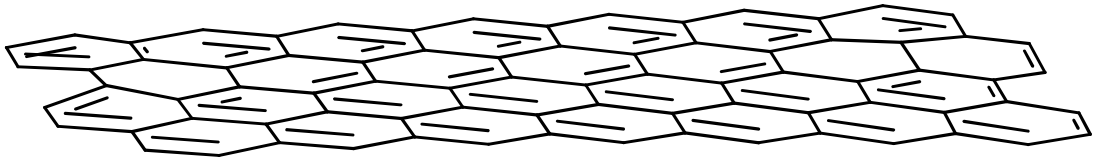
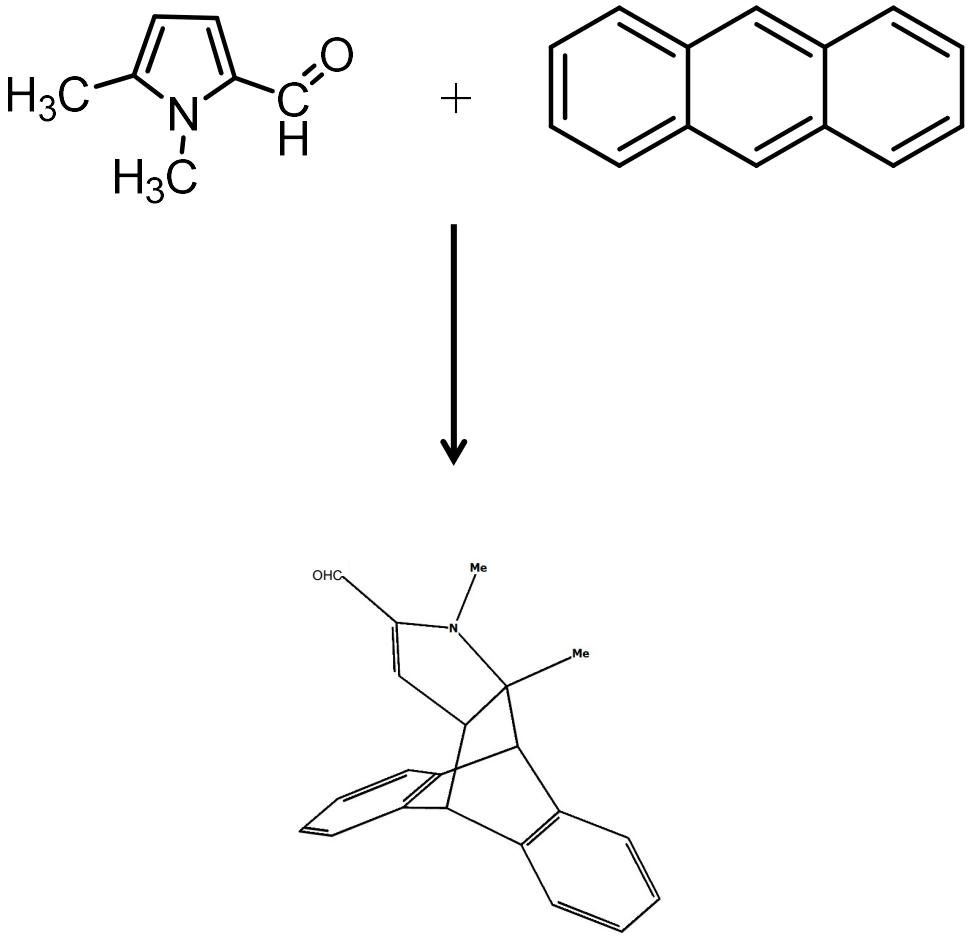


TMP oxidation product - Reaction with a model substrate



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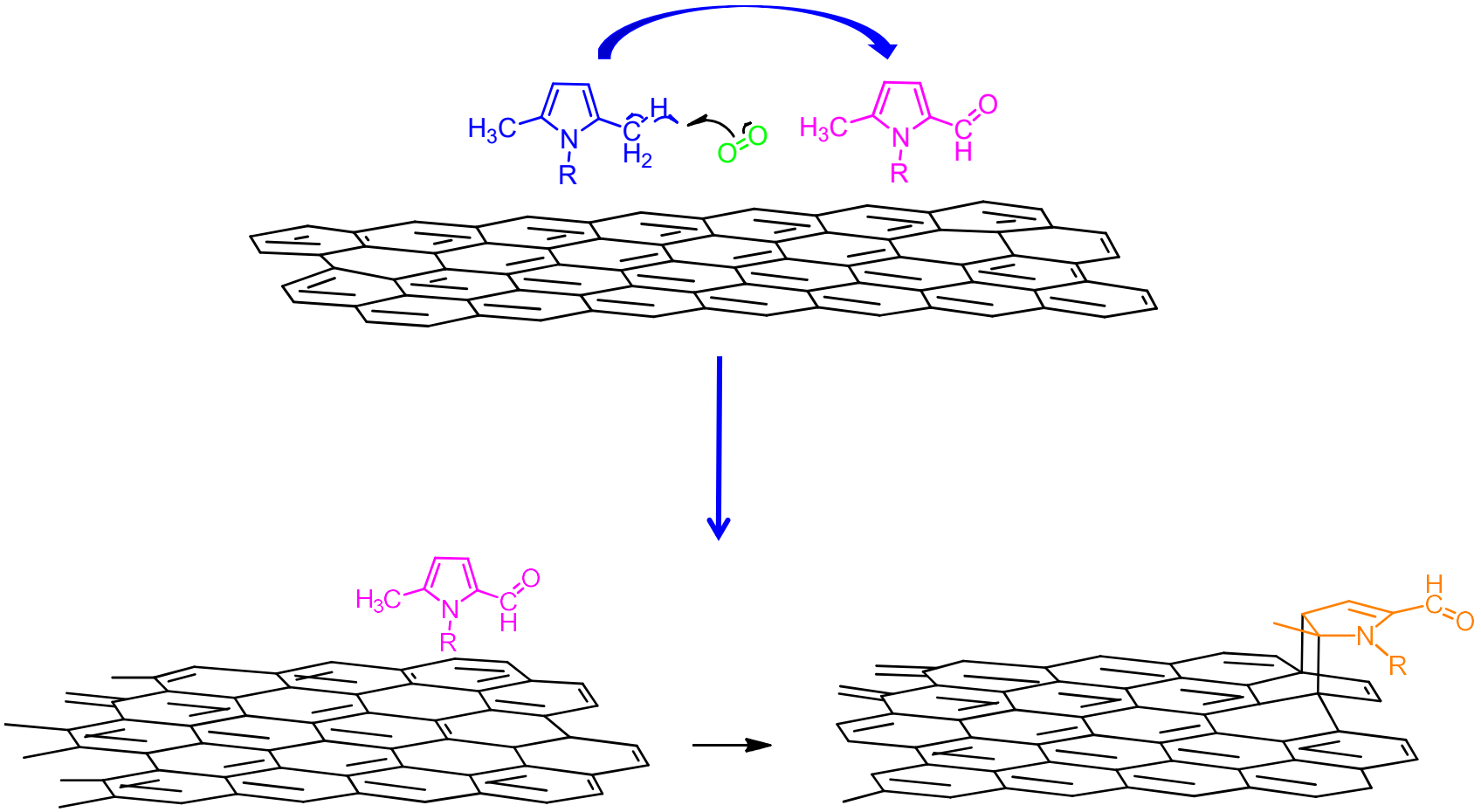
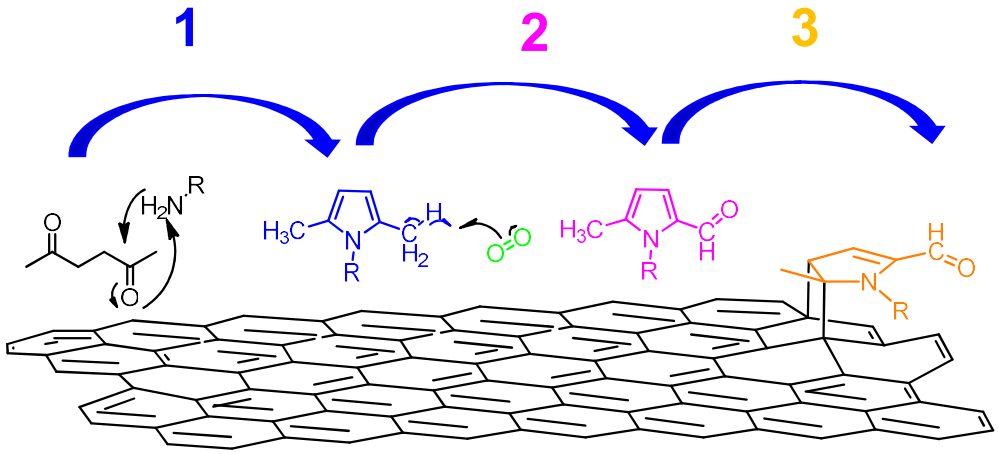


Facile functionalization of carbon materials

Hypothesis for the mechanism



Facile functionalization of carbon materials

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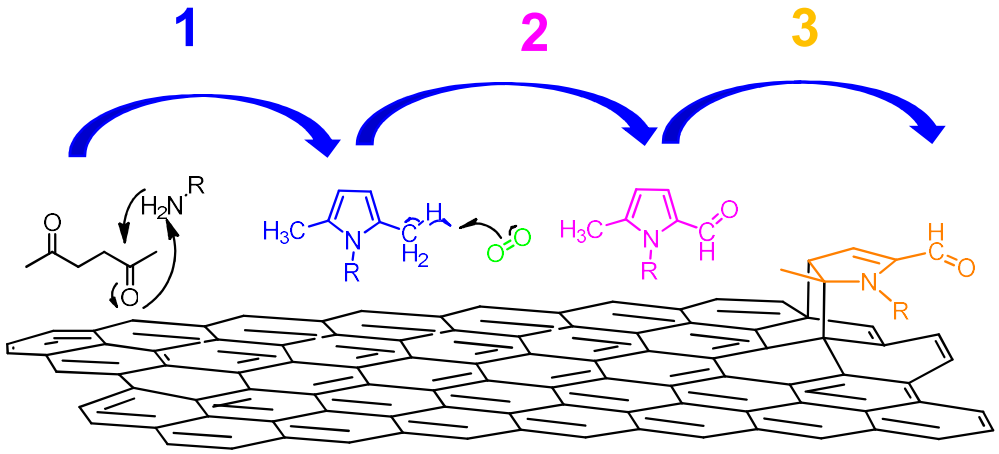
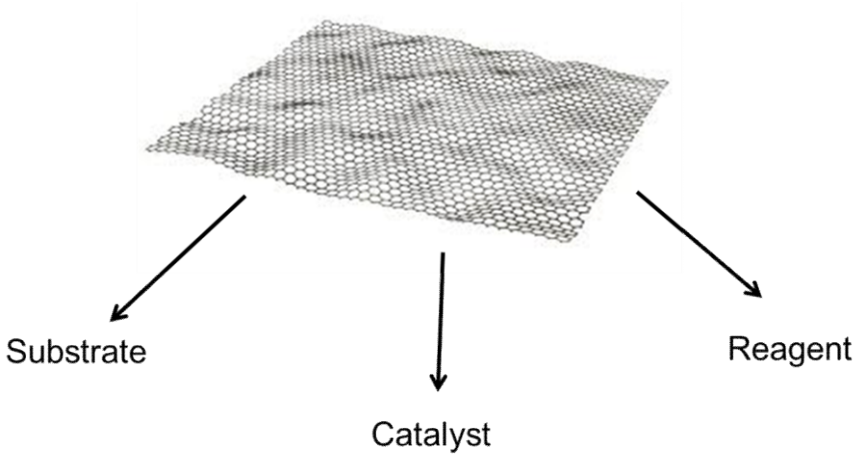
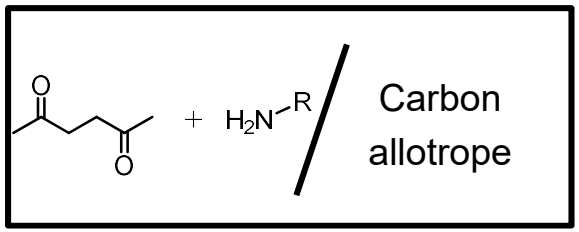




Facile functionalization of carbon materials

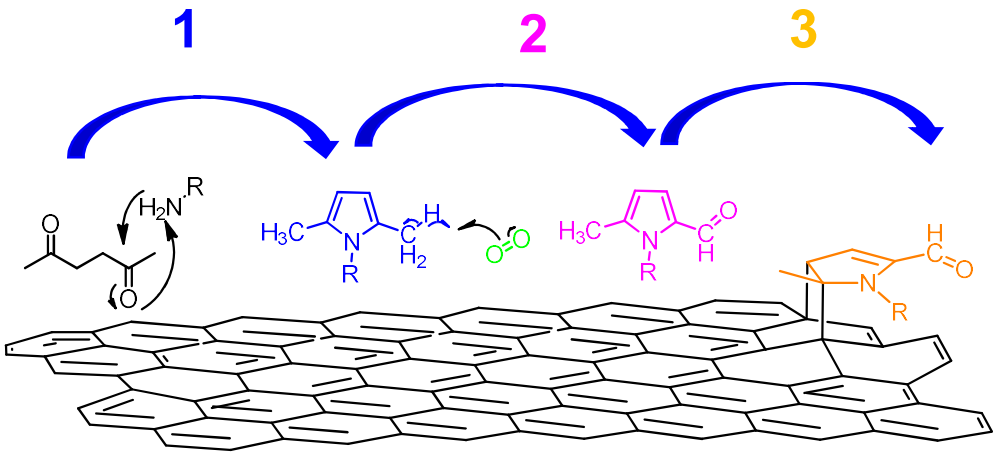
Hypothesis for the mechanism



Paal – Knorr Reaction

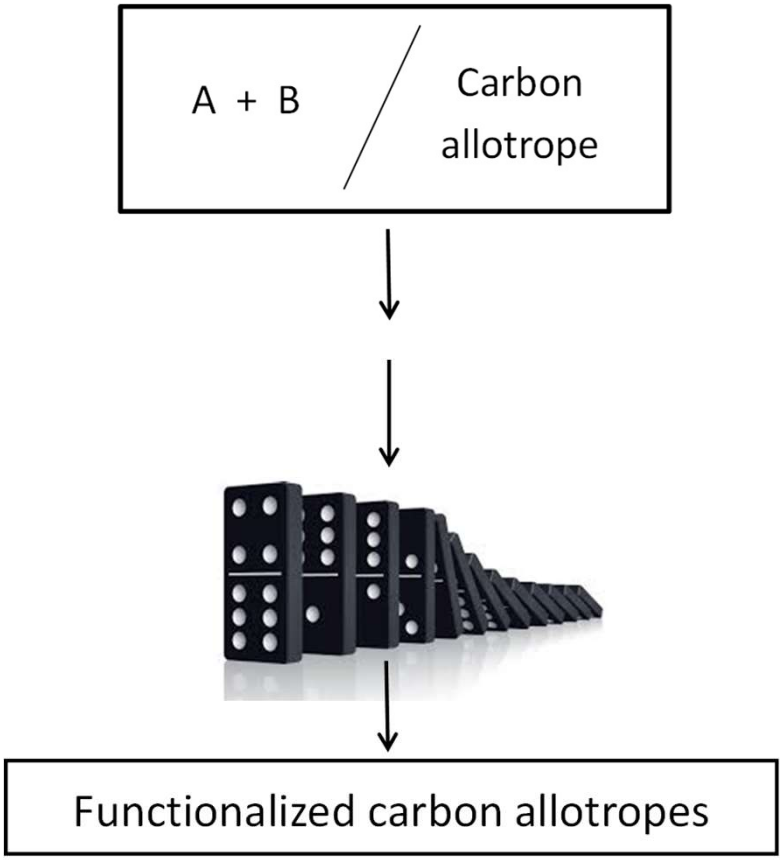
Carbocatalyzed Oxidation

Diels-Alder reaction



Domino reaction

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

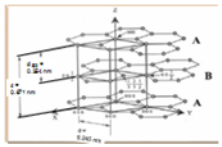
V. Barbera, A. Citterio, M. Galimberti, G. Leonardi, R. Sebastiano, S.U. Shisodia, A.M. Valerio. WO/2015/189411 A1 (2015)
M. Galimberti, V. Barbera, R. Sebastiano, A. Citterio, G. Leonardi, A.M. Valerio. WO/2016/050887 A1 (2016)
M. Galimberti, V. Barbera, R. Sebastiano, A. Truscello, A.M. Valerio. WO/2016/023915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

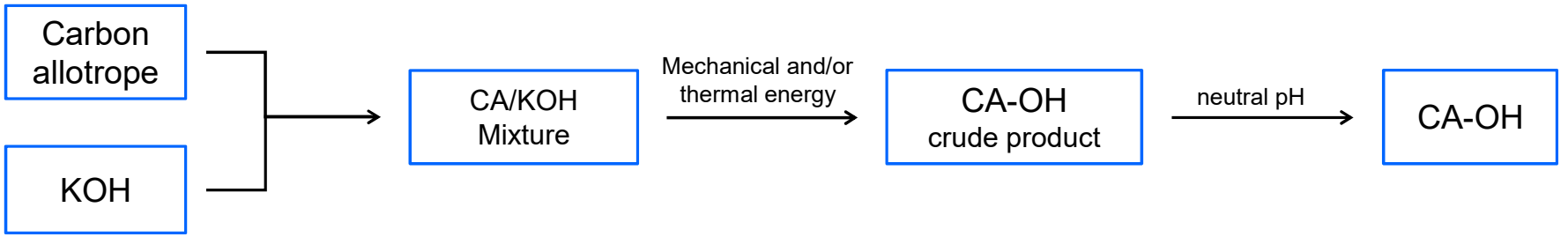
Functionalization of carbon materials with KOH

Synthesis of CA-OH

sp^2 carbon allotropes (CA)

+ KOH ⟶ CA-OH

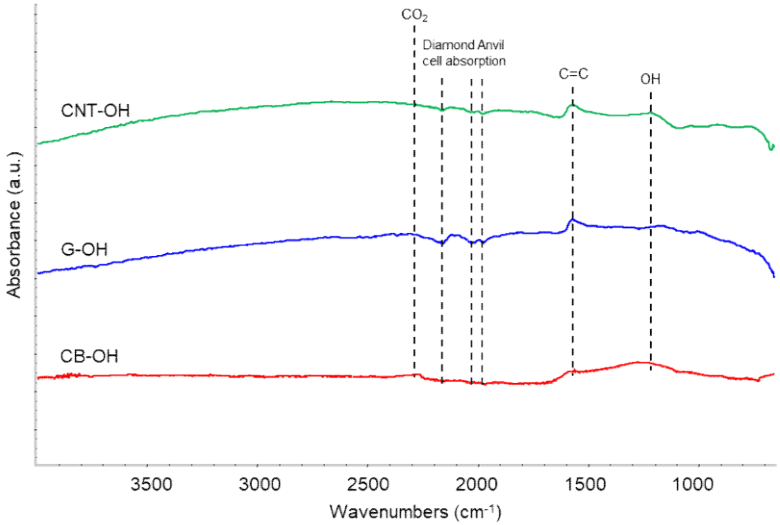




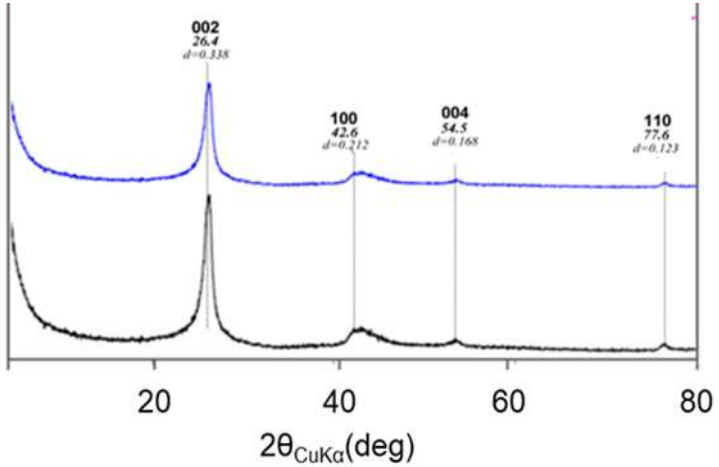
V. Barbera, A. Porta, L. Brambilla, S. Guerra, A. Serafini, A. M. Valerio, A. Vitale, M. Galimberti, RSC Adv., 2016, 6, 87767-87777
V. Barbera, A. Bernardi, G. Torrisi, A. Porta, M. Galimberti, Elastomery, 2017, 21(4), 235-251

Synthesis of CA-OH

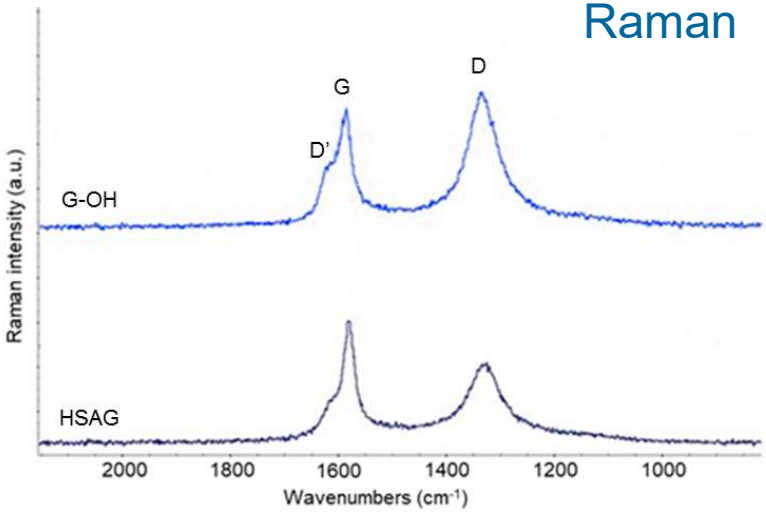
FT-IR



WAXD



Raman



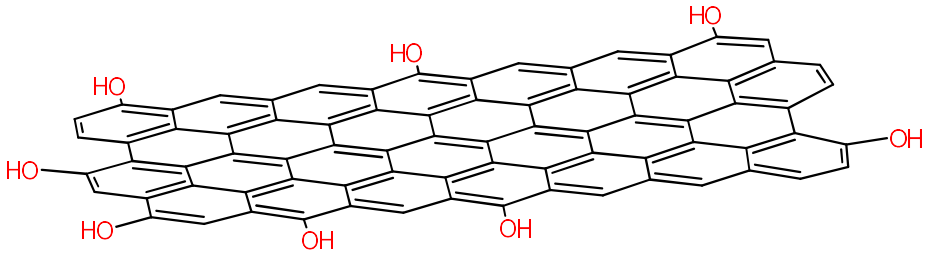
Boehm titration

	CB	HSAG	CNT
Initial functional groups [mmol/g]	1.8	1.8	2.0
Final functional groups [mmol/g]	4.2	6.8	5.0

V. Barbera, A. Porta, L. Brambilla, S. Guerra, A. Serafini, A. M. Valerio, A. Vitale, M. Galimberti, RSC Adv., 2016, 6, 87767-87777

V. Barbera, A. Bernardi, G. Torrisi, A. Porta, M. Galimberti, Elastomery, 2017, 21(4), 235-251

Oxidation of HSAG with KOH



Polyhydroxylated
few layers graphene

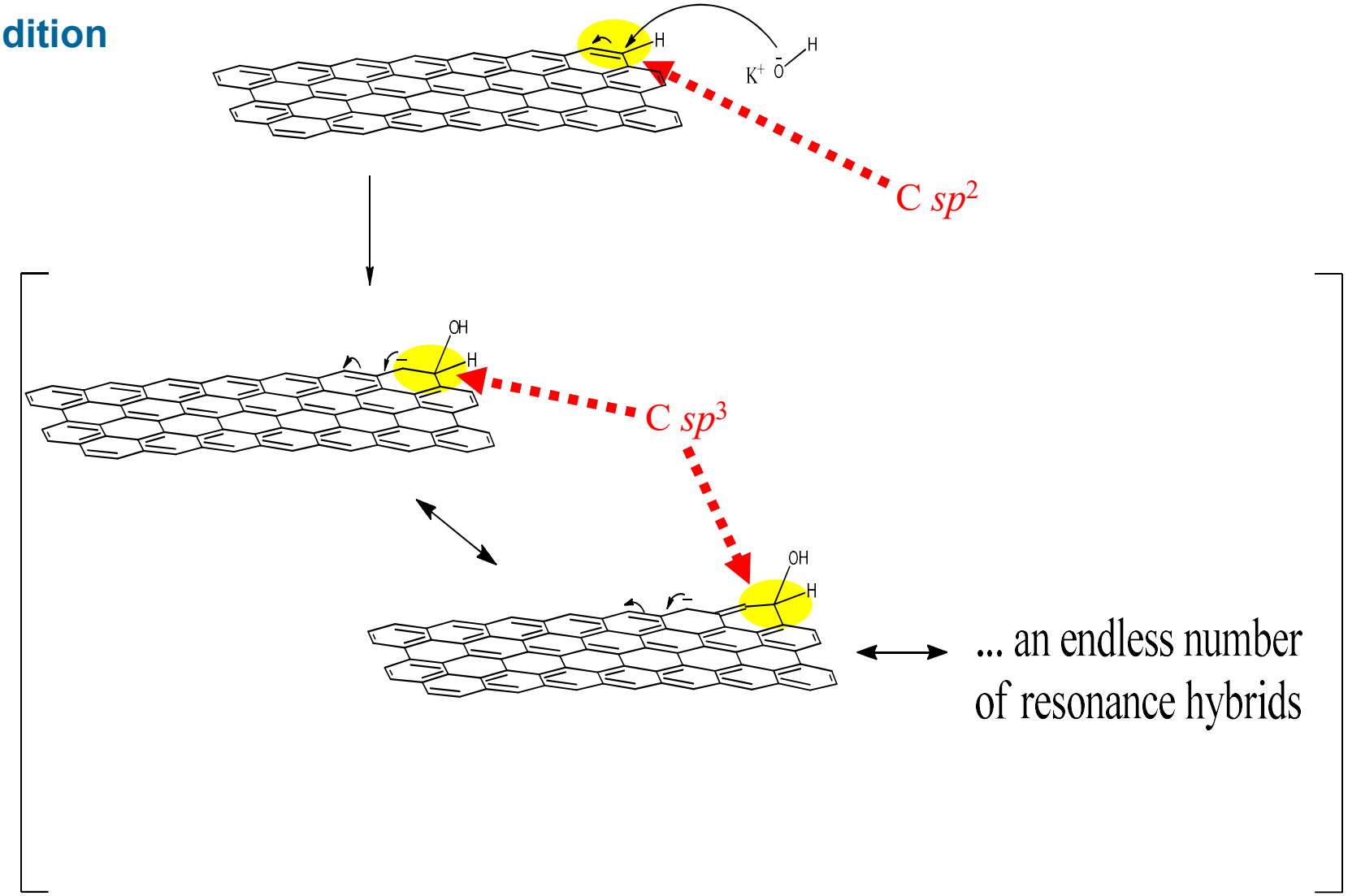
- Selective introduction of OH groups up to 15 mass%
- In plane order substantially unaltered
- No expansion of interlayer distance

sustainable oxidation

Porta, A. Master Thesis, Politecnico Milano, 2015
Barbera, V., Porta, A., Brambilla, L., Guerra, S., Serafini, A., Valerio, M.A., Vitale, A., Galimberti, M. RSC Adv., 2016, 6, 87767-8777

Oxidation with KOH – Proposed mechanism

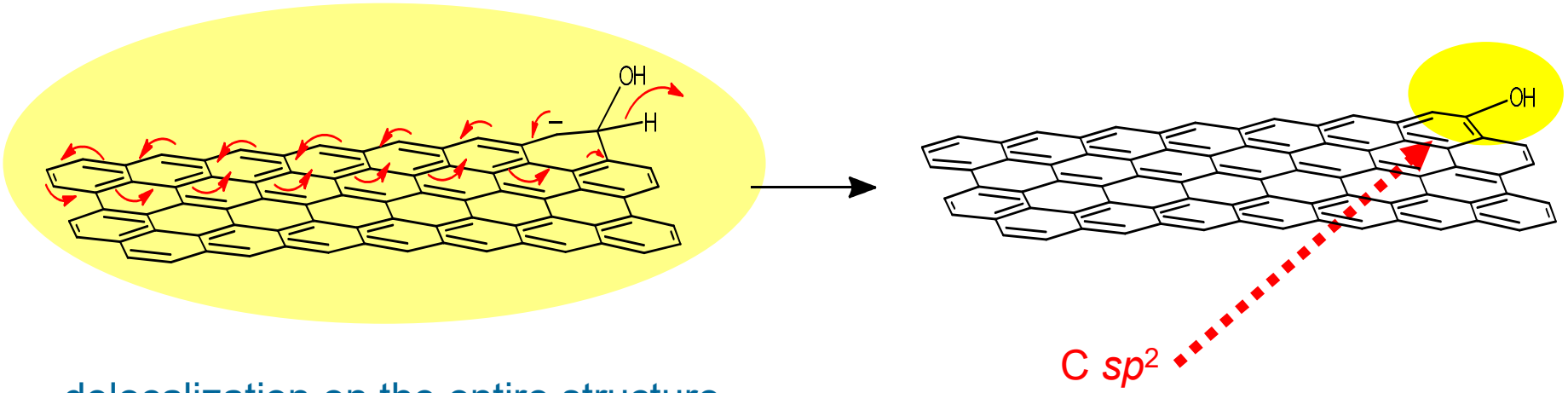
Addition



Barbera, V., Porta, A., Brambilla, L., Guerra, S., Serafini, A., Valerio, M.A., Vitale, A., Galimberti, M. RSC Adv., 2016, 6, 87767-87777

Oxidation with KOH – Proposed mechanism

Elimination



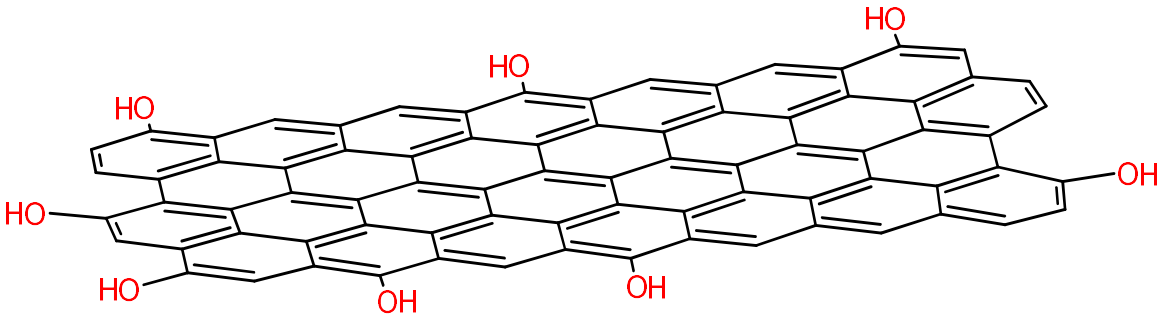
delocalization on the entire structure

"*wave effect*"

More elettronrich structure,
the oxygen lone pairs delocalized
on the polyconjugated system

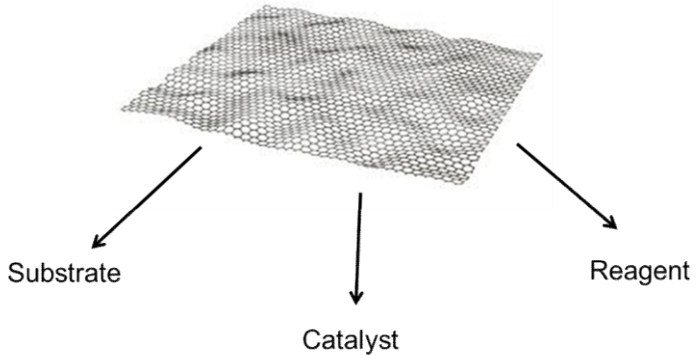
Barbera, V., Porta, A., Brambilla, L., Guerra, S., Serafini, A., Valerio, M.A., Vitale, A., Galimberti, M. RSC Adv., 2016, 6, 87767-87777

Synthetic strategy



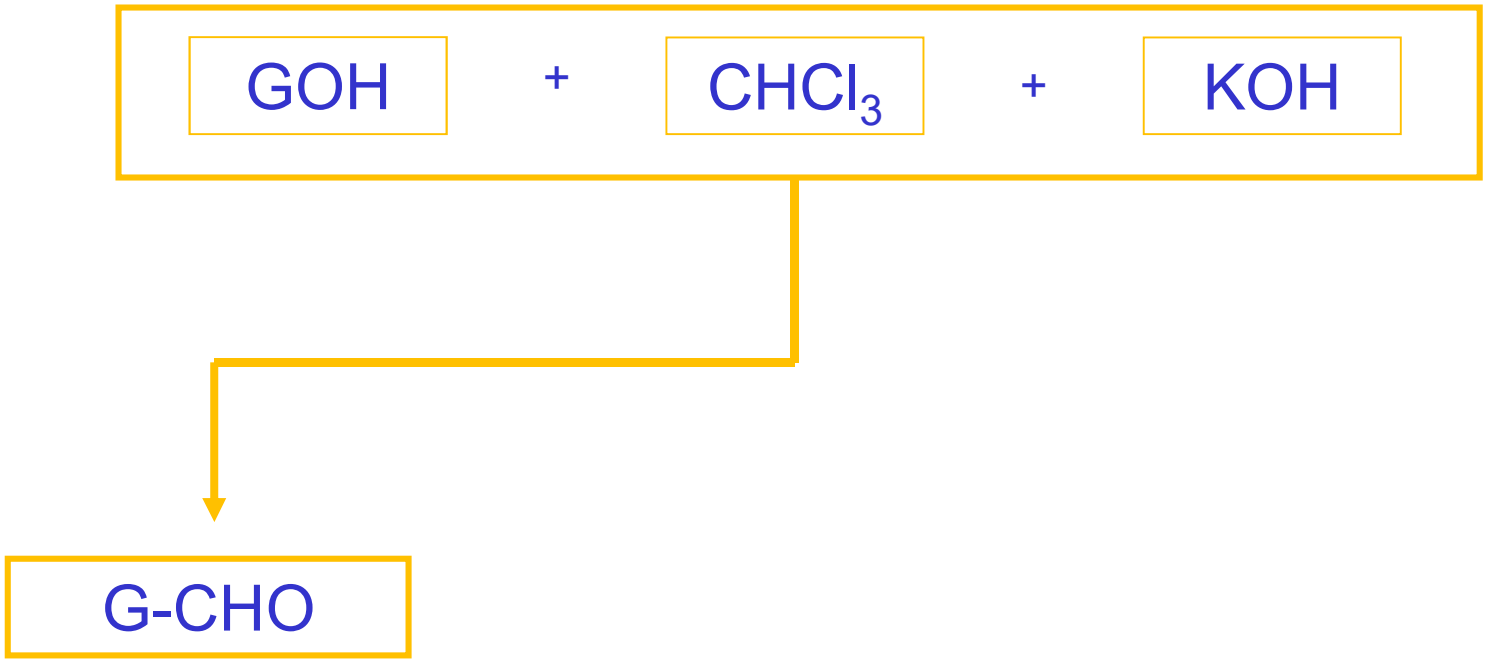
Hydroxyl
few layer graphene

Polyphenolic few layer graphene



Selective introduction of oxygenated functional groups
by means of typical reactions performed on phenol ring

Selective introduction of aldehydic functional groups



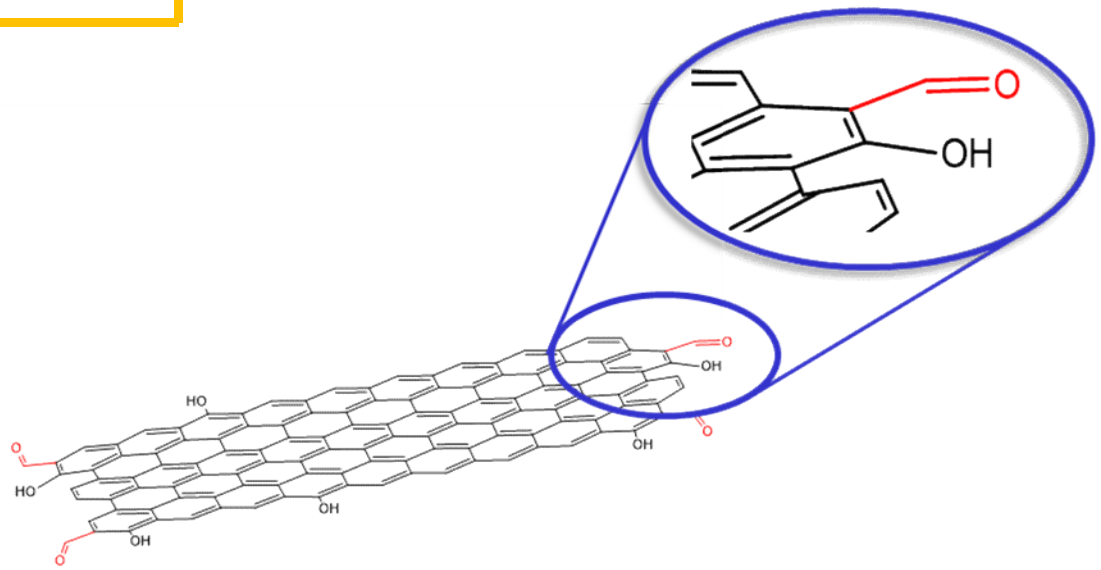
Selective ortho aldehyde

Selective introduction of aldehydic functional groups

GOH + $CHCl_3$ + KOH

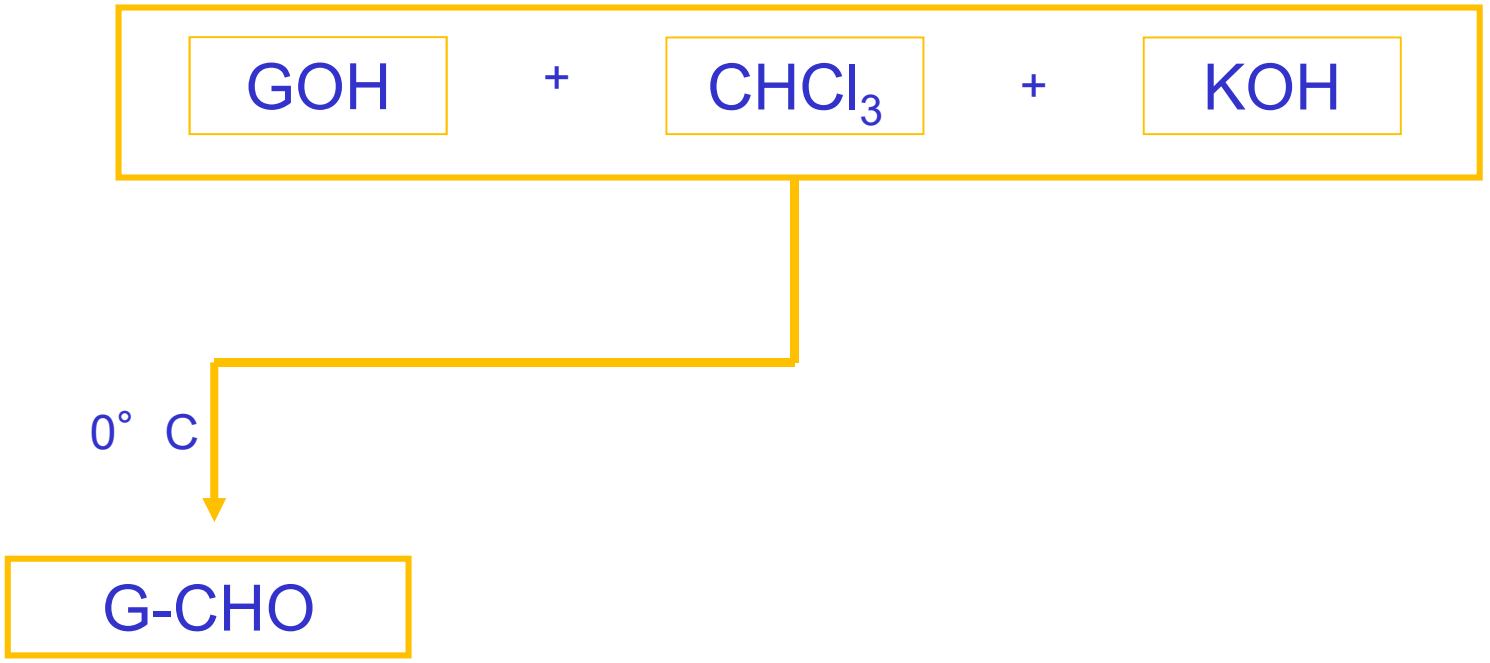
G-CHO

Selective ortho aldehyde



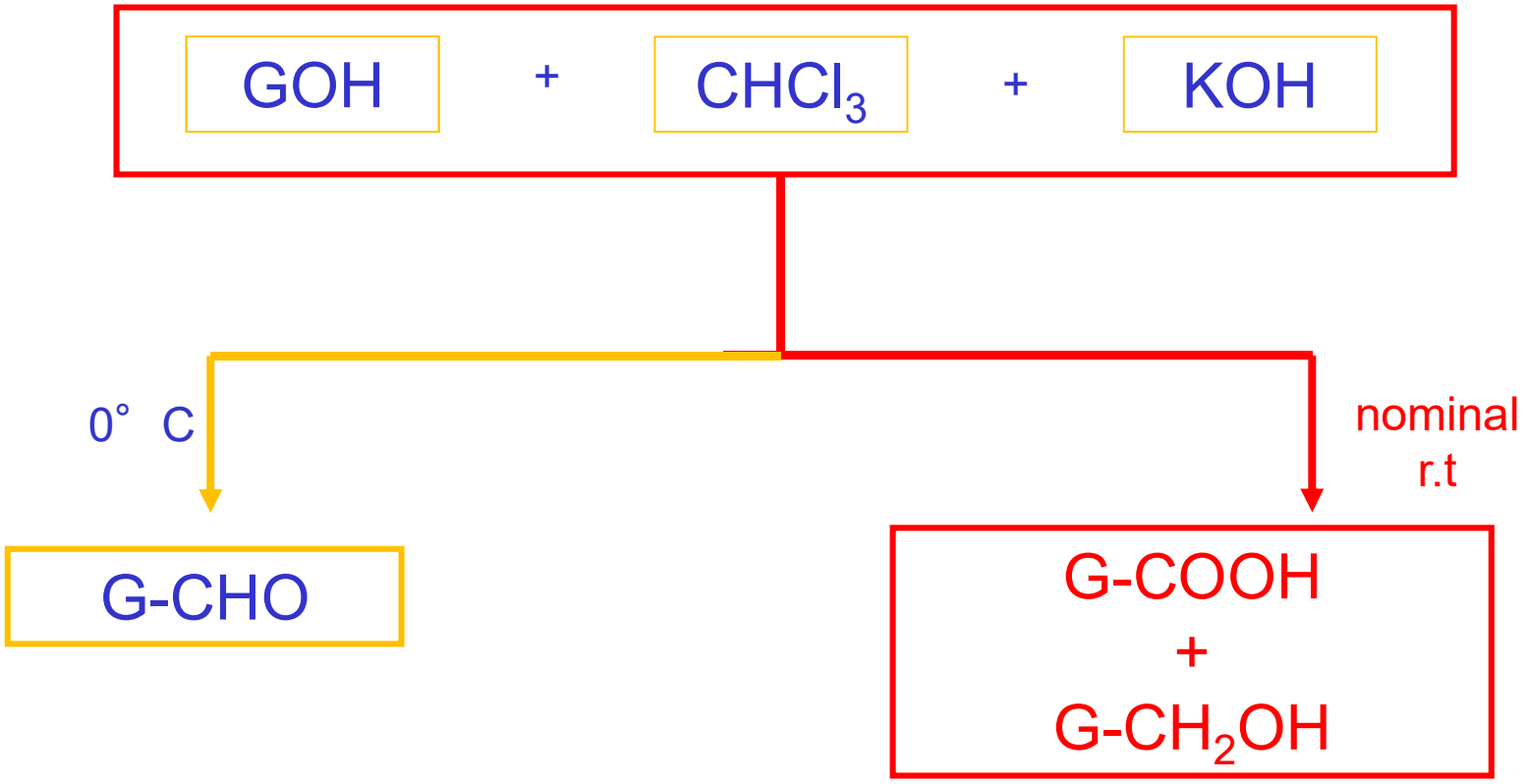
Reimer-Tiemann reaction

GOH – Polyphenolic Graphite



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

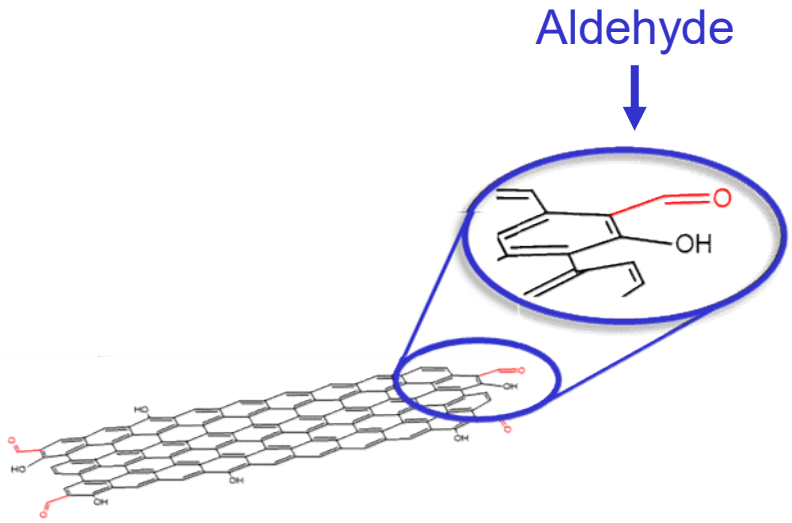
GOH – Polyphenolic Graphite

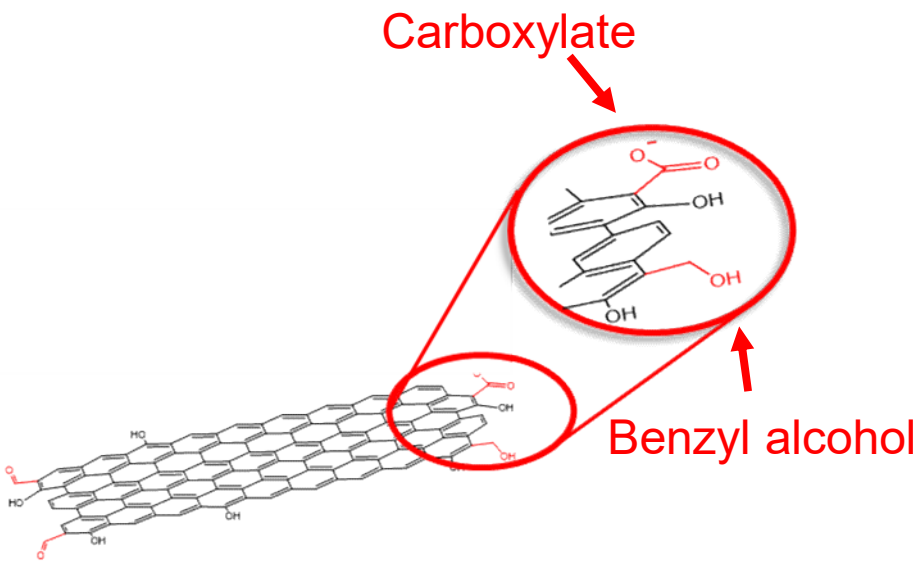


FT-IR, XPS analysis

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

GOH – Polyphenolic Graphite derivatives





G-CHO

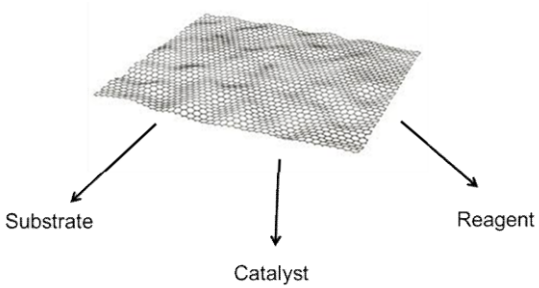
G-COOH
+
G-CH_2OH

Reimer -Tiemann

Cannizzaro

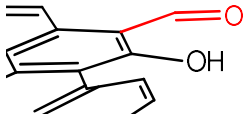
Barbera V., Brambilla L., Porta A., Bongiovanni R., Vitale A., Torrisi G., Galimberti M., Journal of Materials Chemistry A, (2018) 6, 7749-7761.

Reimer-Tiemann - Cannizzaro Domino reaction



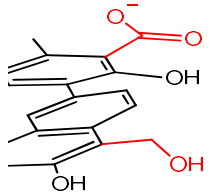
G-OH

G-CHO



Reimer-Tiemann

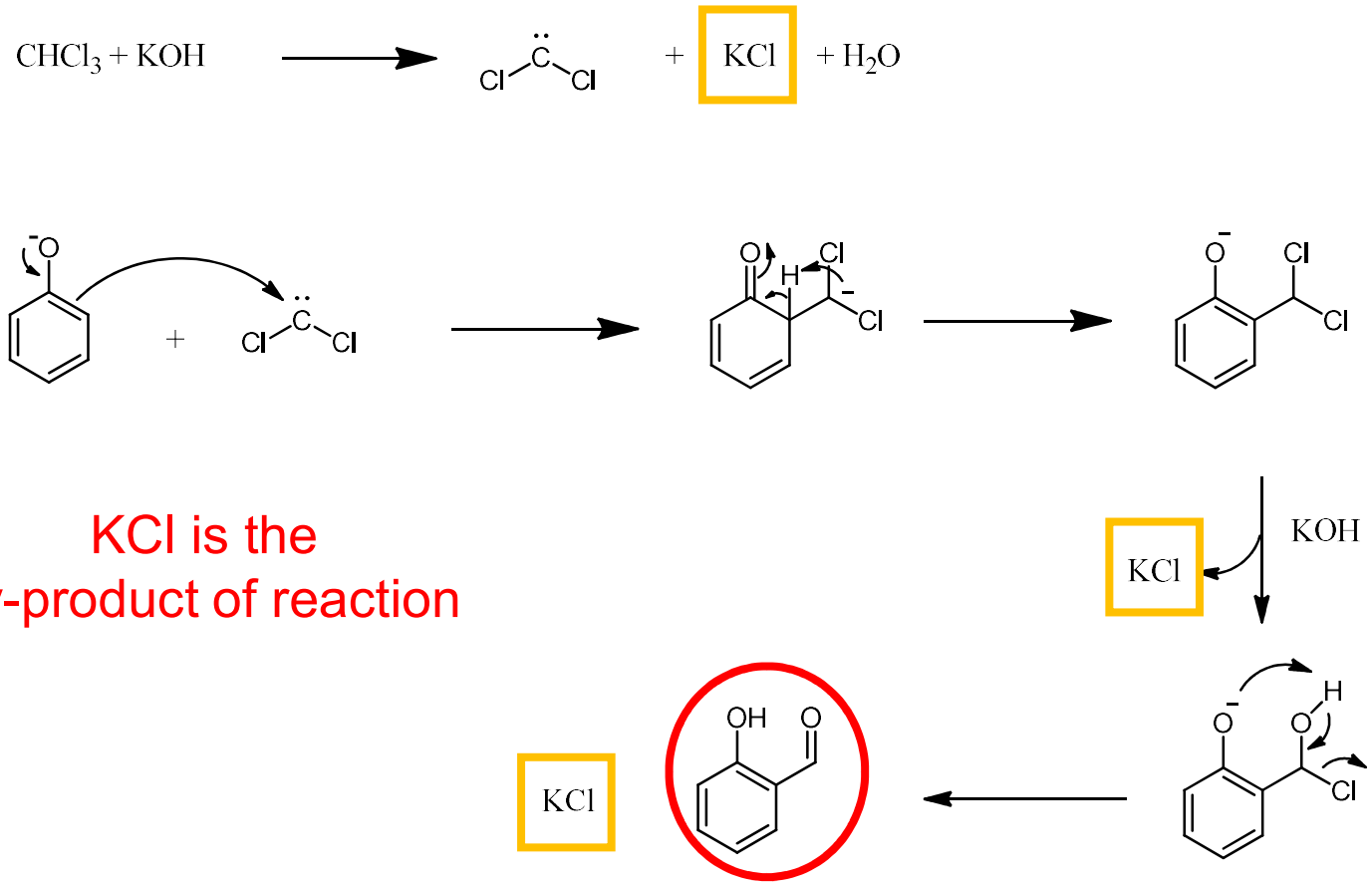
G-COOH



Domino Reimer-Tiemann/Cannizzaro

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

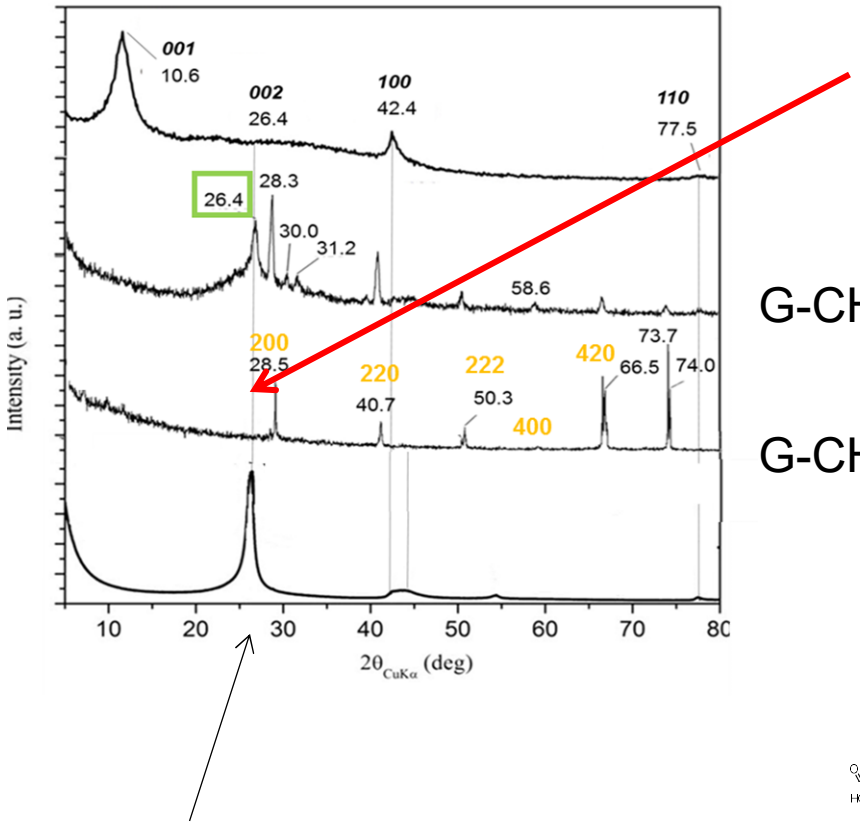
Mechanistic pathway: the Reimer-Tiemann reaction



KCl is the
by-product of reaction

For each Aldehyde formed
there are also 3 KCl molecules

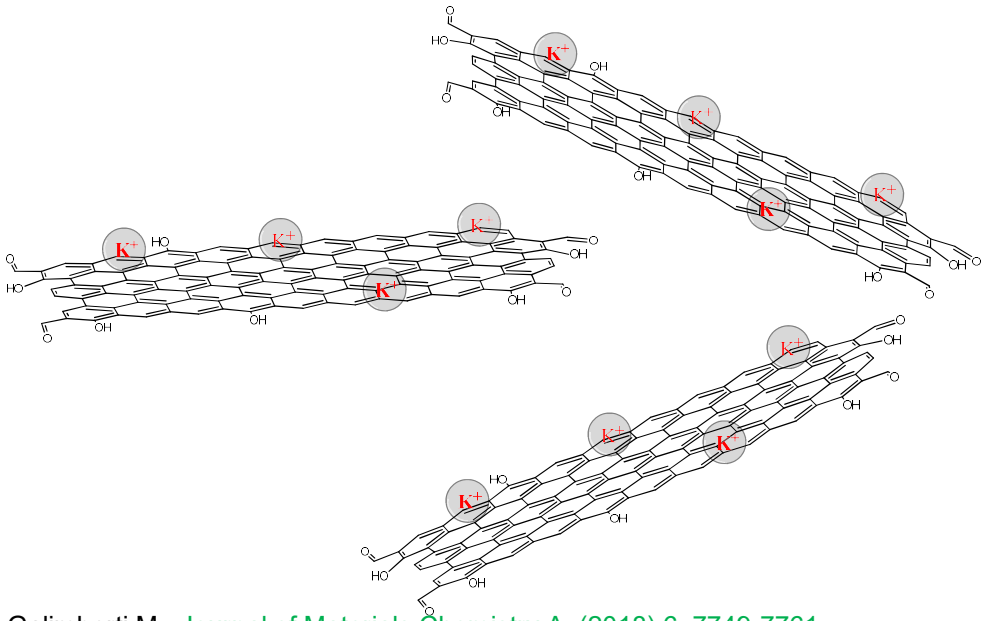
Exfoliation of nanographite



G-CHO after KCl removal

G-CHO in the presence of KCl

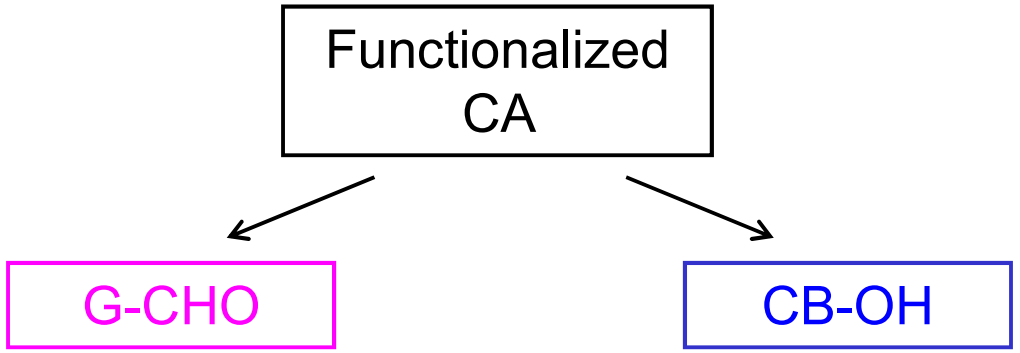
(002) reflection of graphite



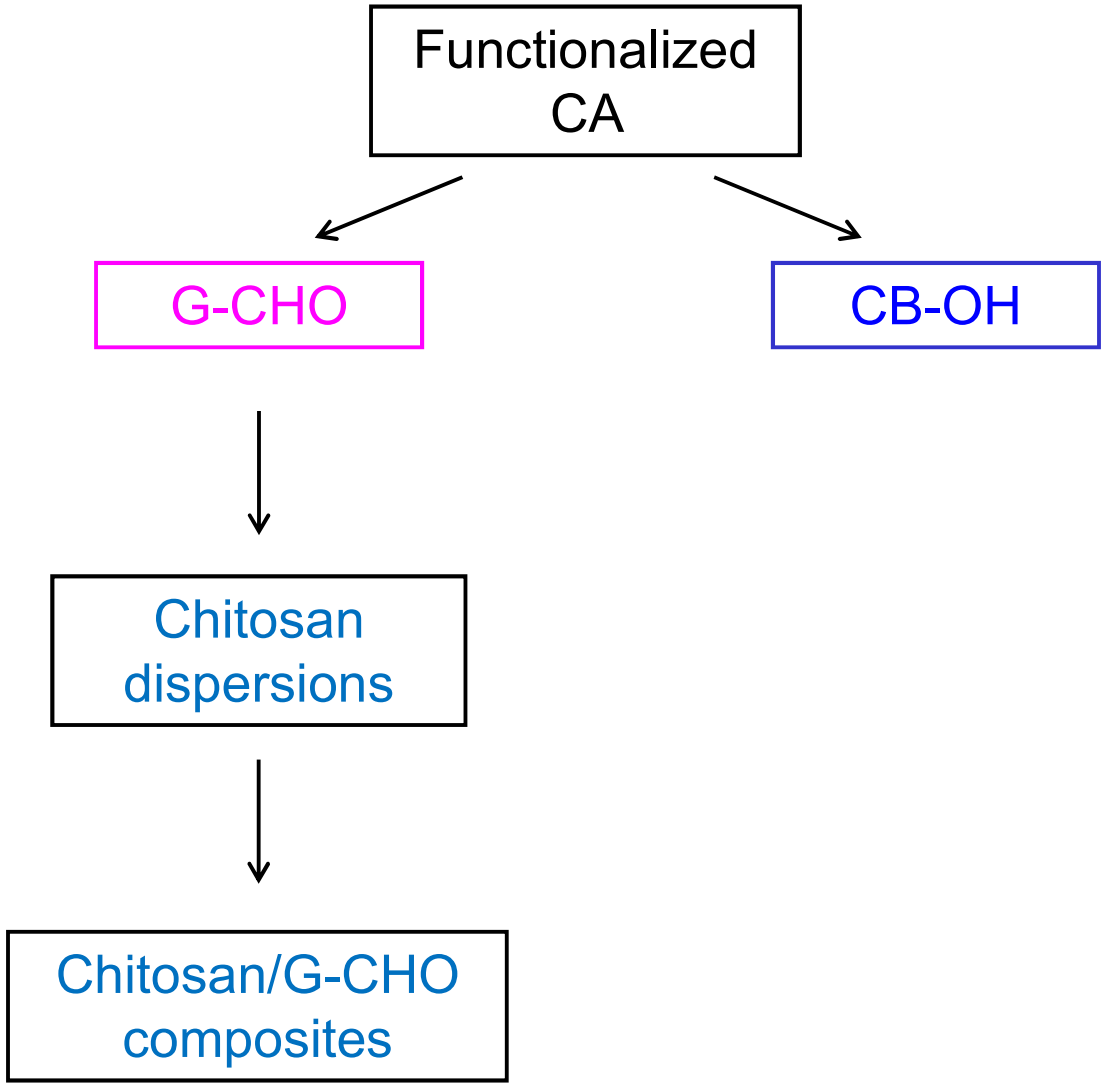
Barbera V., Brambilla L., Porta A., Bongiovanni R., Vitale A., Torrisi G., Galimberti M., Journal of Materials Chemistry A, (2018) 6, 7749-7761.

Composites based on CB-OH and G-CHO

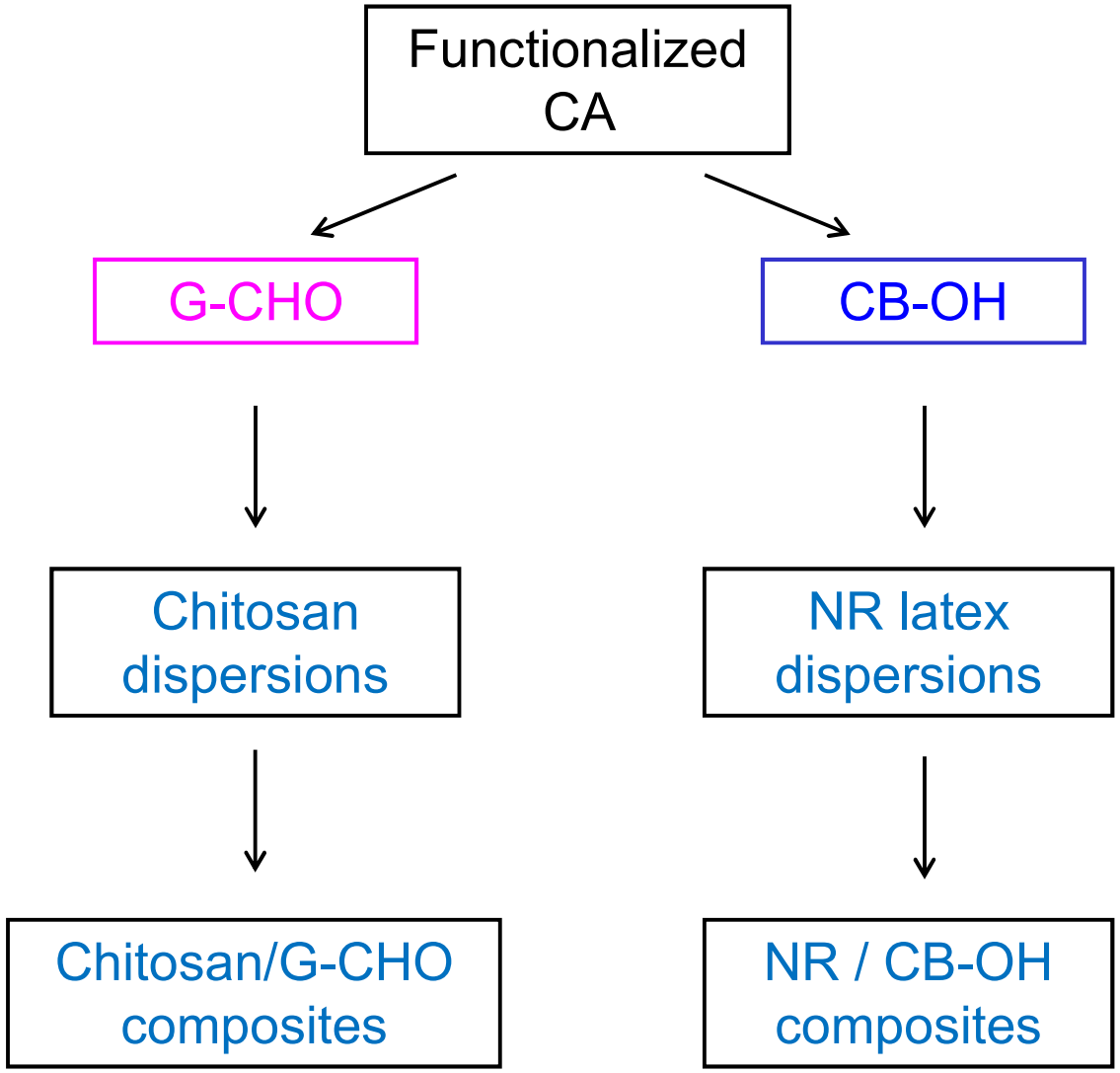
Composites based on CB-OH and G-CHO



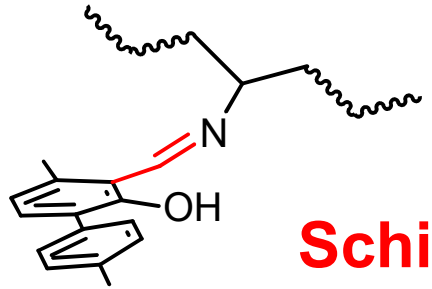
Composites based on CB-OH and G-CHO



Composites based on CB-OH and G-CHO

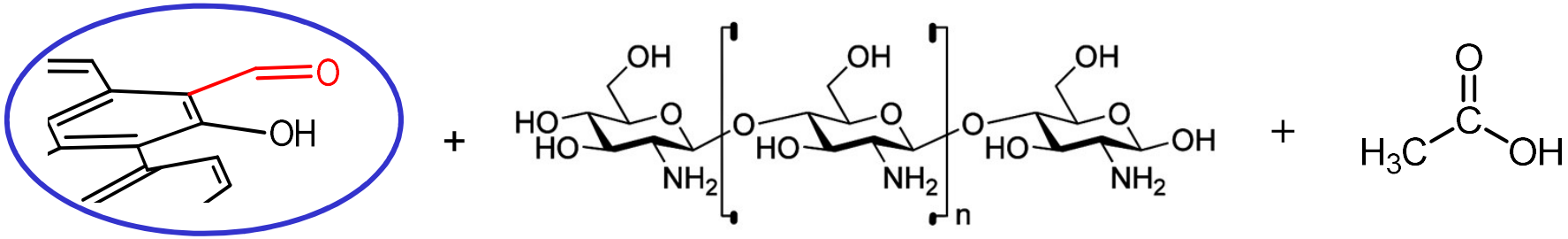


G-CHO – Composites materials



Schiff base

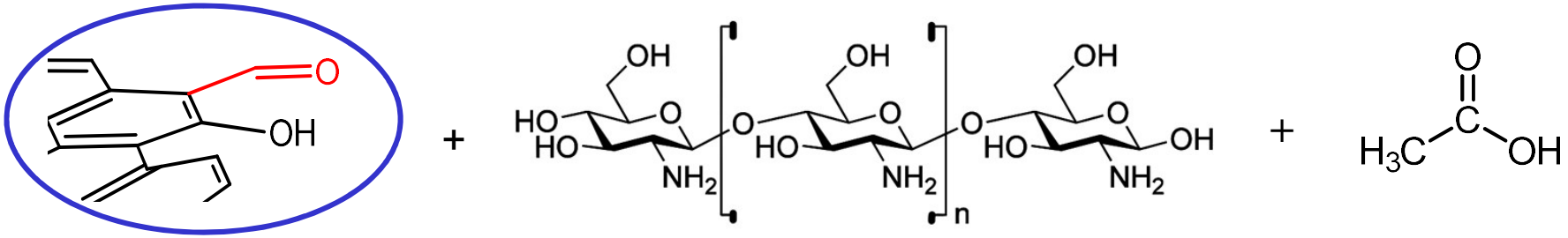
with Chitosan



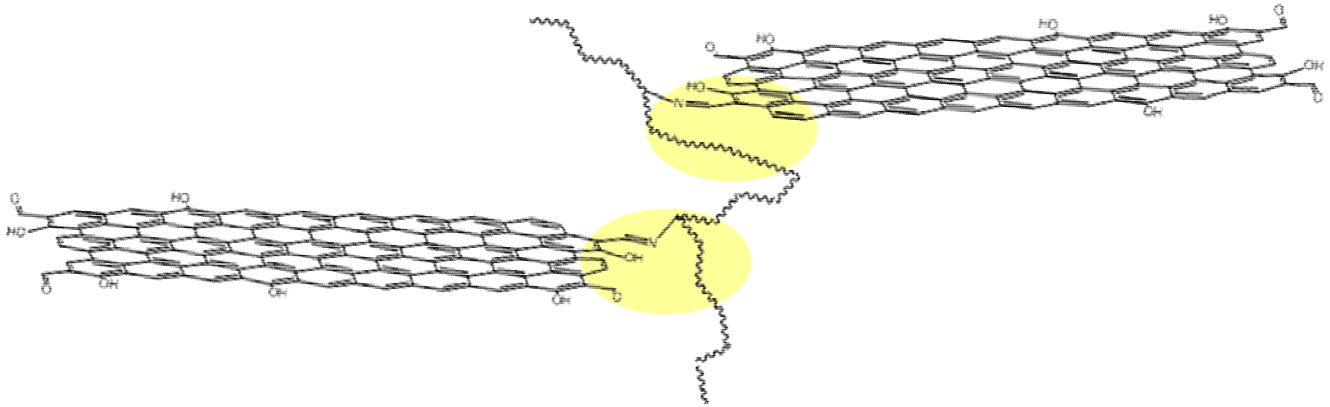
Barbera V., Brambilla L., Porta A., Bongiovanni R., Vitale A., Torrisi G., Galimberti M., Journal of Materials Chemistry A, (2018) 6, 7749-7761.

G-CHO – Composites materials

Only by mixing



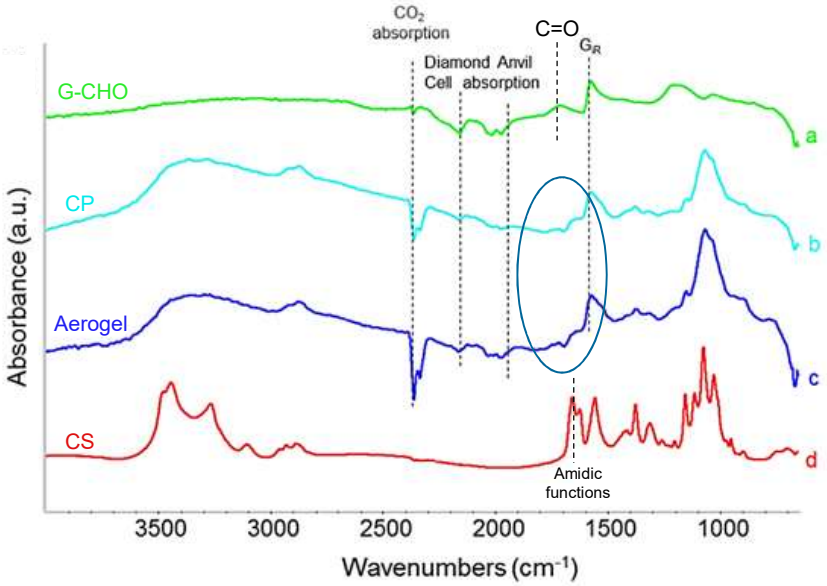
Water as solvent
Room temperature



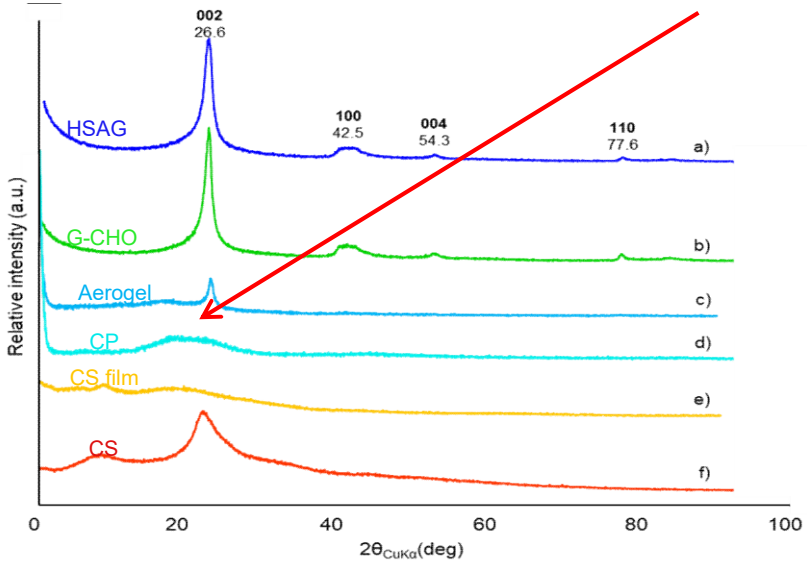
Barbera V., Brambilla L., Porta A., Bongiovanni R., Vitale A., Torrisi G., Galimberti M., Journal of Materials Chemistry A, (2018) 6, 7749-7761.

G-CHO – Composites materials

Imine formation



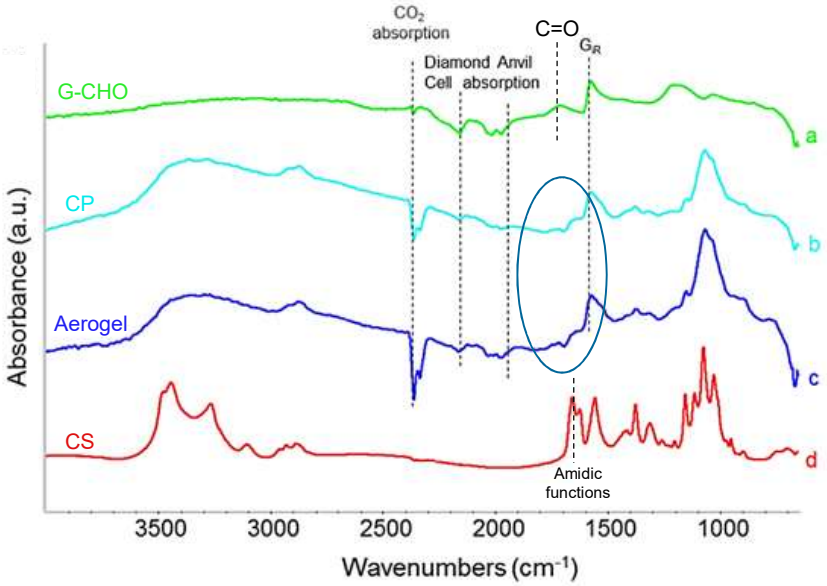
Graphite exfoliation



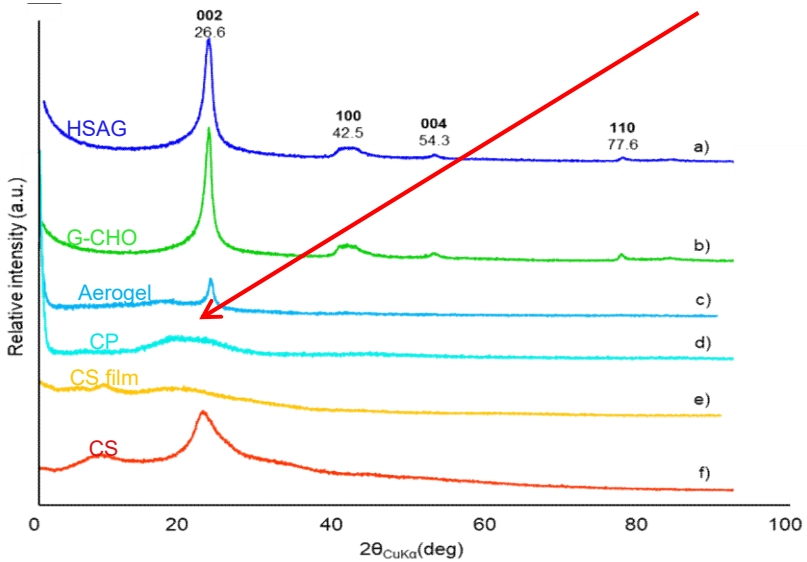
Barbera V., Brambilla L., Porta A., Bongiovanni R., Vitale A., Torrisi G., Galimberti M., Journal of Materials Chemistry A, (2018) 6, 7749-7761.

G-CHO – Composites materials

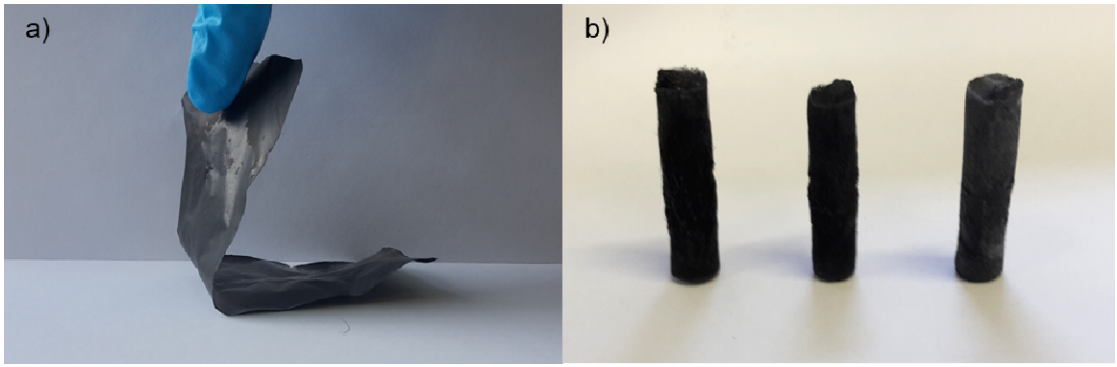
Imine formation



Graphite exfoliation



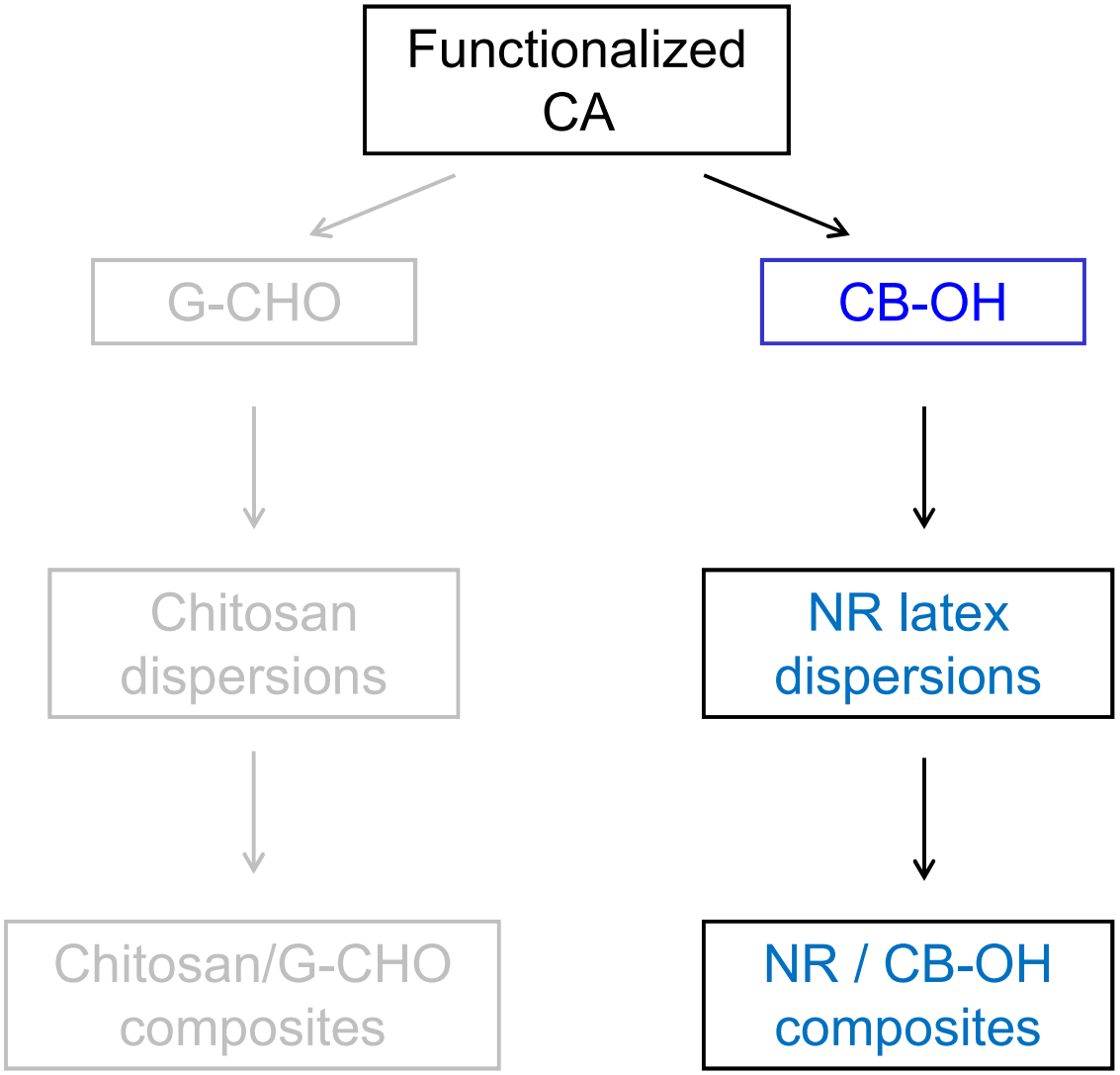
Carbon paper



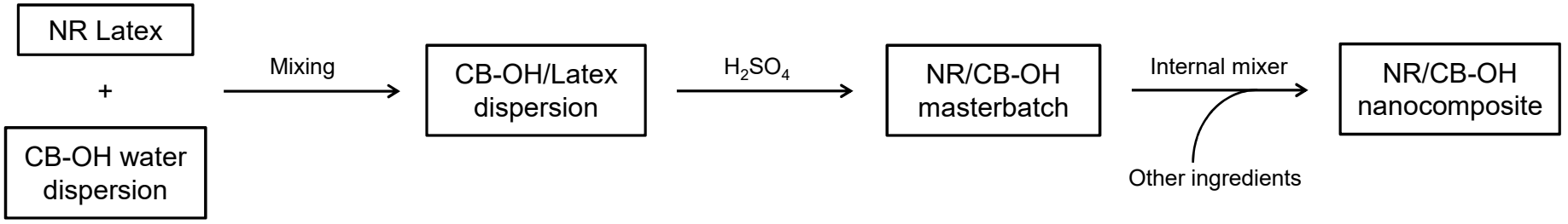
Aerogels

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

Composites based on CB-OH and G-CHO



Natural rubber based nanocomposites

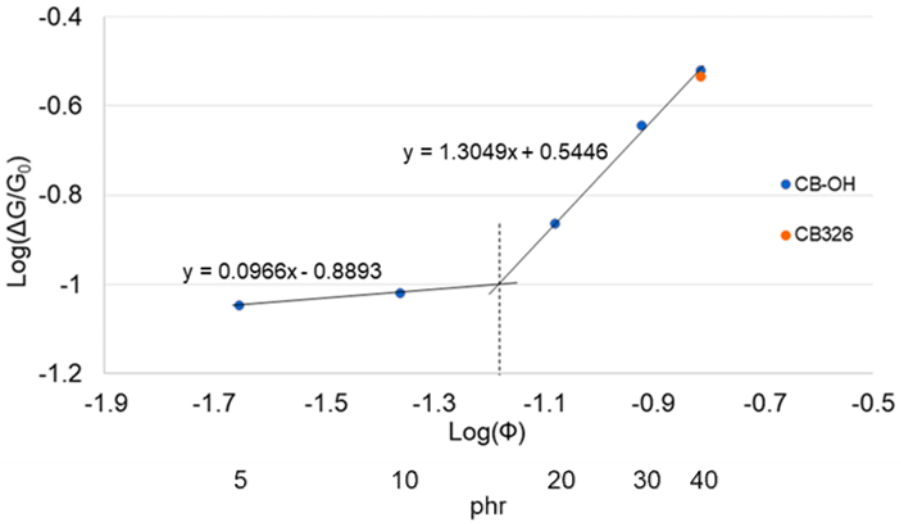


CB-OH

CB

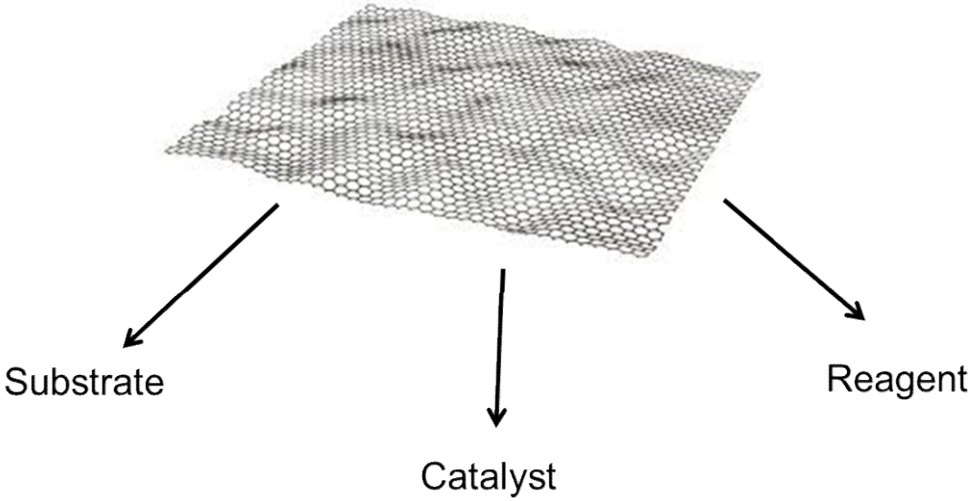
Natural rubber based nanocomposites

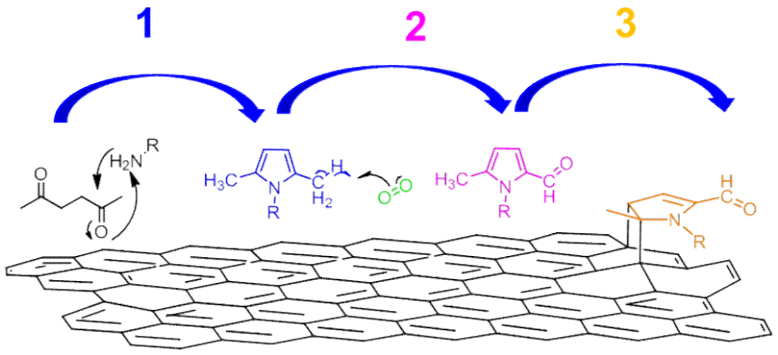
Huber-Vilgis plot

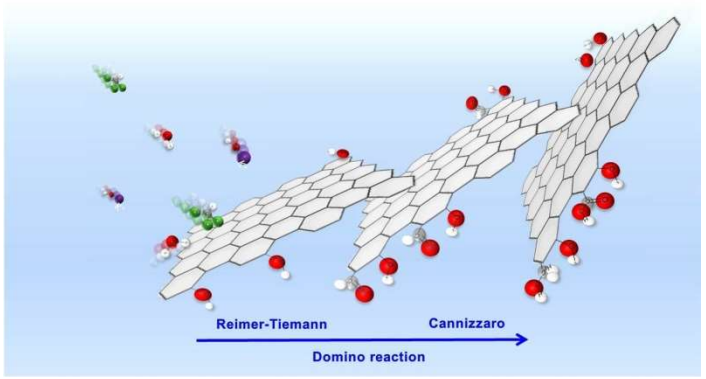


Percolation threshold	
Value from literature for CB	Value for CB-OH
30 to 35 phr	15 phr

Conclusions







Thanks
for the attention!

RICETTE PESO	densità	CB-OH_0	CB-OH_5	CB-OH_10	CB-OH_20	CB-OH_30	CB-OH_40
	gr/cm3	phr	phr	phr	phr	phr	phr
Gomma NR - SIR20	0.87	100.00	100.00	100.00	100.00	100.00	100.00
CB-OH	1.80	0.00	5.00	10.00	20.00	30.00	40.00
Ac Stearico	0.85	2.00	2.00	2.00	2.00	2.00	2.00
ZnO	5.55	4.00	4.00	4.00	4.00	4.00	4.00
6PPD	1.00	2.00	2.00	2.00	2.00	2.00	2.00
TBBS	1.32	1.80	1.70	1.70	1.70	1.70	1.70
Zolfo	2.00	1.80	1.20	1.20	1.20	1.20	1.20
totale		111.60	115.90	120.90	130.90	140.90	150.90