Tailor made functionalizations of graphene layers and their application as carbocatalyst for organic reactions

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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”

Objectives of the research activity

- To reduce the synthetic footprint
  in carbon allotropes functionalization

- To perform tailor made functionalization
  of graphene layers
  with a sustainable, facile, versatile method,
  preserving the sp^2 hybridization

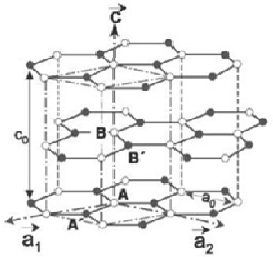
Functionalization of graphene layers

Facile preparation of graphene layers and

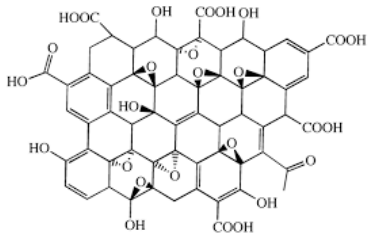
graphene layers with controlled functionalities

is a Holy Grail in the field of materials chemistry.

Suitable approach



GO



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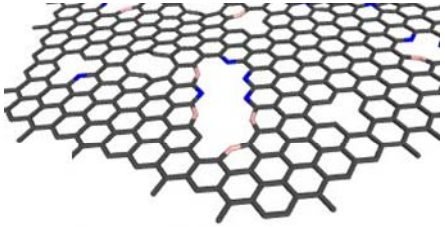
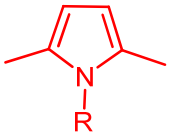


Functionalization of graphene layers

Functionalization of graphene layers

+

- Pyrrole derivatives



- KOH

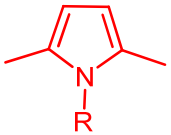
- Reactions
- Products' characterization
- Hypothesis of mechanisms

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

Functionalization of graphene layers

+

- Pyrrole derivatives



- KOH

- Reactions
- Products' characterization
- Hypothesis of mechanisms

- Catalyst for organic reactions

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
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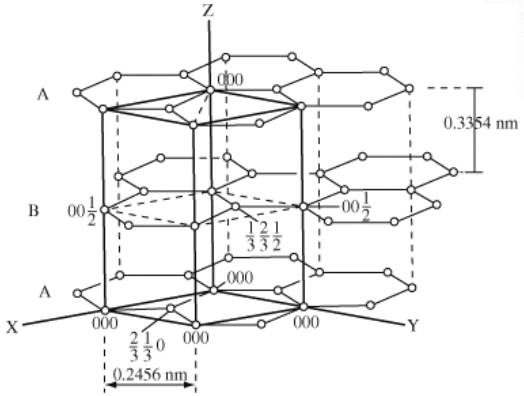
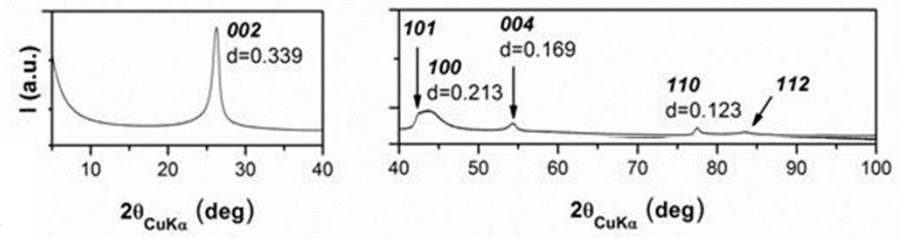
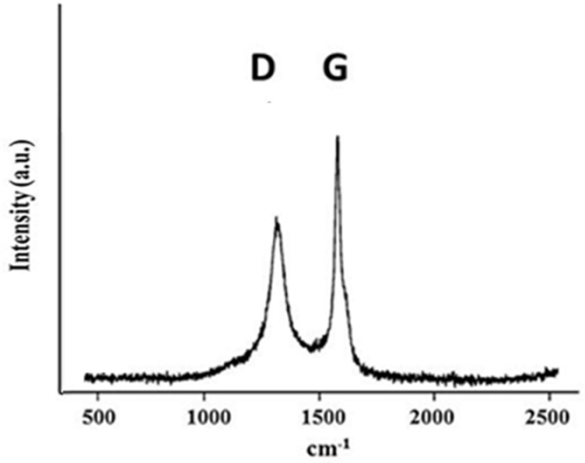
High Surface Area Graphite (HSAG)





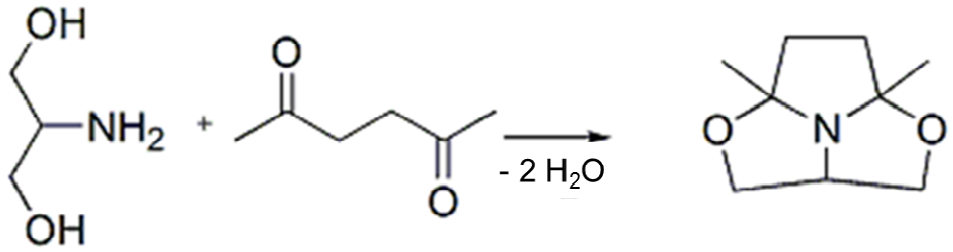
Surface area (m^2/g)	number of layers	$D_{\parallel} / D_{\perp}$
330	35	3.1



Functionalization of carbon materials

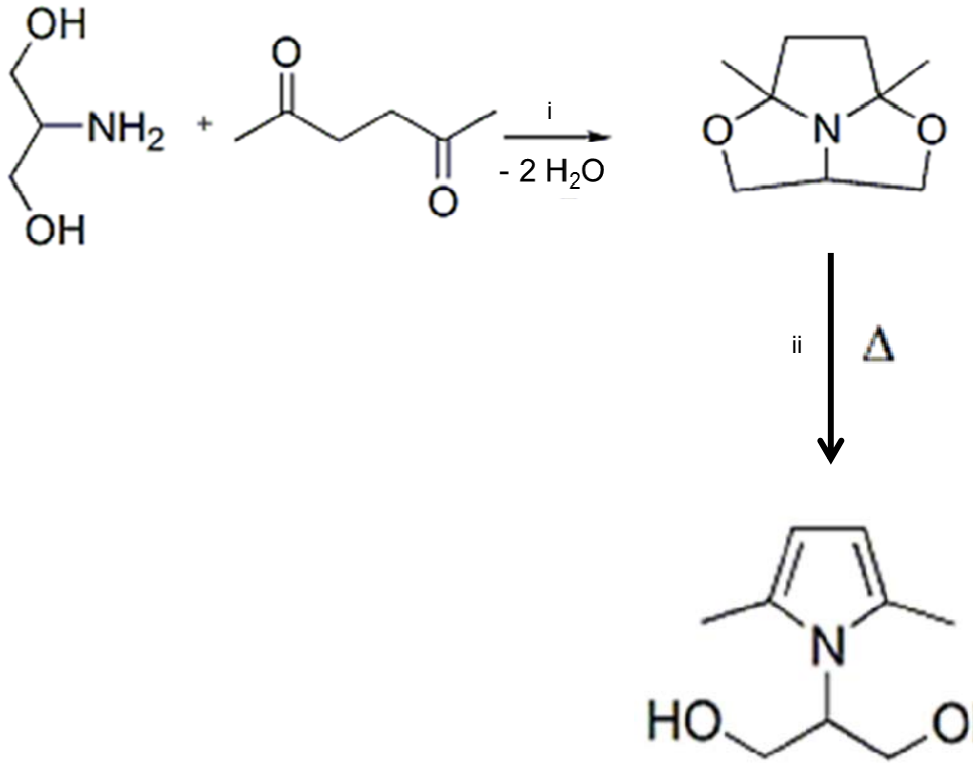
with pyrrole derivative

Reaction of serinol with dicarbonyl compound



V. Barbera, A.Citterio, M. Galimberti, G. Leonardi, R. Sebastiano, S.U.Shisodia, A.M. Valerio *WO 2015 189411 A1*
M. Galimberti, V. Barbera, A. Citterio, R. Sebastiano, A. Truscello, A. M. Valerio, L. Conzatti, R. Mendichi, *Polymer*, vol 63, 20 April 2015, Pages 62–70
M. Galimberti, V. Barbera, S. Guerra, L. Conzatti, C. Castiglioni, L. Brambilla, A. Serafini,, *RSC Adv.,* 2015, *5*, 81142-81152 DOI: 10.1039/C5RA11387C
V. Barbera, S. Musto, A. Citterio, L. Conzatti, M. Galimberti,, *eXPRESS Polymer Letters* 2016, *10* (7) 548–558

Reaction of serinol with dicarbonyl compound



Serinol pyrrole - SP

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

i. r.t. 6h; ii.150°C, 2h

V. Barbera, A.Citterio, M. Galimberti, G. Leonardi, R. Sebastiano, S.U.Shisodia, A.M. Valerio *WO 2015 189411 A1*
M. Galimberti, V. Barbera, A. Citterio, R. Sebastiano, A. Truscello, A. M. Valerio, L. Conzatti, R. Mendichi, *Polymer*, vol 63, 20 April 2015, Pages 62–70
M. Galimberti, V. Barbera, S. Guerra, L. Conzatti, C. Castiglioni, L. Brambilla, A. Serafini,, *RSC Adv.*, 2015, *5*, 81142-81152 DOI: 10.1039/C5RA11387C
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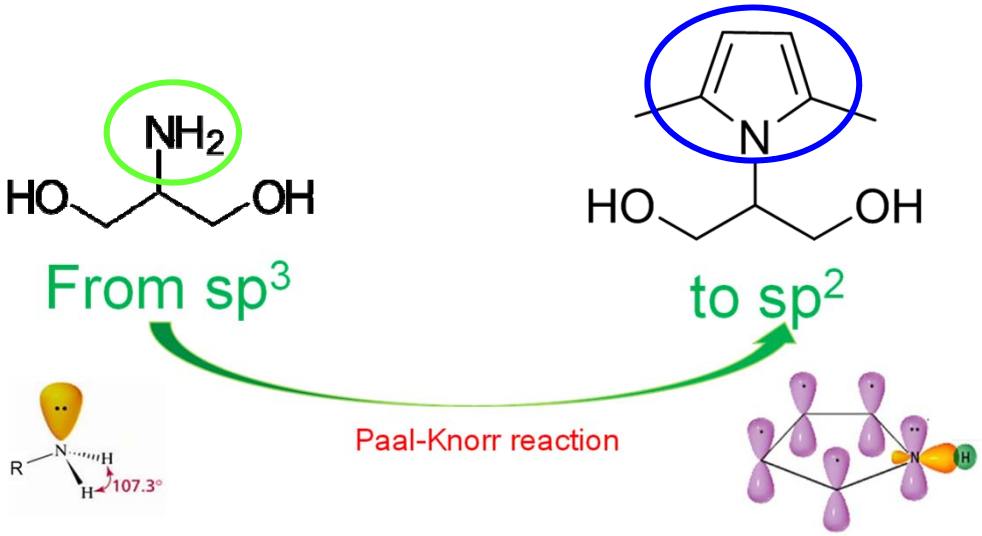
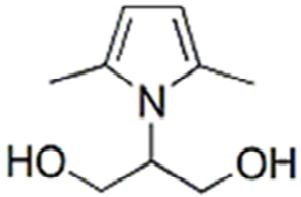
Neat synthesis of Serinol pyrrole



- Yield: at least 96%
- Atom efficiency: 85%
- Easy procedure
- No solvent
- By product: H_2O

Adduct of SP with HSAG

+



HSAG

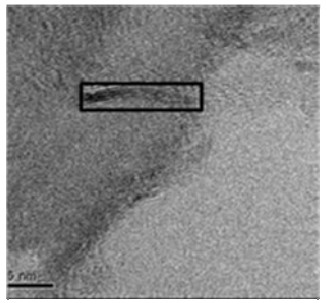
SP = 1 – 20 phc

phc = per hundred carbon

80 - 180 C

0,5 - 4 h

HSAG/SP adduct



Functionalization Yield(%)*: **96**

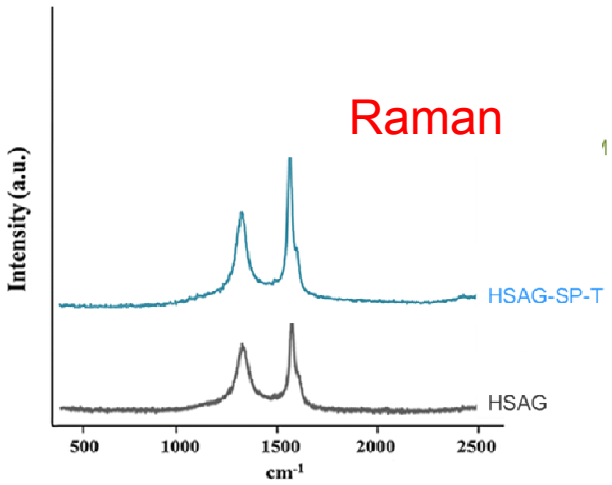
$$\text{Functionalization Yield } (\%) = 100 * \frac{\text{SP mass \% in (CA–SP adduct) after acetone washing}}{\text{SP mass \% in (CA–SP adduct) before acetone washing}}$$

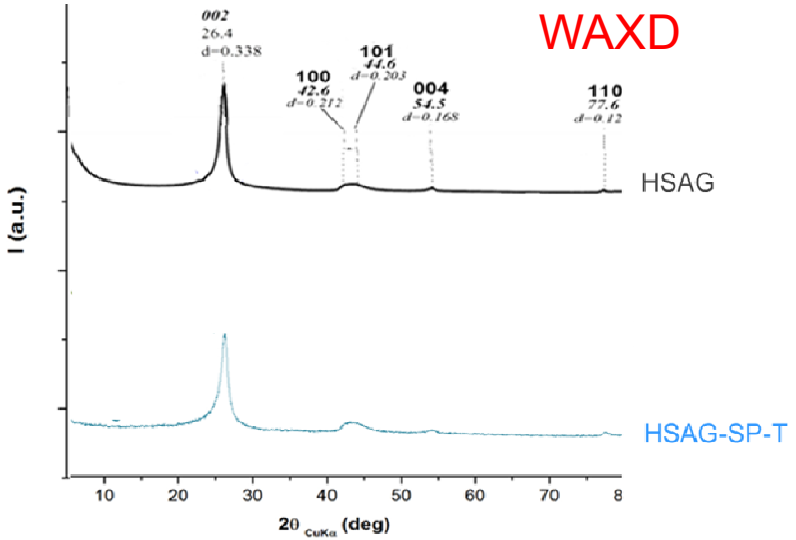
from TGA

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.

Adduct of SP with HSAG





- Unaltered in plane order
- No expansion of the interlayer distance

- Reaction with SP
  does not substantially alter, *per se*,
  the bulk crystalline order of HSAG

Sample	number of stacked layers
HSAG	35
HSAG-SP	24

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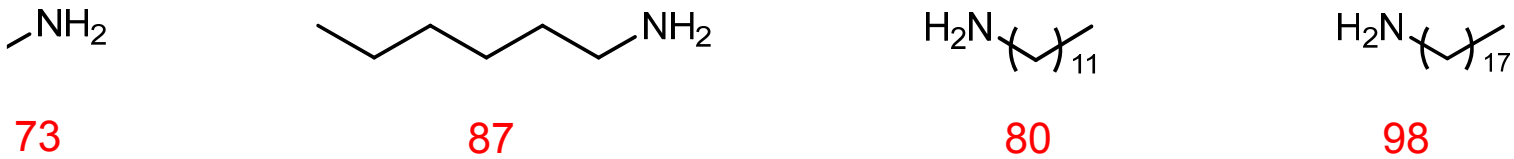
HSAG / PyC adducts

Functionalization Yield %



73 87 80 98

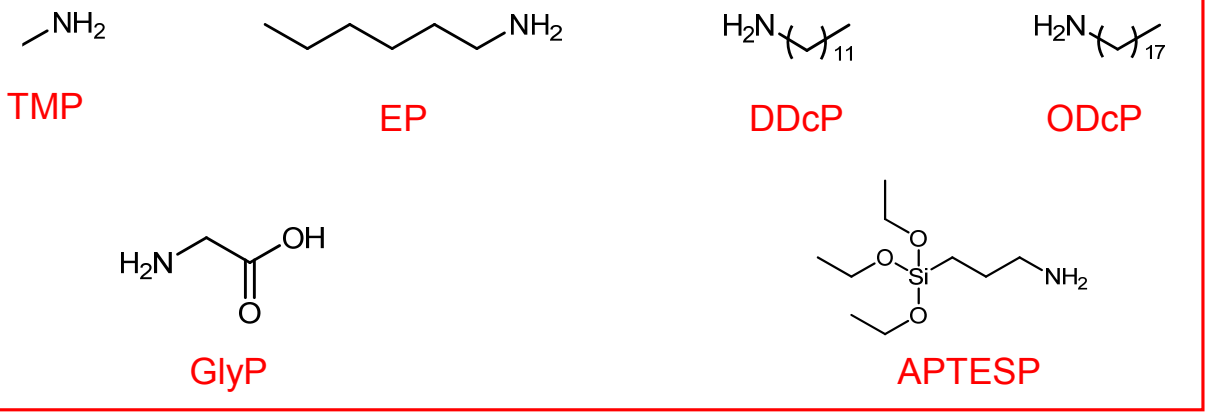
82 78

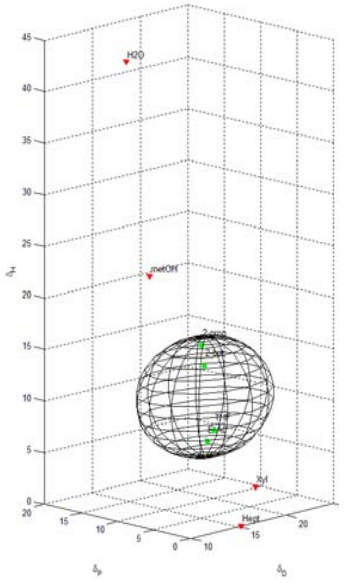
V. Barbera, A. Bernardi, A.Palazzolo, A. Rosengart, L. Brambilla, M. Galimberti Pure and Applied Chemistry 2018, 90(2), 253–270

Evaluation of solubility parameters of HSAG-PyC - δ values

Amount of PyC on HSAG: about 5% mol

Sample	δ_D	δ_P	δ_H	Radius
HSAG	17.8	3.1	5.7	1.0
HSAG-TMP	14.6	10.3	5.6	11.6
HSAG-DDcP	8.5	7.5	8.3	12.3
HSAG-APTESP	12.7	2.3	0.5	8.3
HSAG-SP	12.8	2.0	8.9	13.8
HSAG-GlyP	6.9	12.1	5.3	15.3





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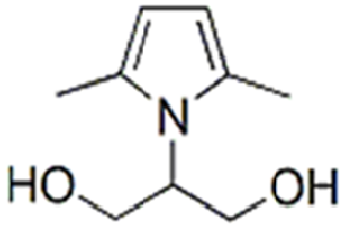
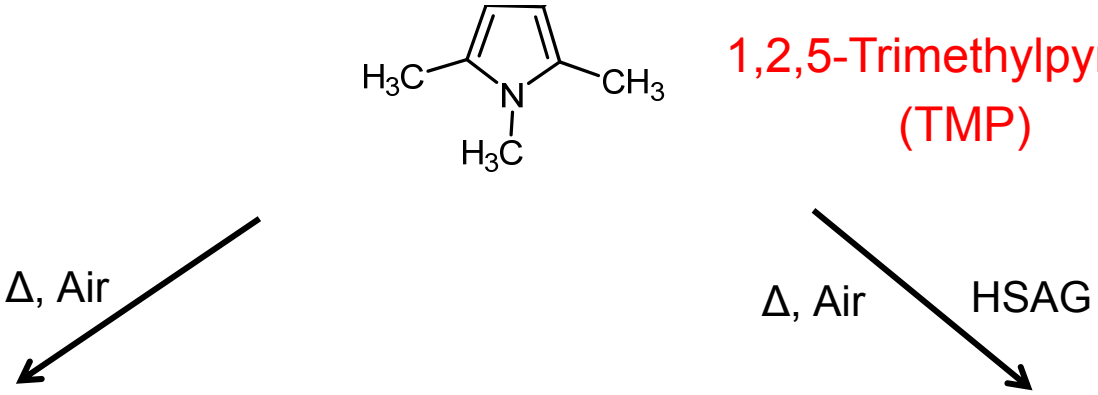
NanoCarbon Up Technology



WO 2015/189411 A1; WO2016/023915A1; WO 2016/050887 A1; WO 2018/087688 A1 ;
Italian patent 102016000113012; Italian Patent 10201800005161; Italian Patent 102018000002919; Italian Patent 102018000005206;
Italian Patent 10201800005164

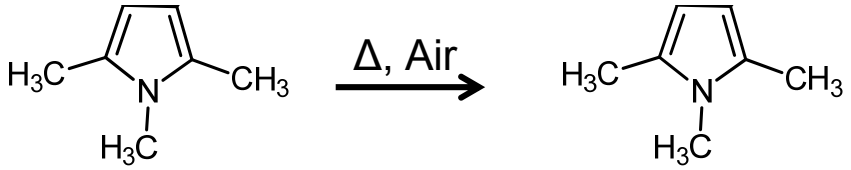
Mechanism of the functionalization reaction

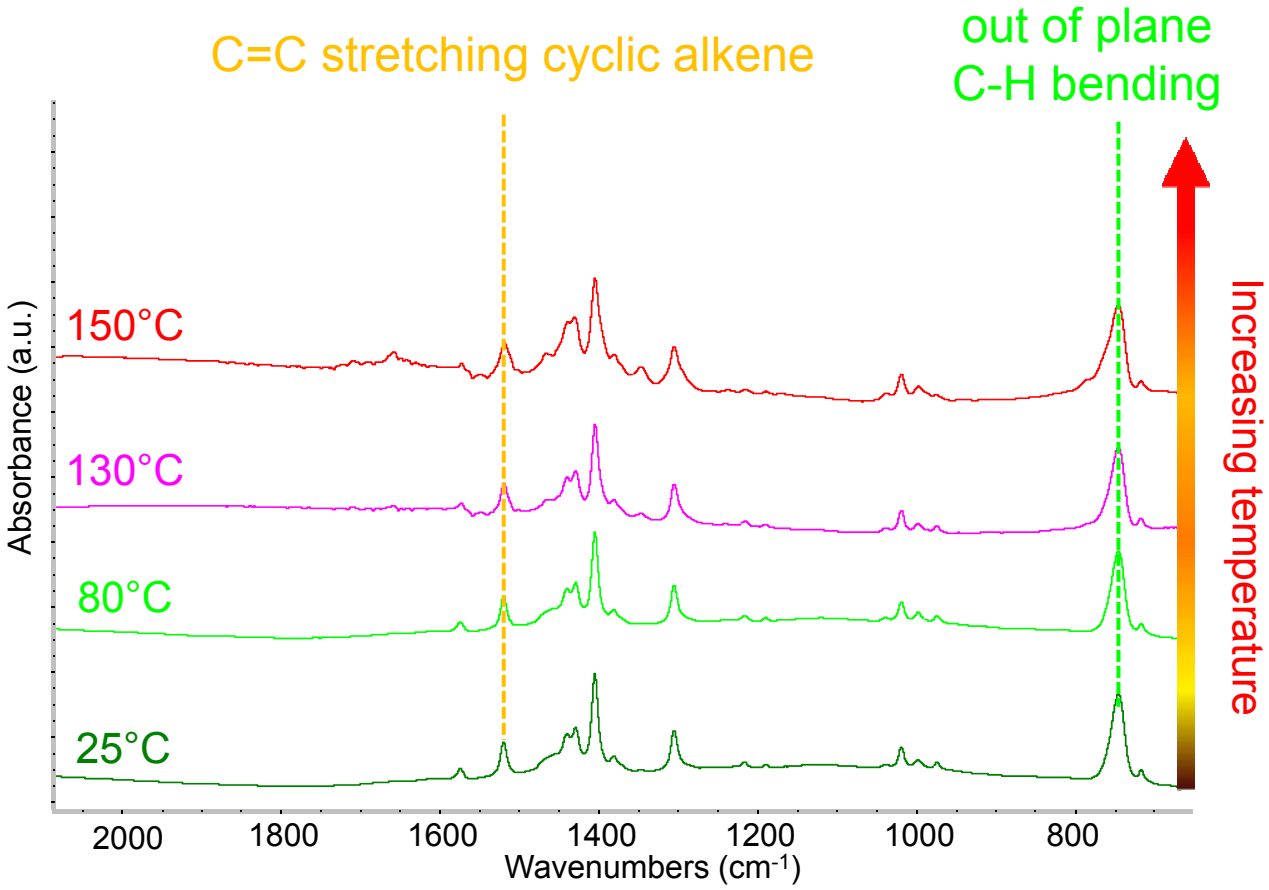
Investigation with a model compound

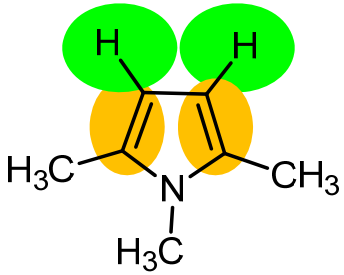


- Analysis of: liquids, HSAG/TMP adducts
- FT-IR and ^{1}H-NMR spectroscopies
- FT-IR spectra generation with Density Functional Theory (DFT) quantum chemical modelling

TMP + Air - From 25°C to 150°C

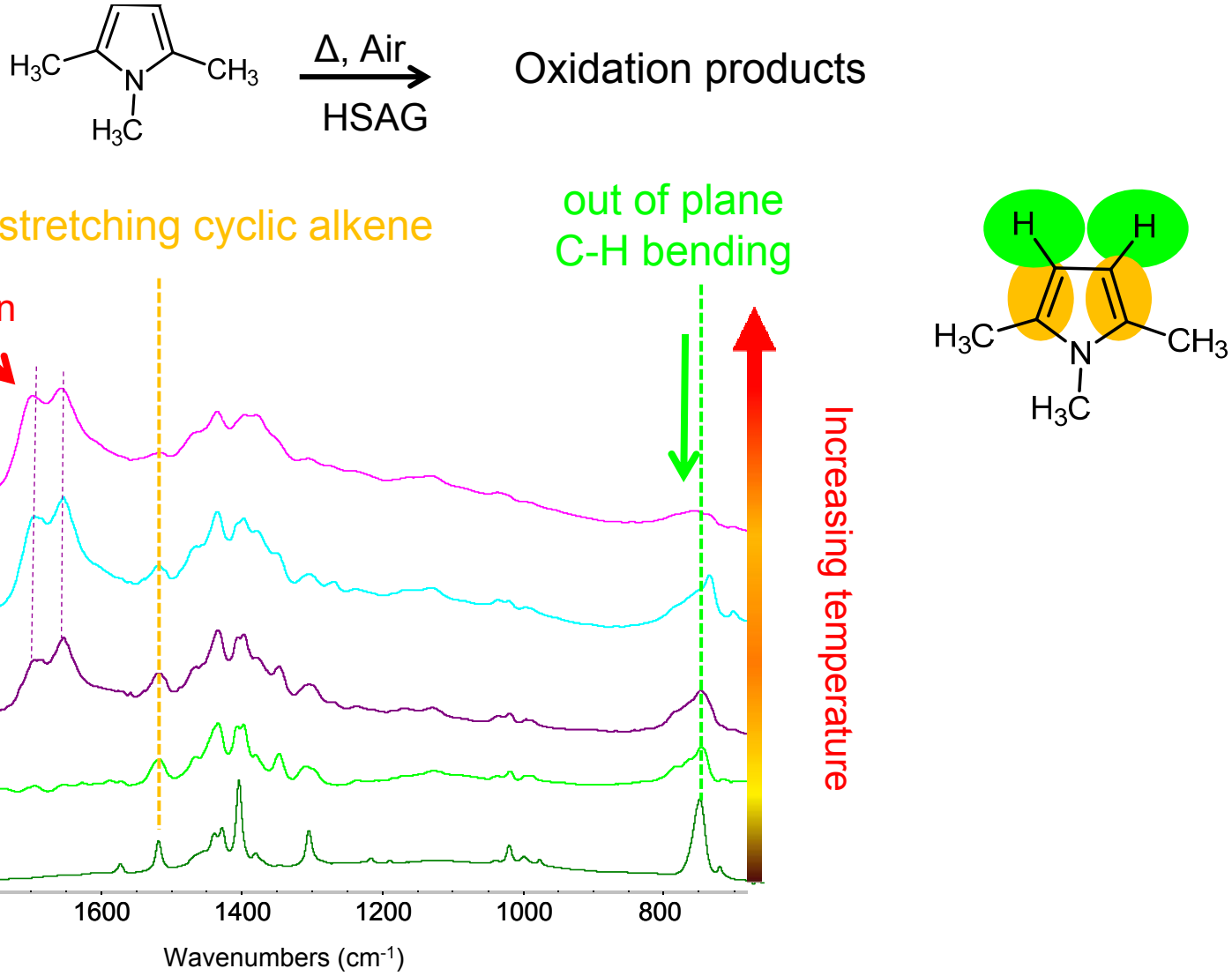






V. Barbera, L. Brambilla, C. Castiglioni, A. Milani, A. Palazzolo, M. Galimberti Submitted manuscript 2018

TMP + HSAG - from 100°C to 150°C



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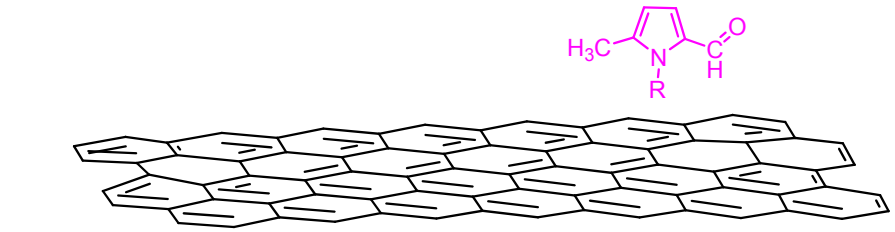
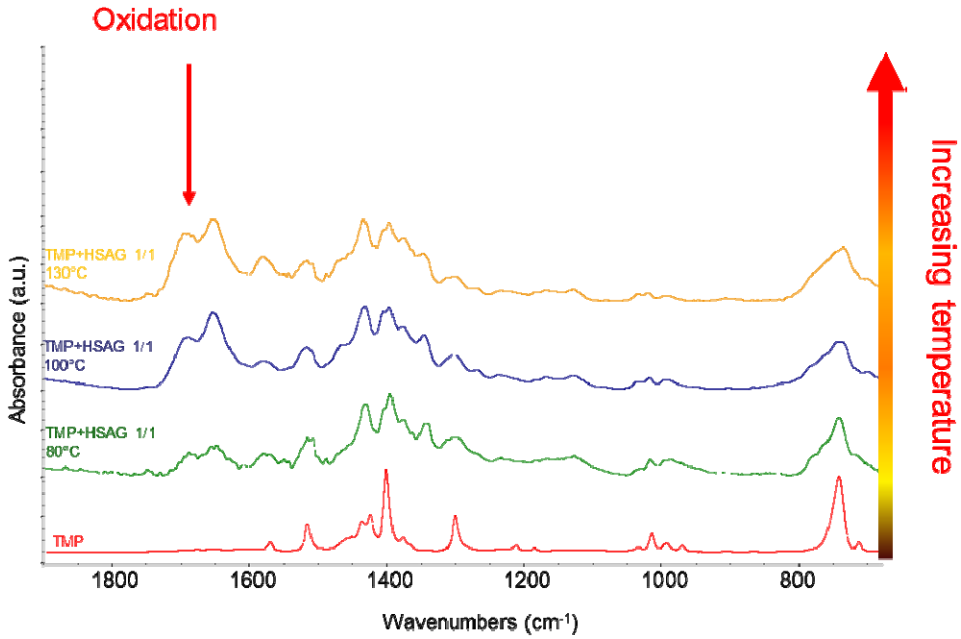
TMP oxidation product



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

* Structure confirmed by means of NMR spectroscopy

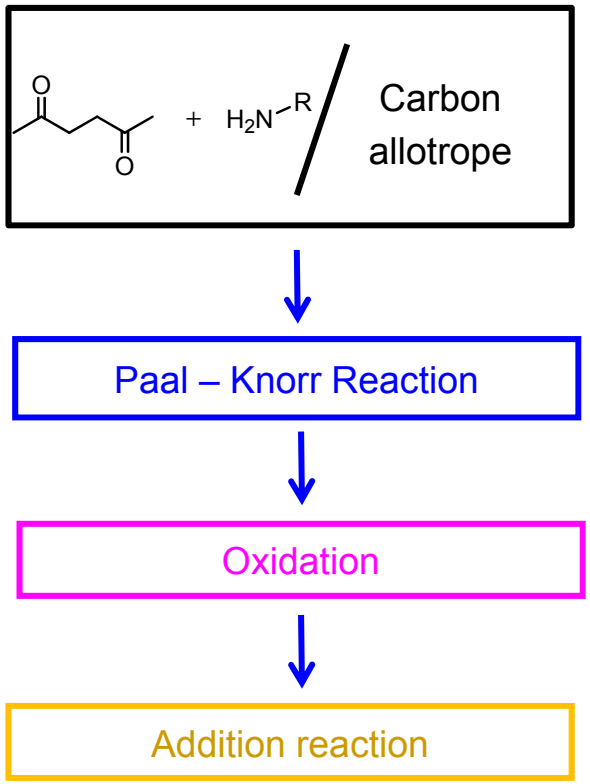


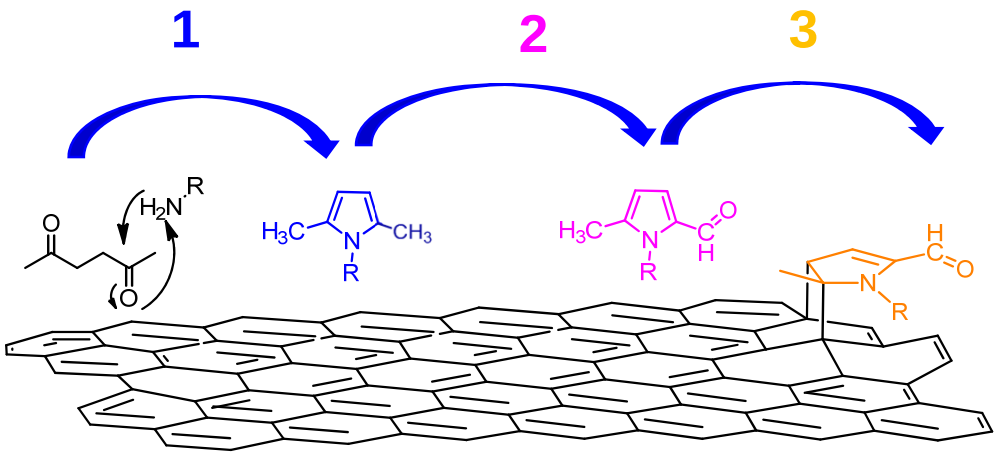
FT-IR and ^{1}H-NMR spectroscopies; FT-IR spectra generation with Density Functional Theory (DFT) quantum chemical modelling

V. Barbera, L. Brambilla, C. Castiglioni, A. Milani, A. Palazzolo, M. Galimberti Submitted manuscript 2018

Facile functionalization of carbon materials

Hypothesis for the mechanism





FT-IR and ^{1}H-NMR spectroscopies; FT-IR spectra generation with Density Functional Theory (DFT) quantum chemical modelling

Functionalization of carbon materials with KOH

Preparation of G-OH

+ KOH

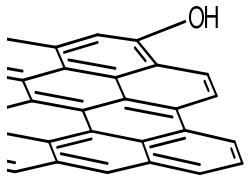
HSAG

130° C, 4h

or by ball milling 6h

G-OH

Polyhydroxylated
few layers graphene



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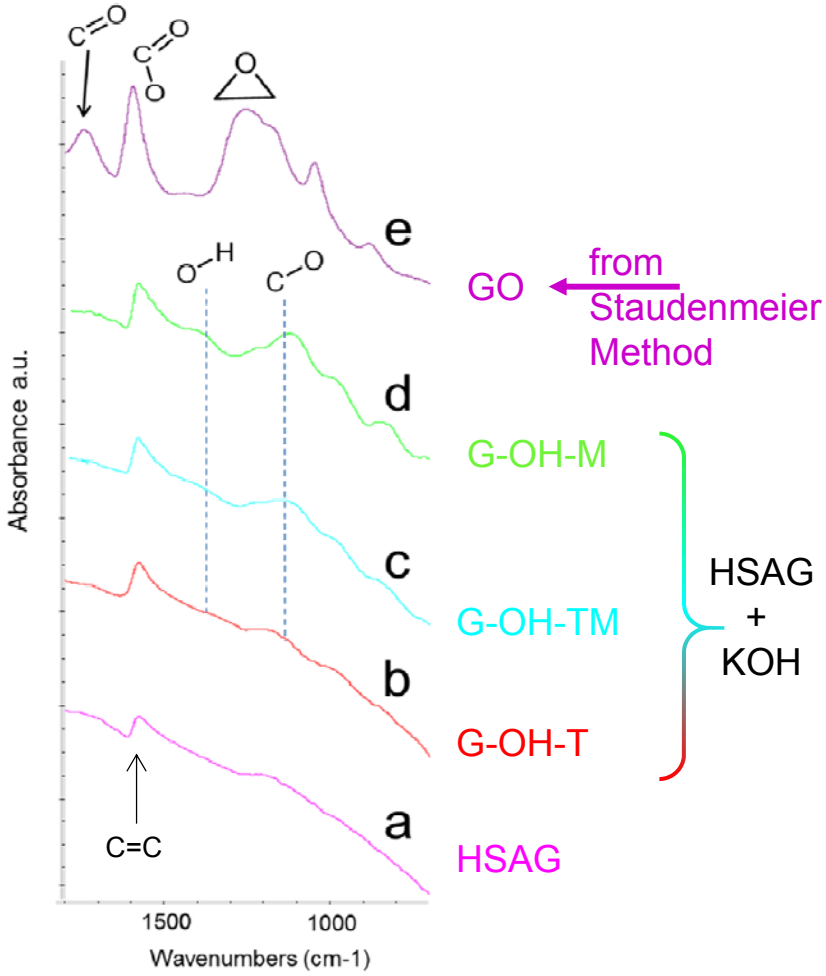
V. Barbera, A. Bernardi, G. Torrisi, A. Porta, M. Galimberti, Elastomery, 2017, 21(4), 235-251

Preparation of G-OH



XPS ☞ Increase of C-O / C=O ratio

	HSAG	G-OH-M
O1s / C1s atomic ratio	0.04	0.07
O atomic %	4.2	6.4

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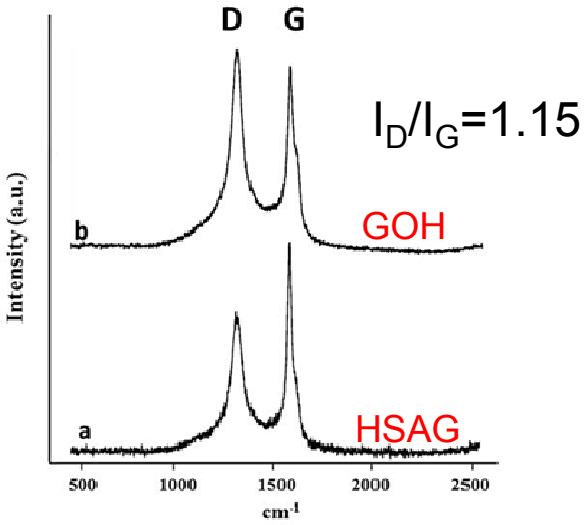

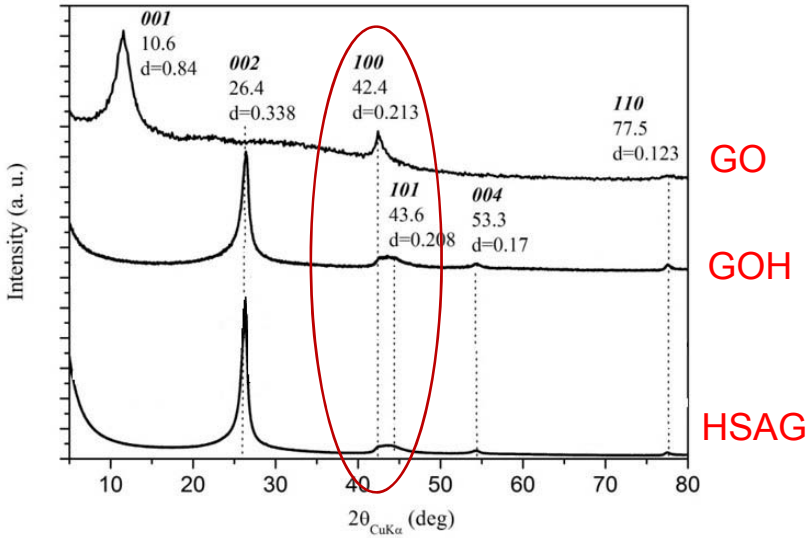

- Selective introduction of OH groups up to 15 mass%
- In plane order substantially unaltered
- No expansion of interlayer distance

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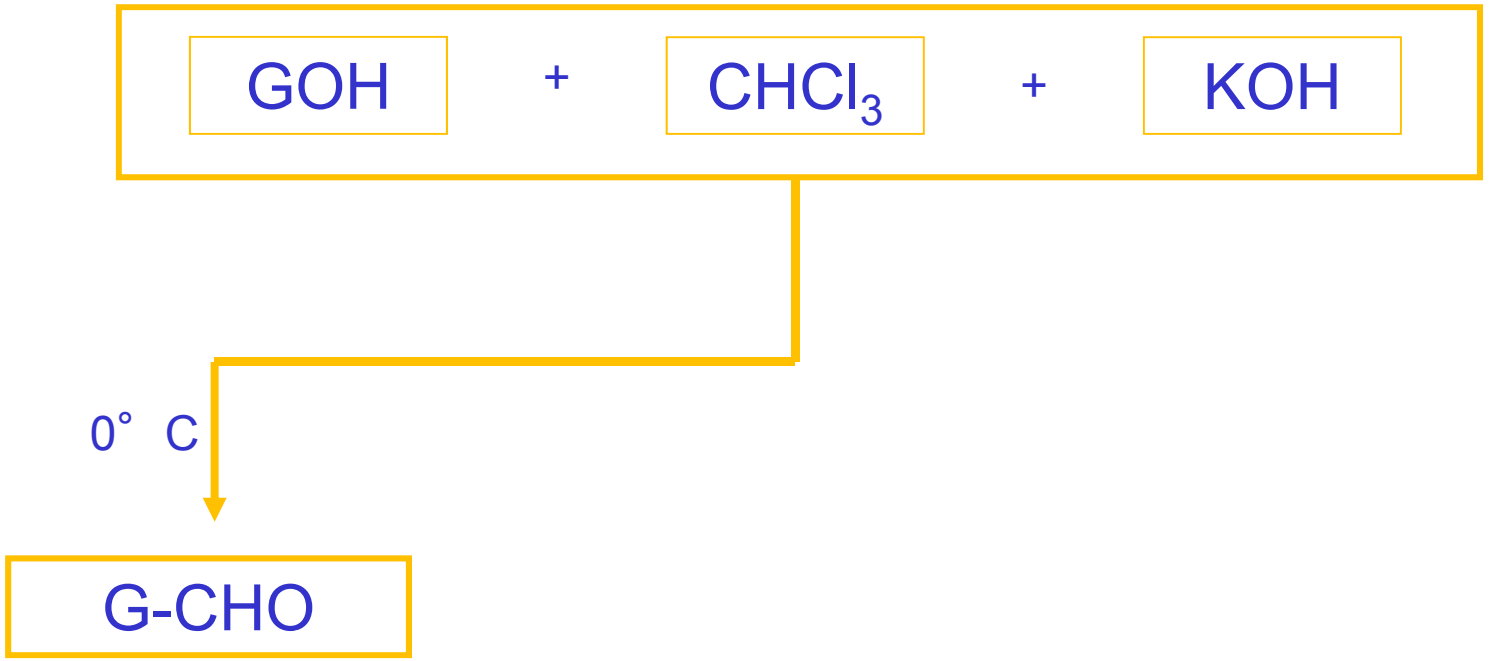
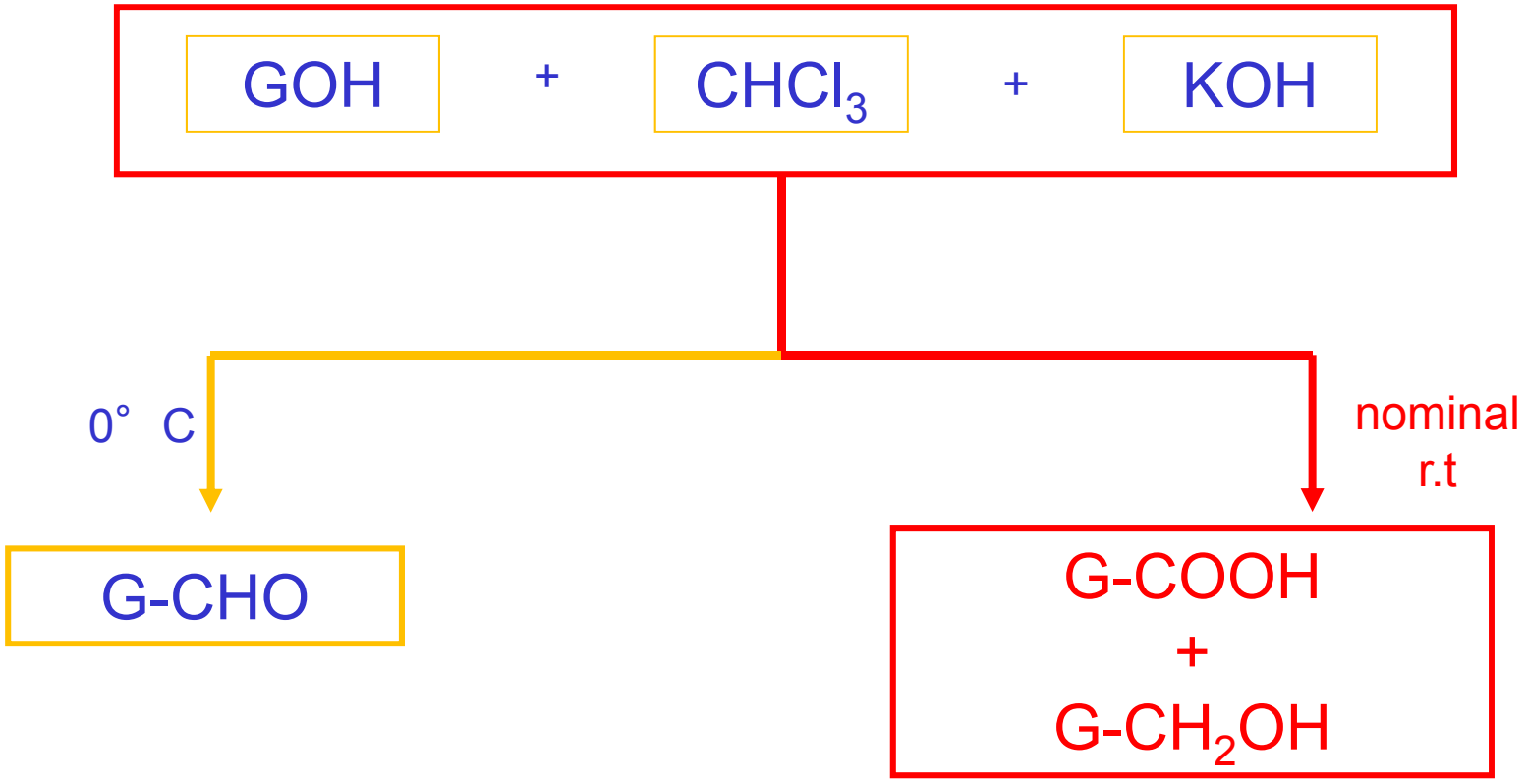
GOH – Polyhydroxylated FLG



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

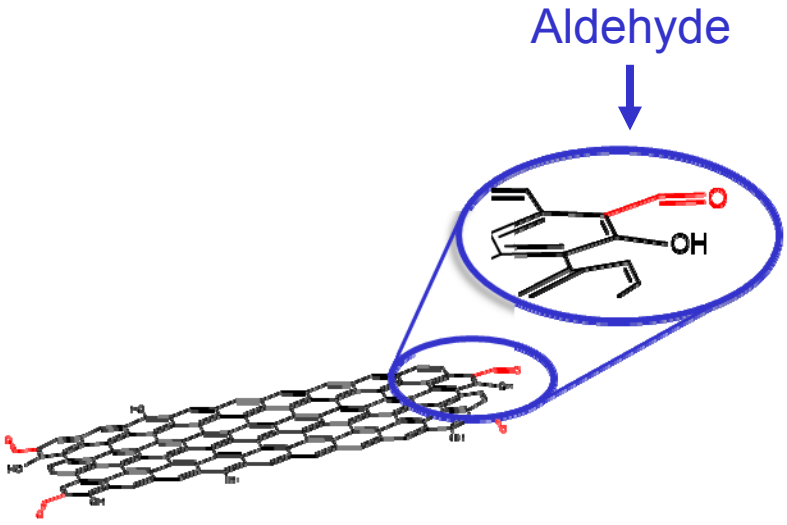
GOH – Polyhydroxylated FLG

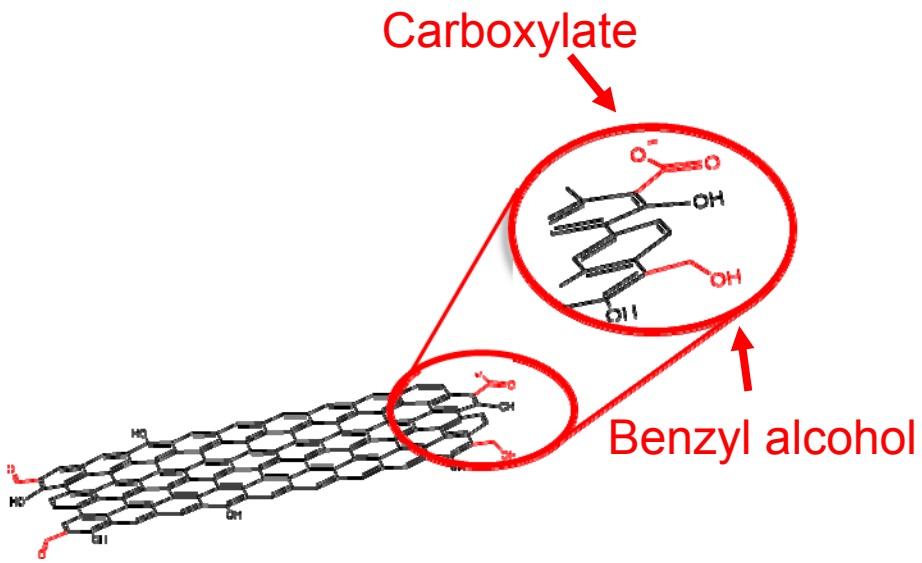


FT-IR, XPS analysis

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

G-CHO and G-COOH FLG





G-CHO

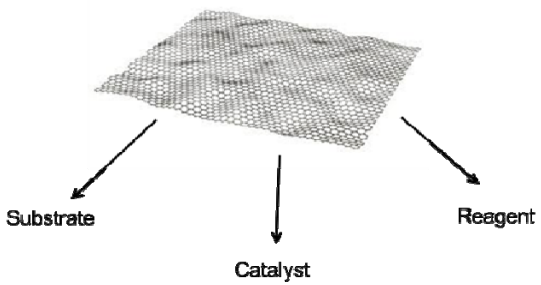
G-COOH
+
G-CH_2OH

Reimer -Tiemann

Cannizzaro

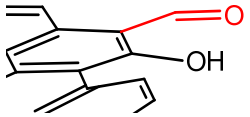
Barbera V., Brambilla L., Porta A., Bongiovanni R., Vitale A., Torrisi G., Galimberti M., Journal of Materials Chemistry A, (2018) 6, 7749-7761.

Reimer-Tiemann - Cannizzaro reactions

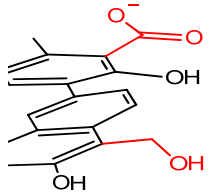


G-OH

G-CHO

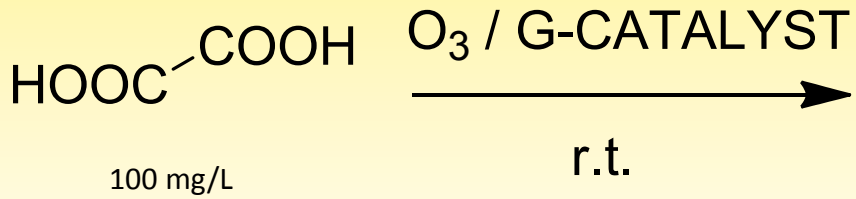


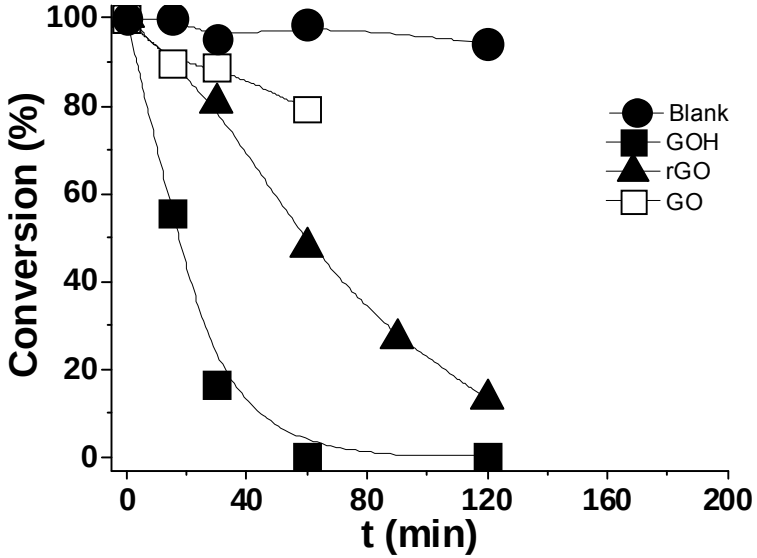
G-COOH



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

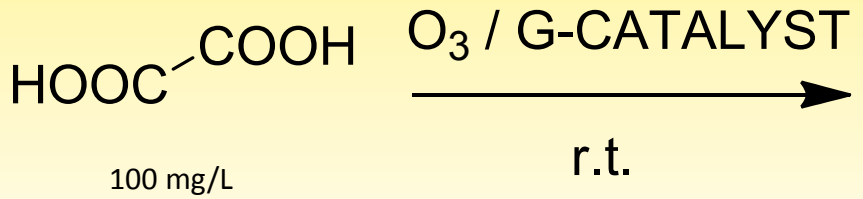
G-OH and derivatives as catalyst for Ozonation

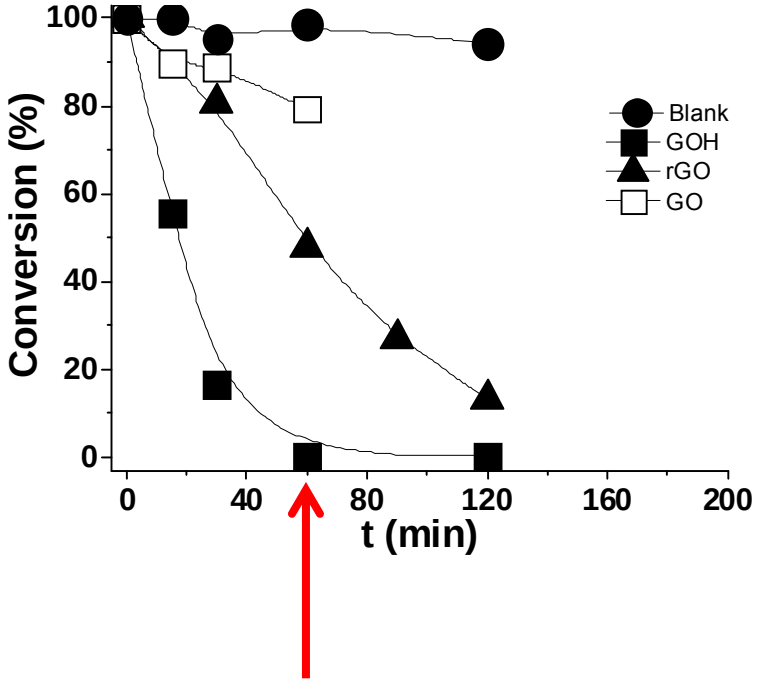




Navalon S., Barbera V., Galimberti M. et al , Manuscript in preparation.

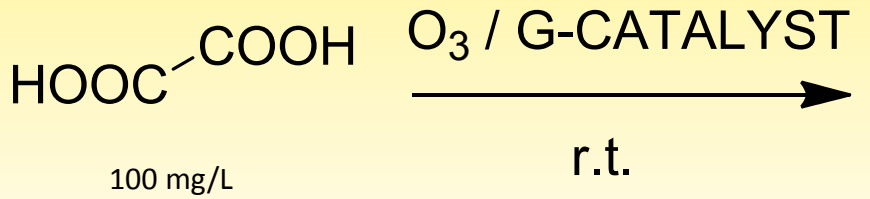
G-OH and derivatives as catalyst for Ozonation

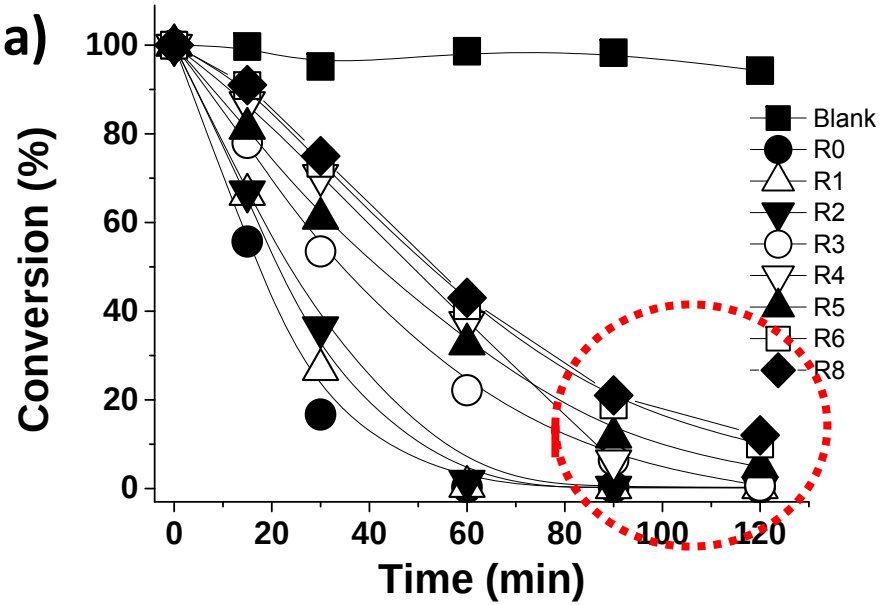


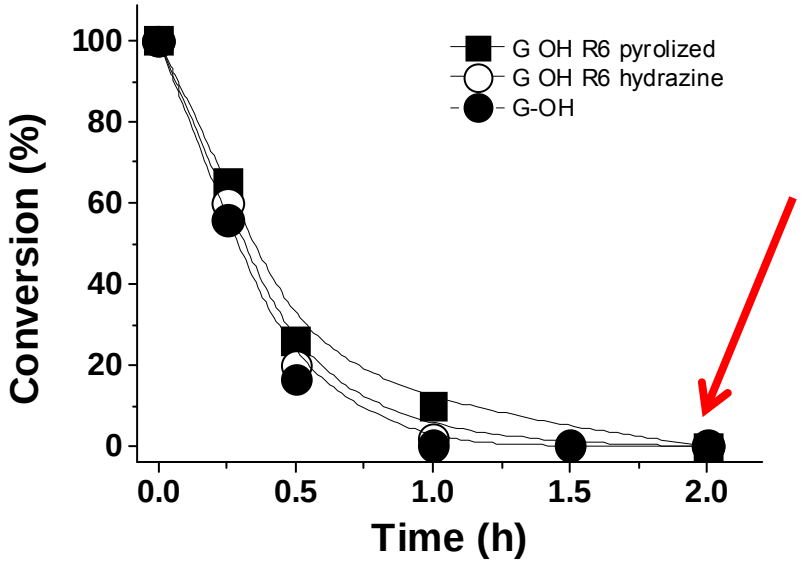


Navalon S., Barbera V., Galimberti M. et al , Manuscript in preparation.

G-OH and derivatives as catalyst for Ozonation







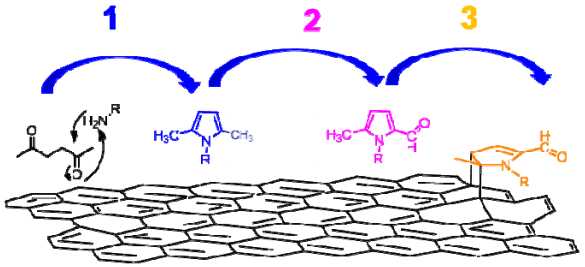
Navalon S., Barbera V., Galimberti M. et al , Manuscript in preparation.

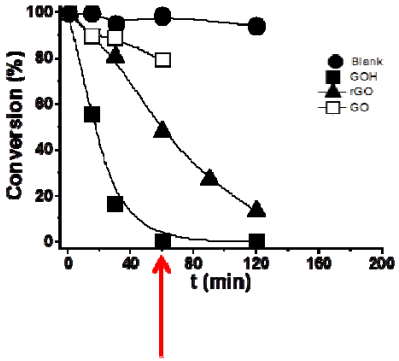
Conclusions

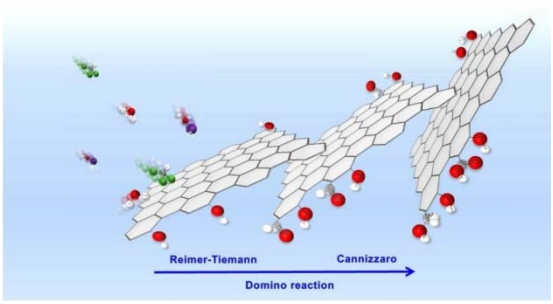
Substrate

Catalyst

Reagent

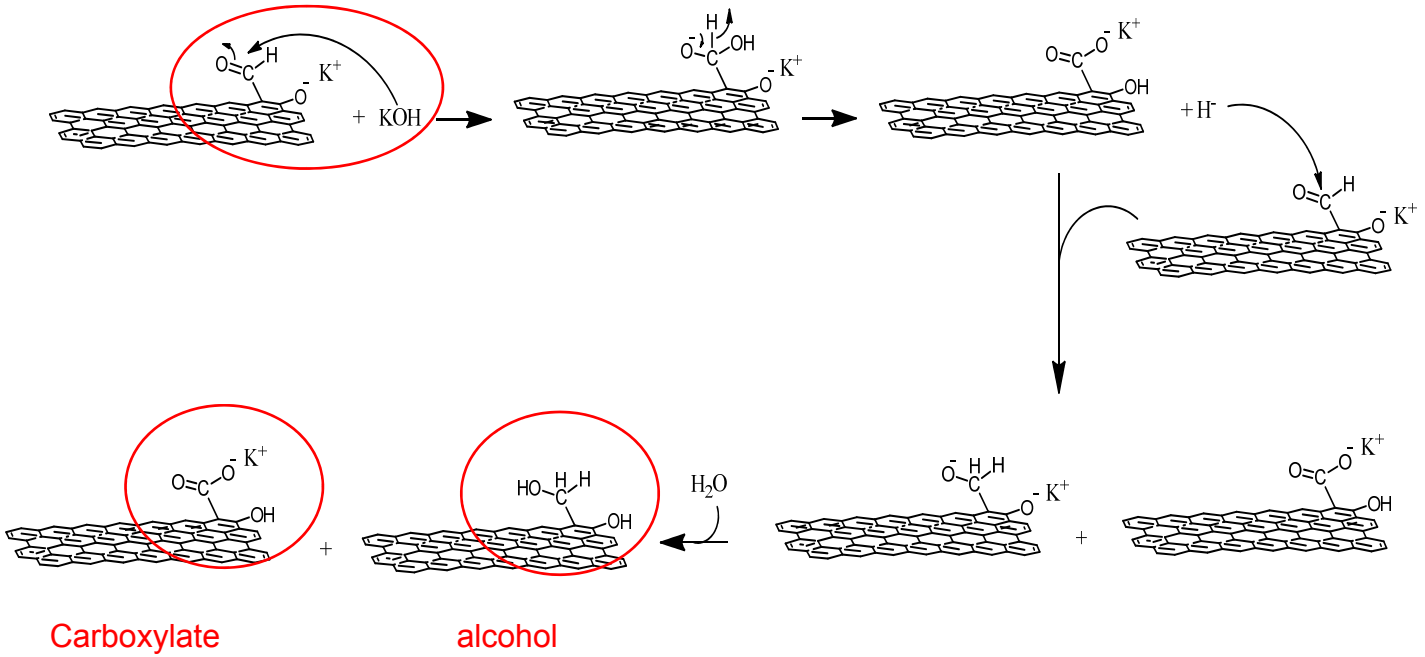






Thanks
for the attention!

Reimer-Tiemann - Cannizzaro carbocatalyzed

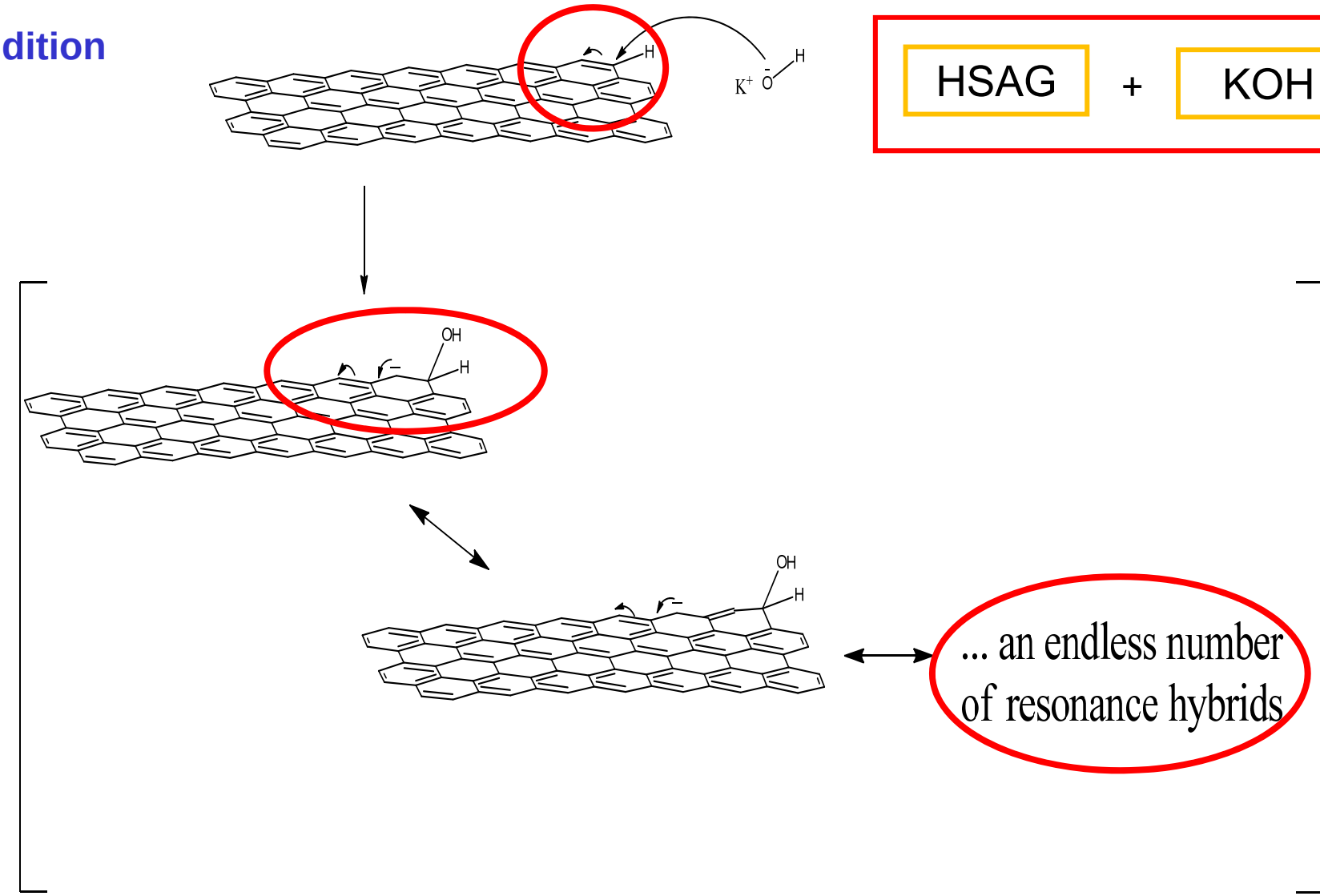


G-(OH)-CH_2(OH)-COOH

V. Barbera, M. Galimberti, Submitted, 2016

Preparation of GOH – Proposed mechanism

Addition



V. Barbera, A. Porta, S. Guerra, A. Serafini, L. Conzatti, M. Galimberti, Submitted, 2016

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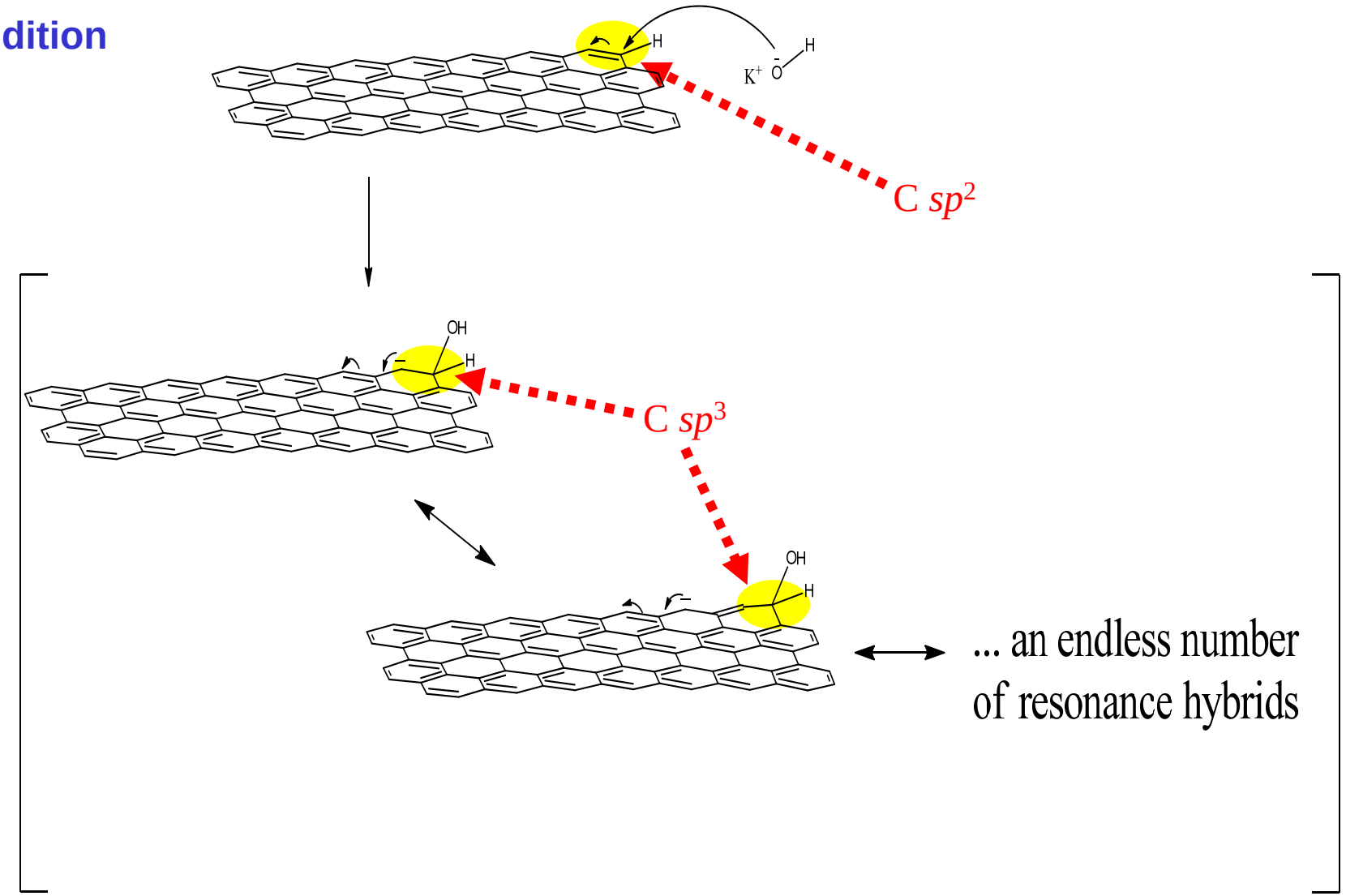
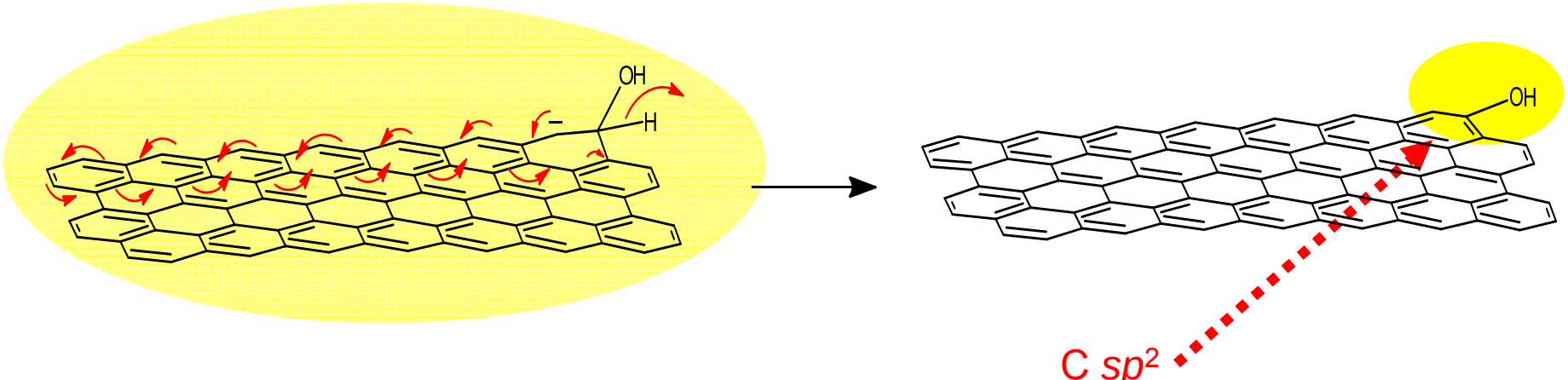


V. Barbera, A. Porta, S. Guerra, A. Serafini, L. Conzatti, M. Galimberti, Submitted, 2016

Preparation of GOH – Proposed mechanism

Elimination

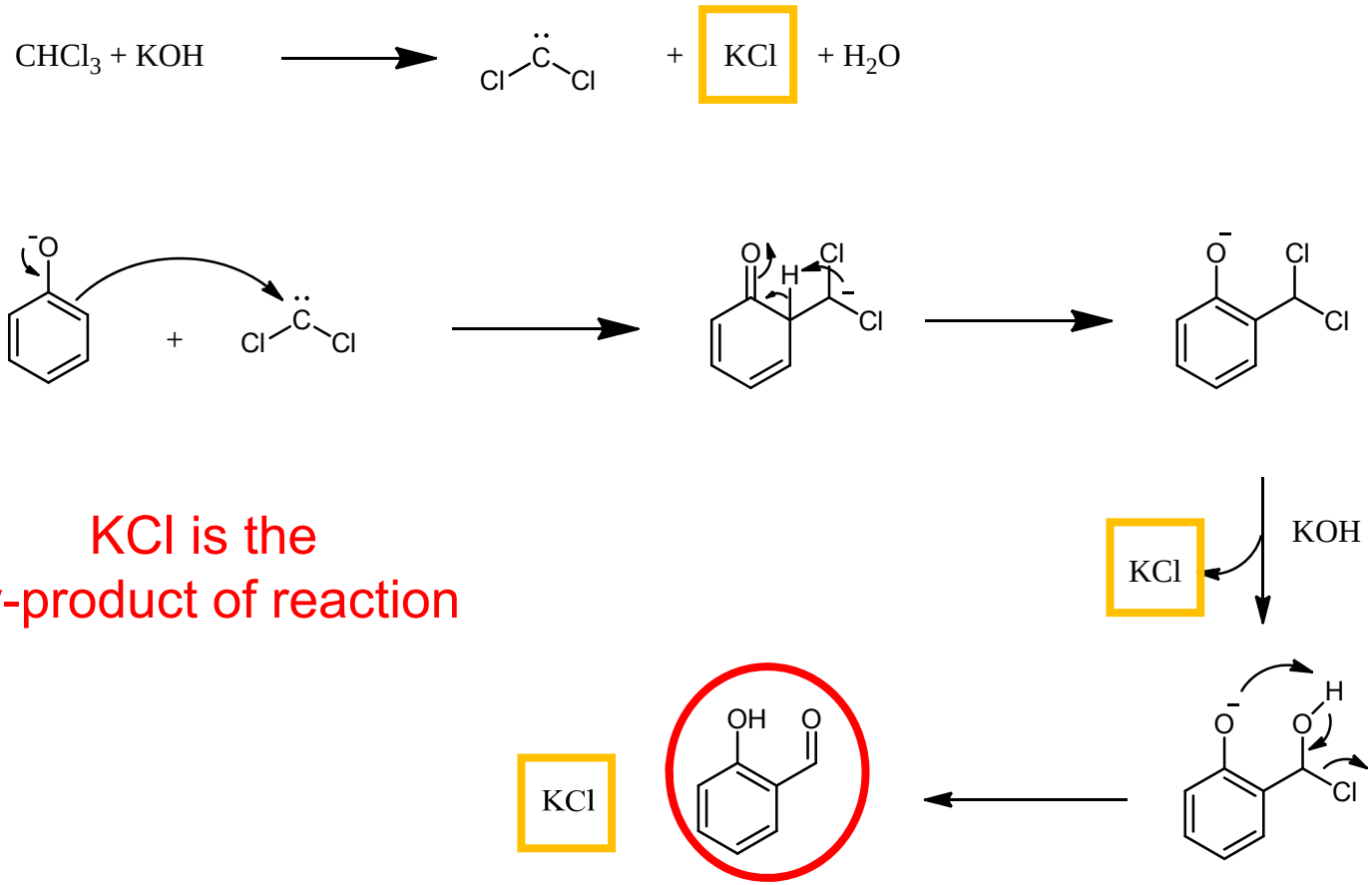


The delocalization on the entire structure and the sp^3 carbon atom in the intermediates,
favour the expulsion of an hydride ion!

"*wave effect*"

More elettronrich structure,
the oxygen lone pairs delocalize on the polyconiugate system

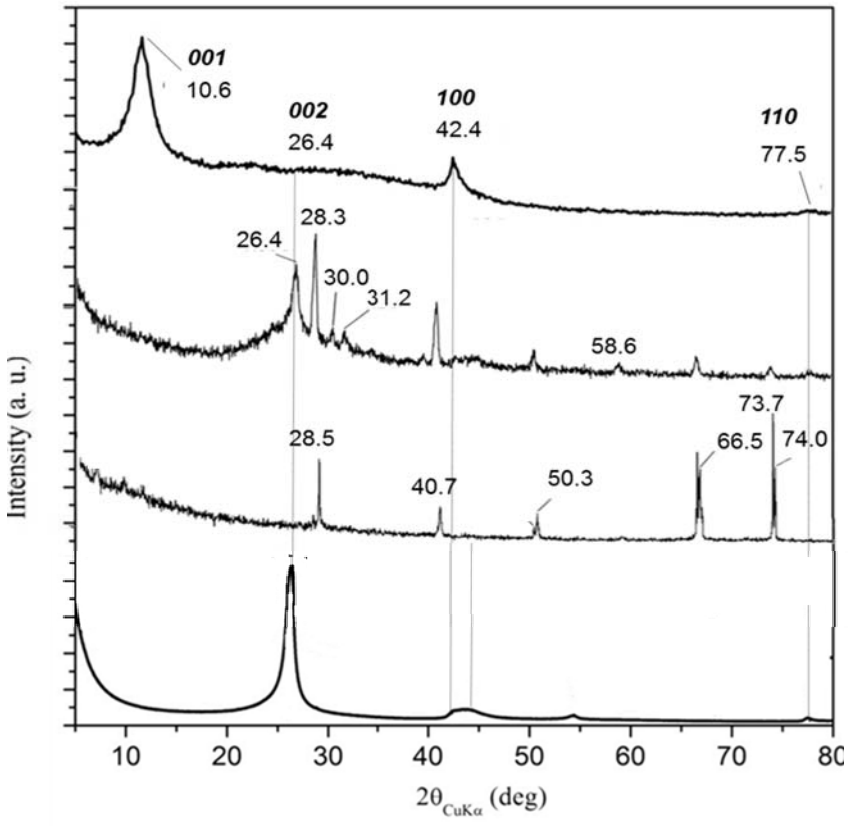
Mechanistic pathway: the Reimer-Tiemann reaction



For each Aldehyde formed
there are also 3 KCl molecules

GOH – The Reimer-Tiemann reaction

XRD patterns



GO Staudenmeier

G(OH)-CHO after purification

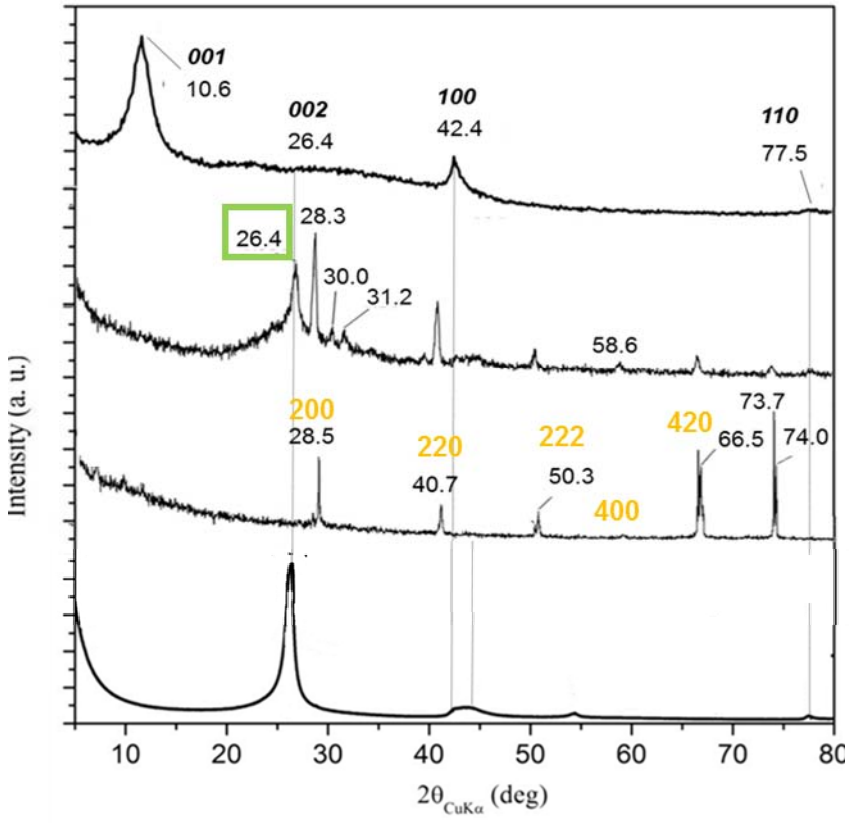
G(OH)-CHO before purification

HSAG

V. Barbera, M. Galimberti, Submitted, 2016

GOH – The Reimer-Tiemann reaction

XRD patterns



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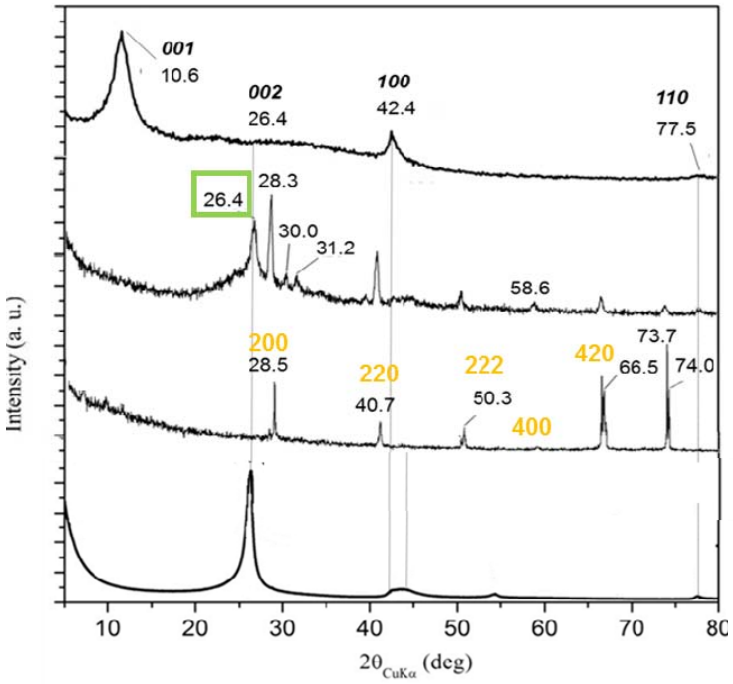
V. Barbera, M. Galimberti, Submitted, 2016

GOH – The Reimer-Tiemann reaction



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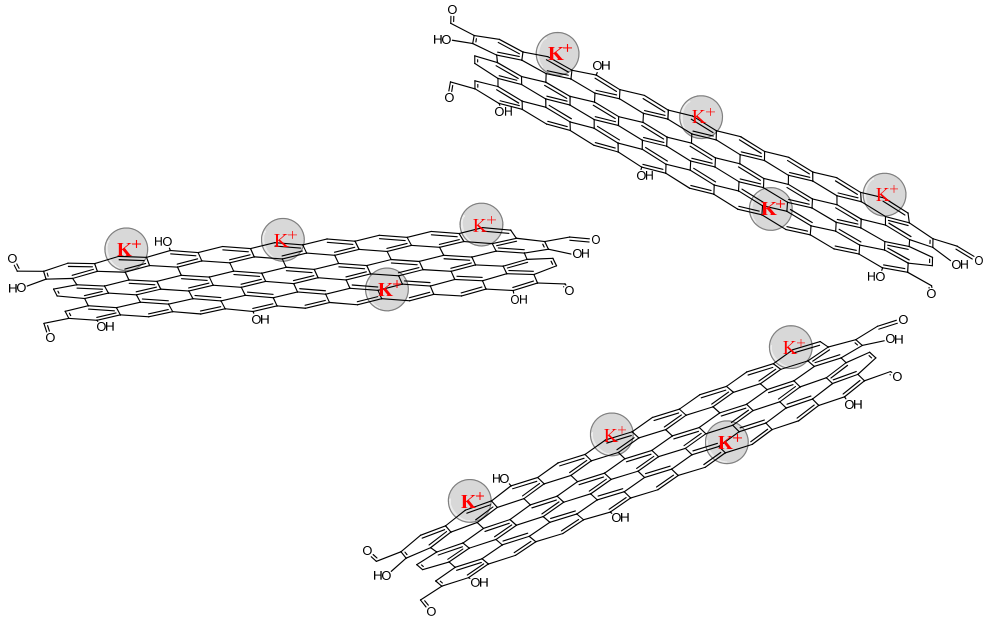

KCl
has the ability to interact
with graphene layers!

V. Barbera, M. Galimberti, Submitted, 2016