Controlled functionalization of sp^2 carbon allotropes for the reinforcement of diene elastomers

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ISCaMaP

Innovative Sustainable Chemistry and Materials and Proteomics Group

Objectives of the research activity

- To reduce the synthetic footprint in carbon allotropes functionalization

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

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

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  in view of the final application: reinforcement of diene elastomers

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

Graphene

stacked

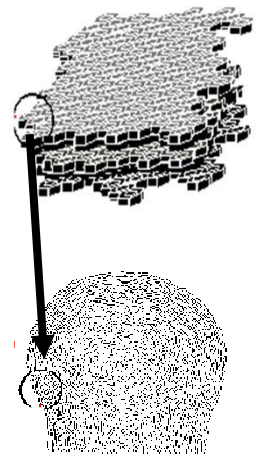
wrapped

stacked graphene layers

randomly arranged

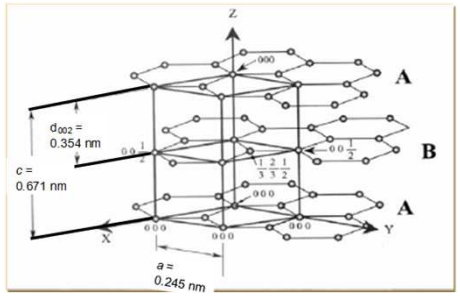
with different shape anisotropy

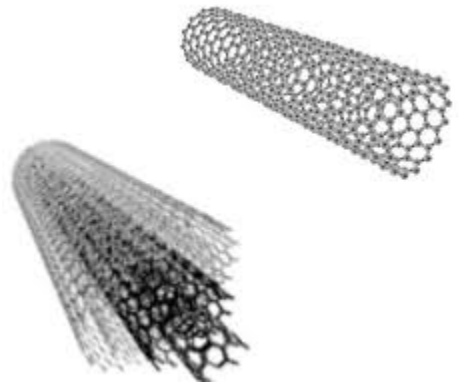
CNT



carbon black

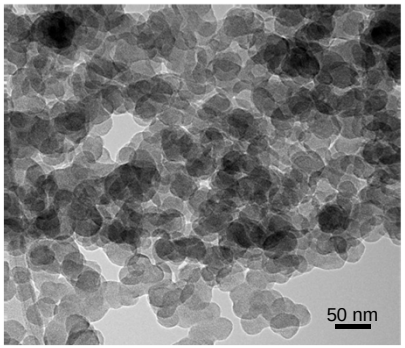
graphite, nano-graphite, graphene

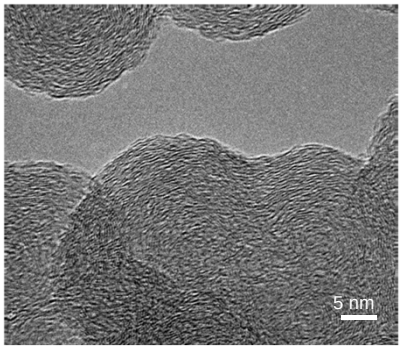




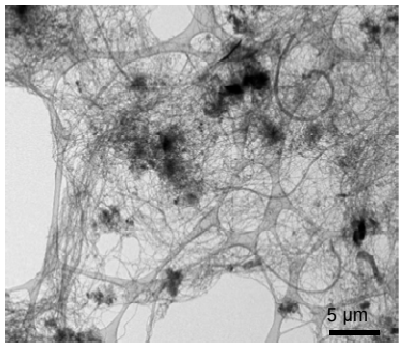
Characterization of carbon allotropes (CA)

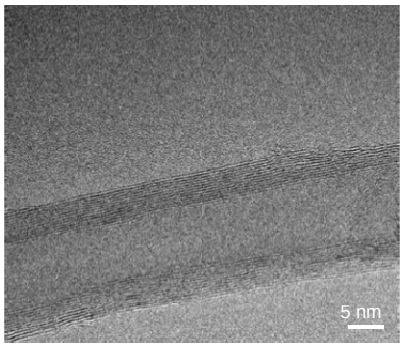
CB



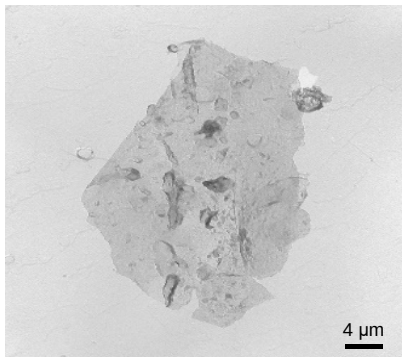


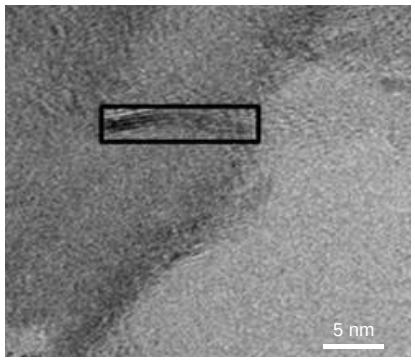
CNT





FLG





High-resolution
transmission electron microscopy
(HR-TEM)

Characterization of carbon allotropes (CA)

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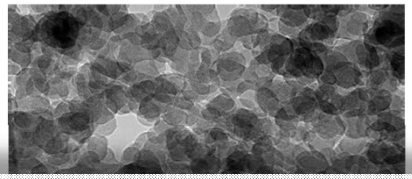
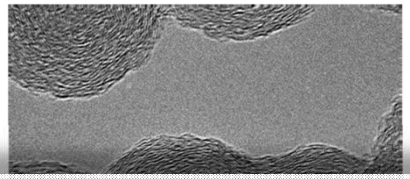




TGA, Elemental Analysis: carbon purity

BET: surface area, activity

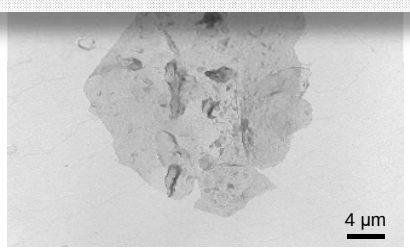
CNT

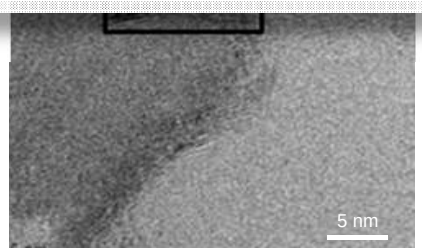
Infrared, XPS: functional groups

Raman, X-ray: bulk structure

FLG

TEM, HRTEM: morphology





High-resolution
transmission electron microscopy
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The starting point: sustainable oxidation

- KOH
- H_2O_2
- Serinol derivative

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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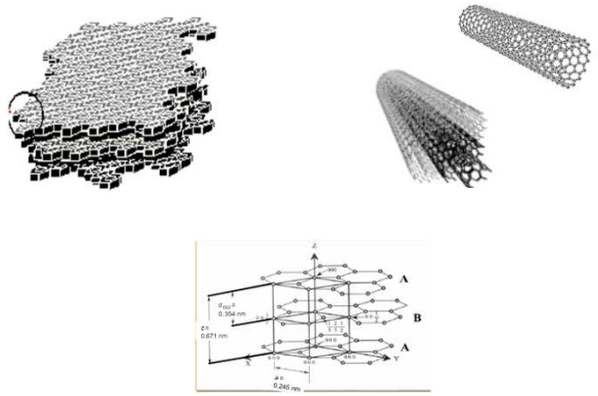

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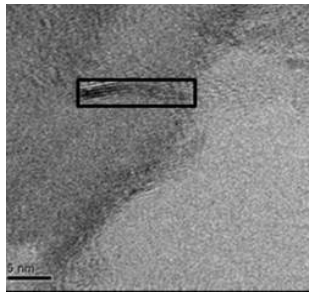
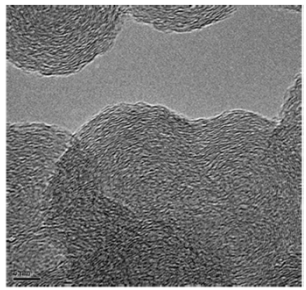
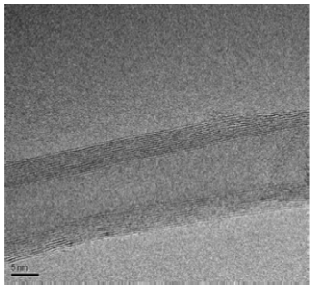

BET Surface area: [m^2/g]	**300**	**77**	**275**
Initial functional groups*: [mmol/g]	**1.7**	**0.9**	**2.0**

* By means of Boehm titration

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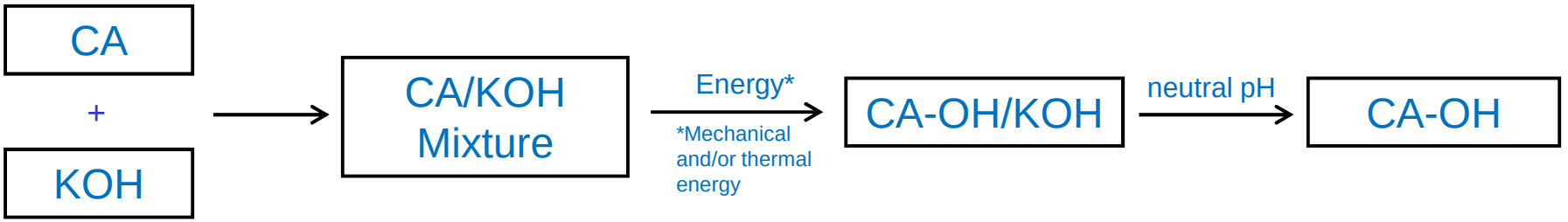

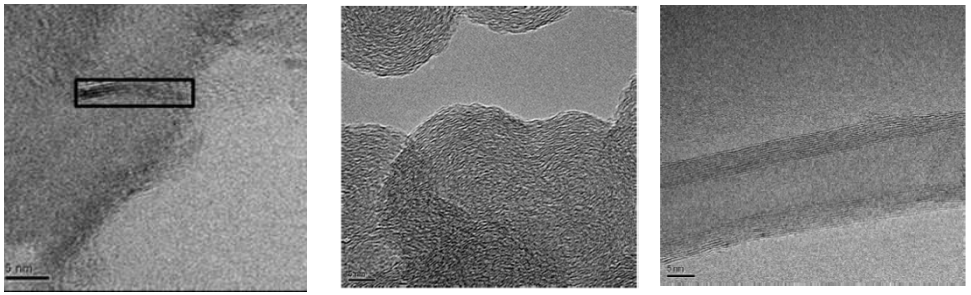

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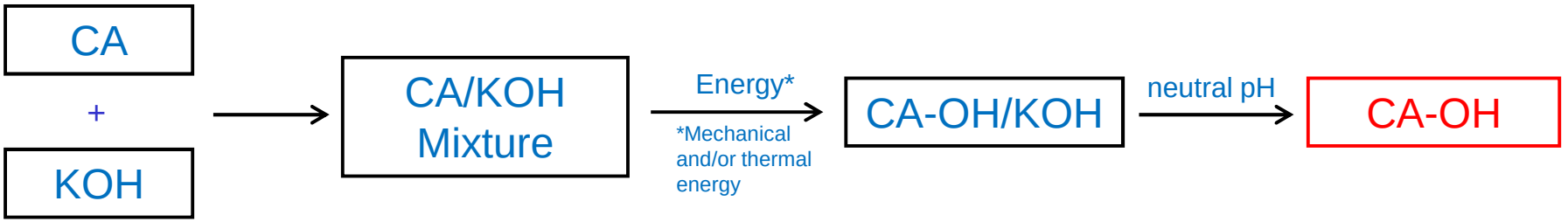

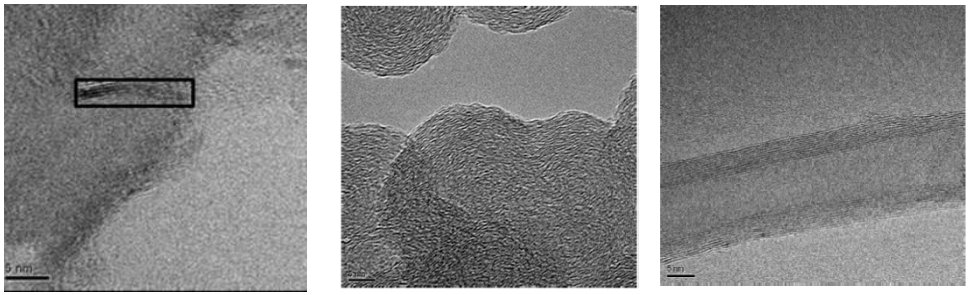

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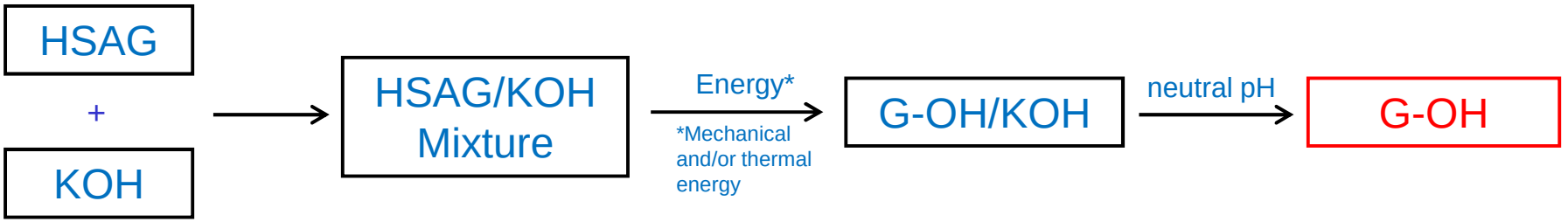
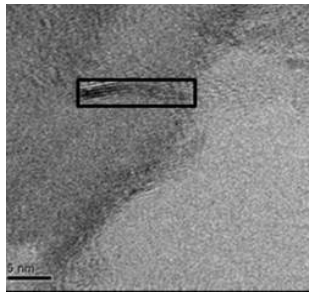
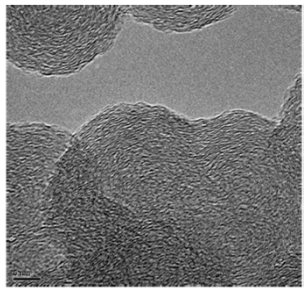
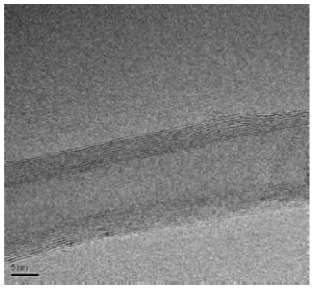
Oxidation of high surface area graphite (HSAG) with KOH









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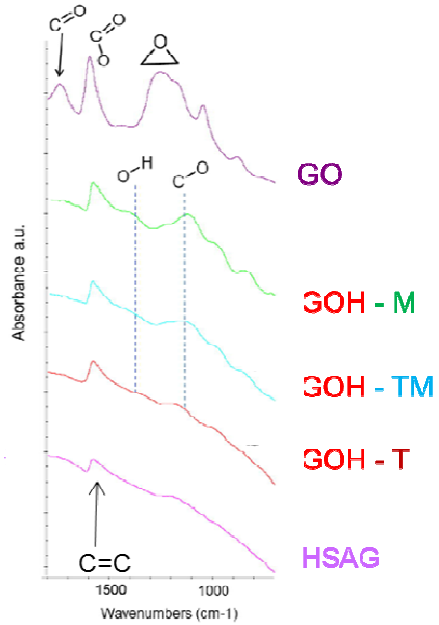
Polyhydroxylated graphene layers from HSAG + KOH



XPS

☞ Increase of C-O / C=O ratio

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

Results from elemental, TGA, IR, XPS, Raman, XRD, HRTEM analysis

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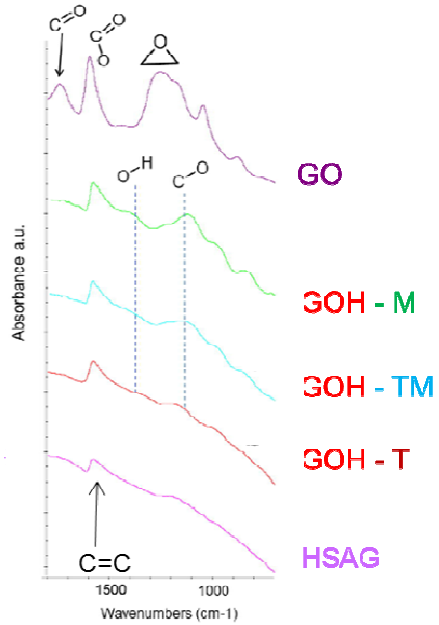

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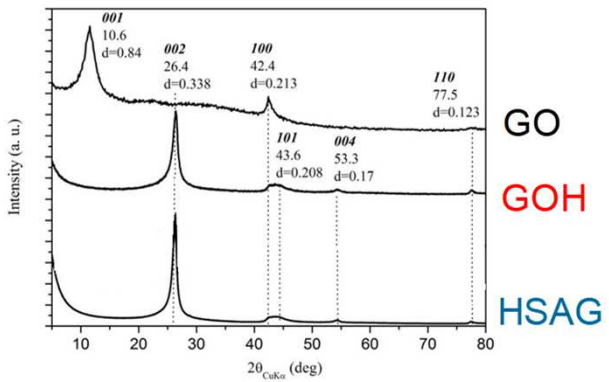
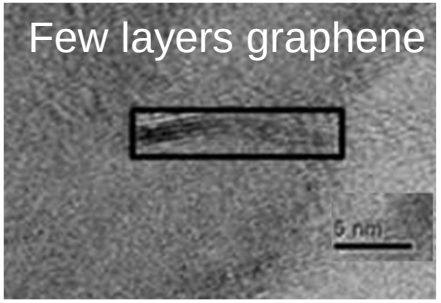
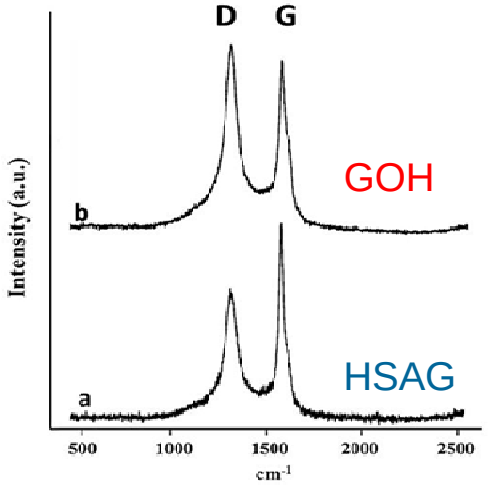




From water suspension



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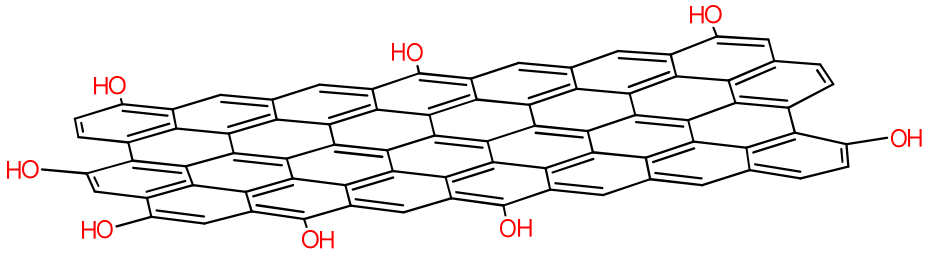
Oxidation of HSAG with KOH



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

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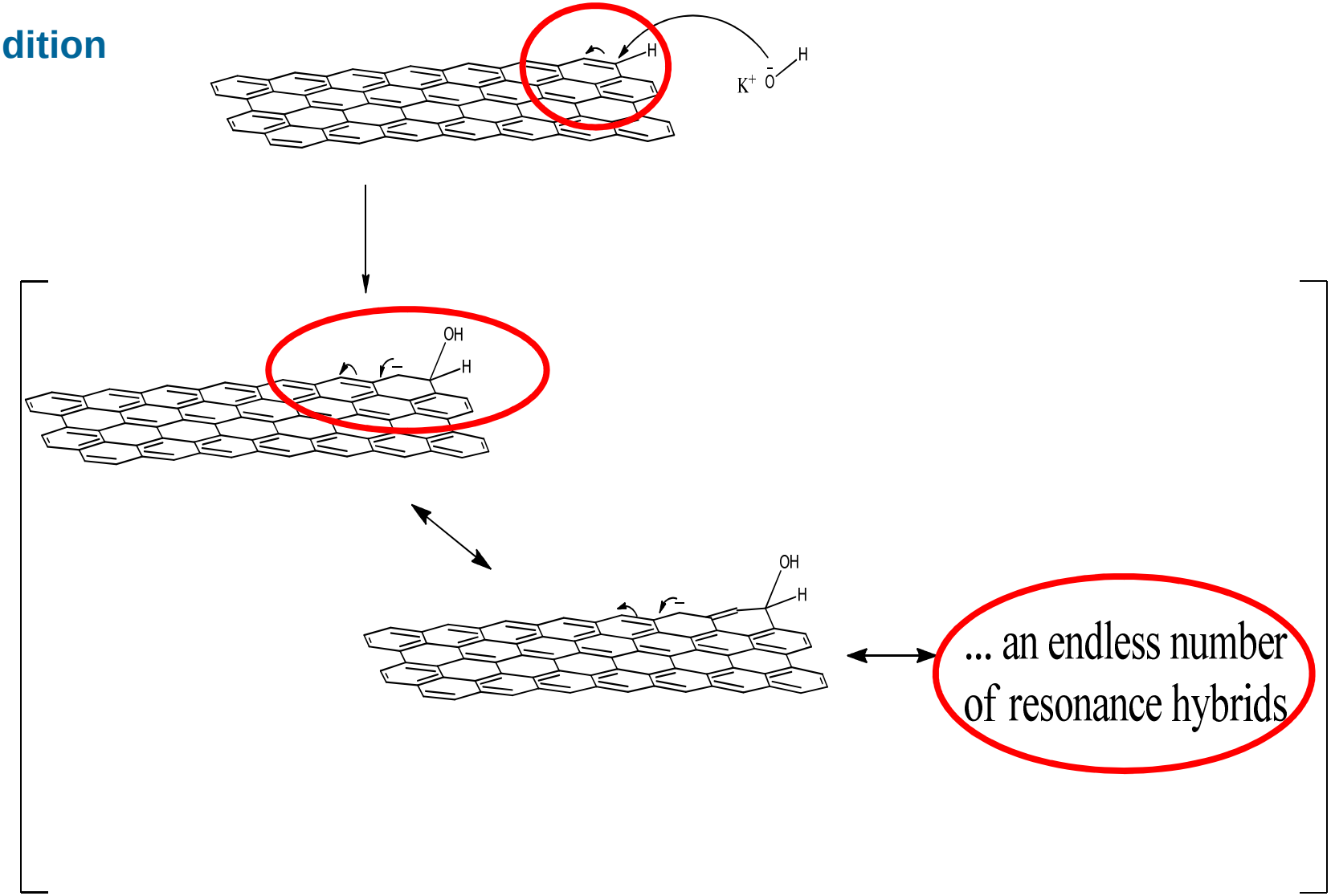
Oxidation with KOH – Proposed mechanism

Addition



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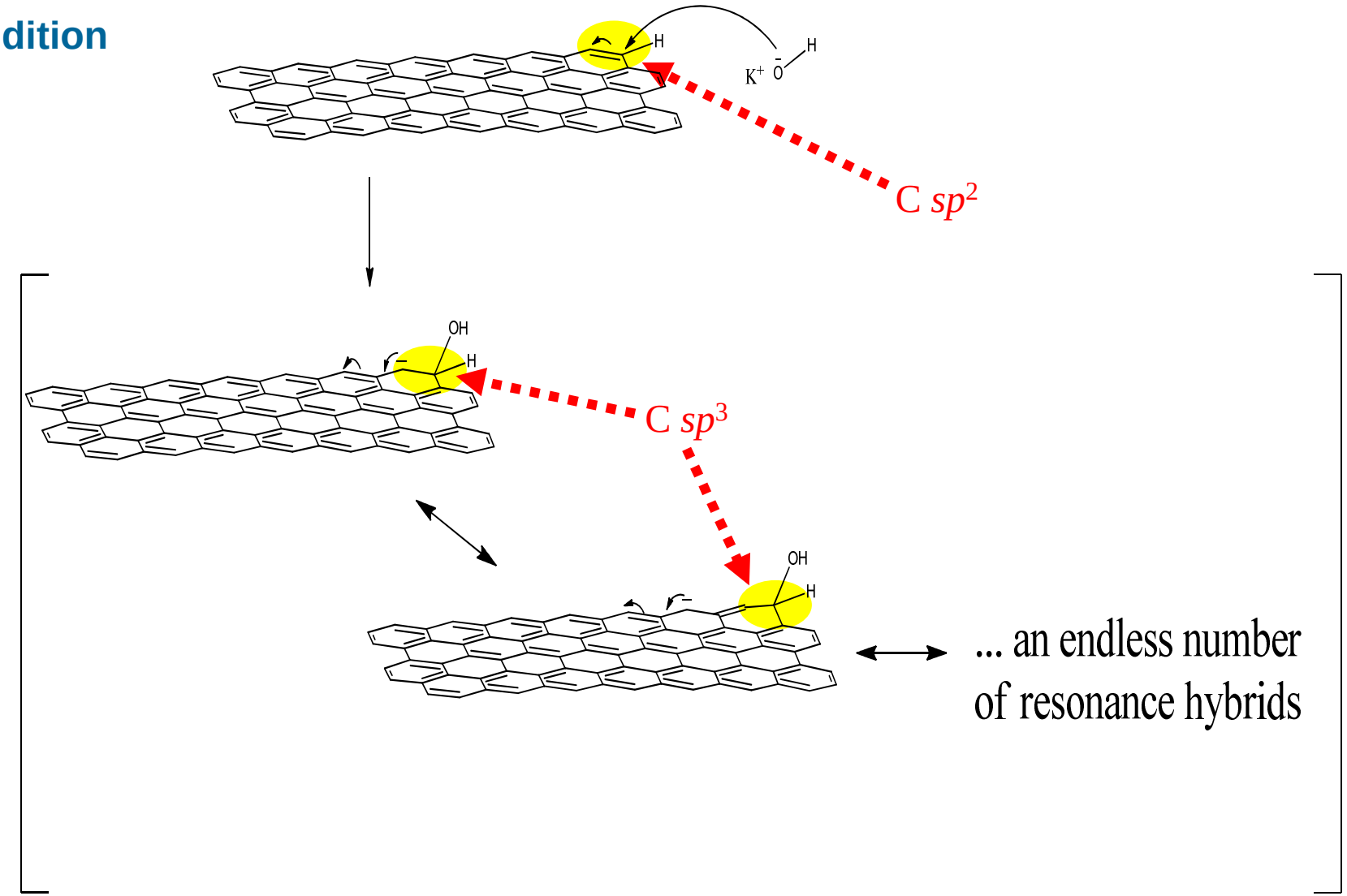

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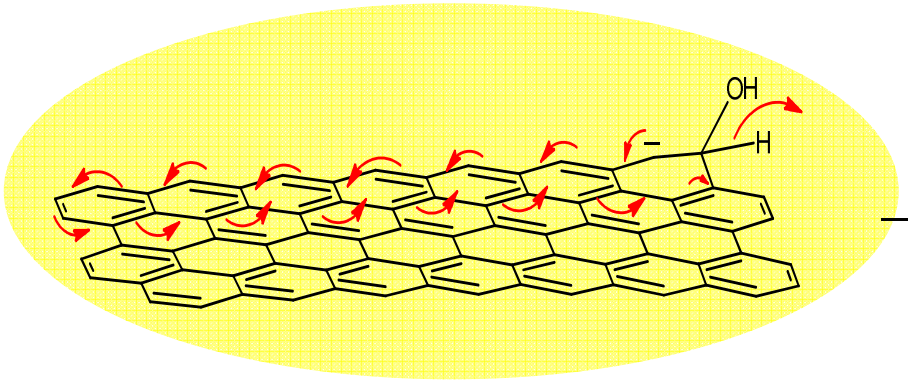
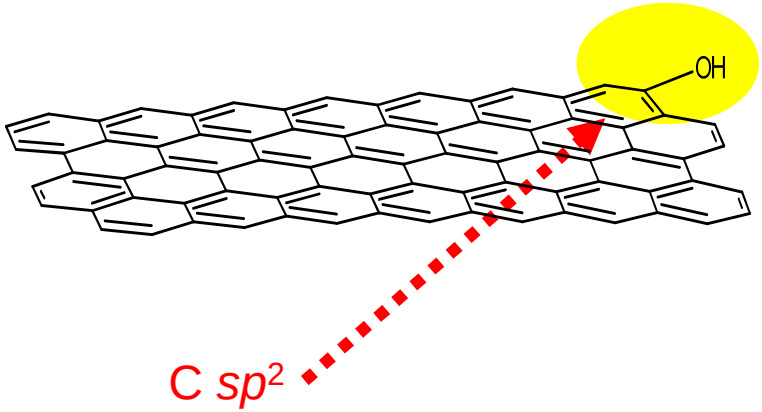
Oxidation with KOH – Proposed mechanism

Elimination





delocalization on the entire structure

"*wave effect*"

<u>More elettronrich structure</u>,
the oxygen lone pairs delocalized
on the polyconjugated system

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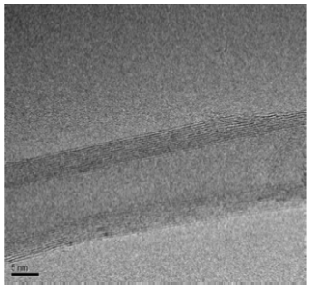
Oxidation of CNT with KOH



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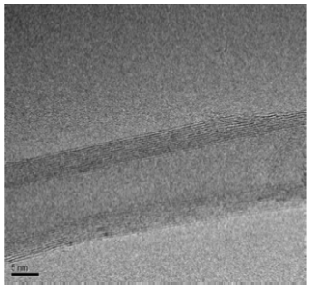

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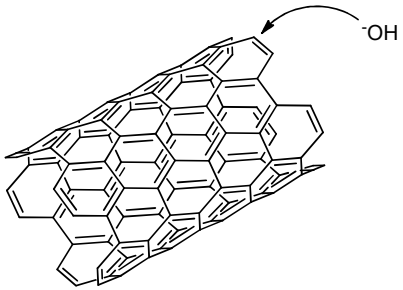
CNT reactivity:



- on defects
- on pentagon or heptagon rings
- Fullerene like cap

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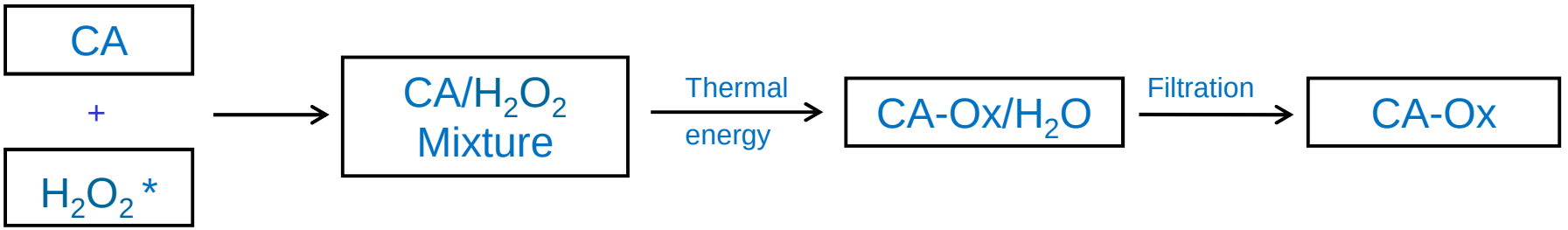
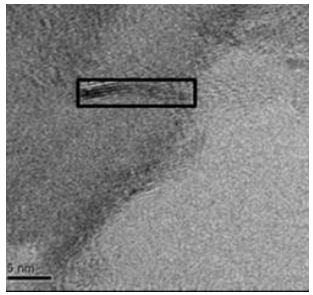
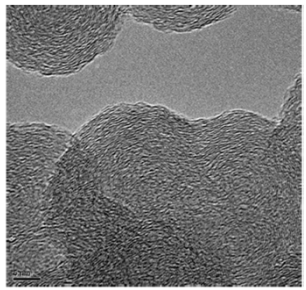
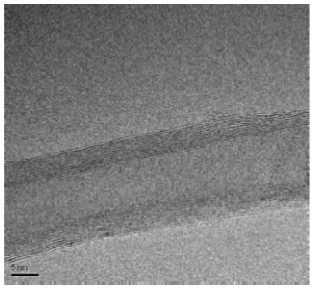
Oxidation of CA with H_2O_2



* 30 % (w/w) in H_2O







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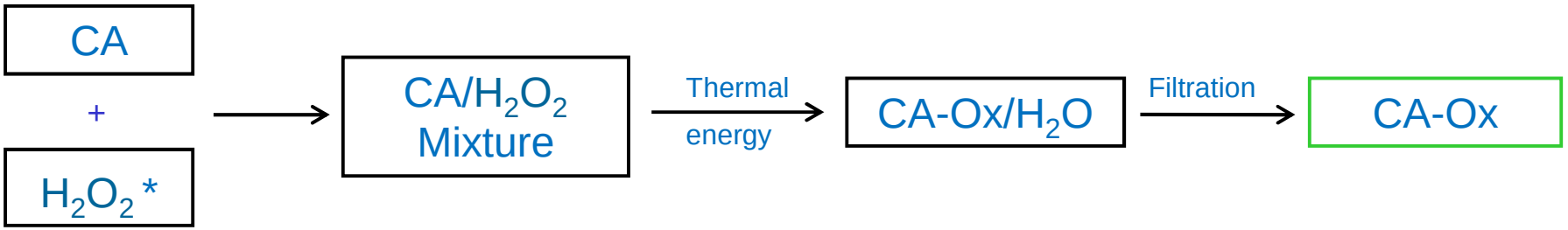
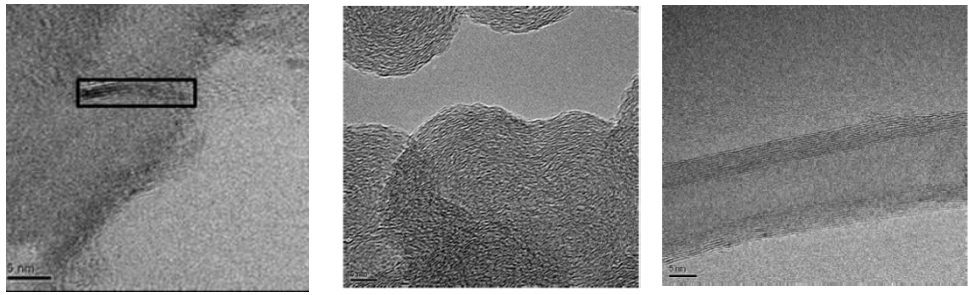
Oxidation of CA with H_2O_2



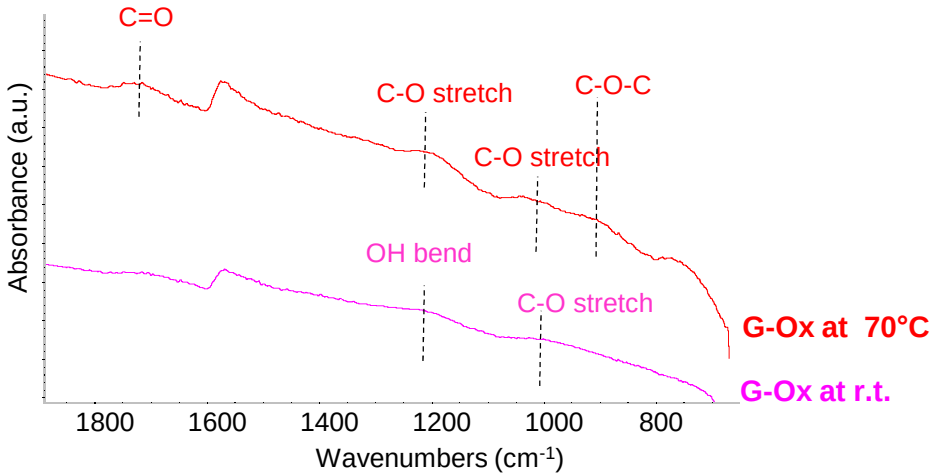
* 30 % (w/w) in H_2O



BET Surface area: [m^2/g]	**300**	**77**	**275**
Initial functional groups: [mmol/g]	**1.7**	**0.9**	**2.0**
Adducts' functional groups: [mmol/g]	**3.1**	**5.8**	**3.2**

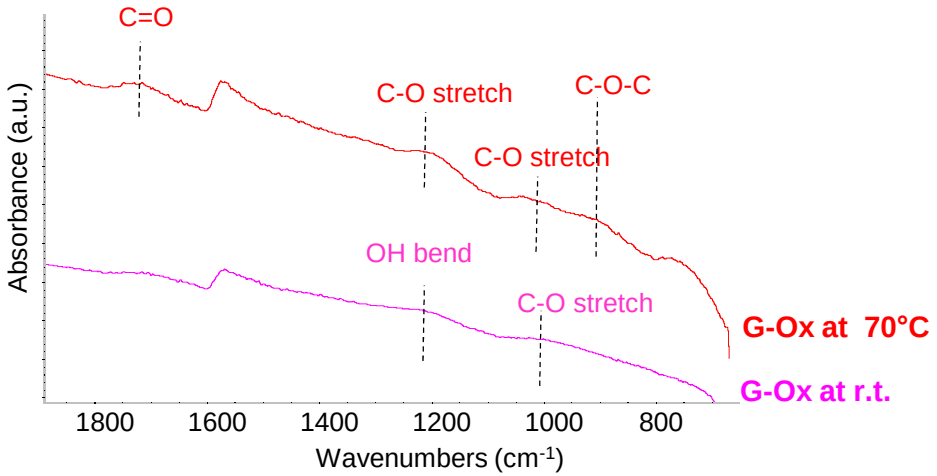
Barbera, V., Bernardi, A., Torrisi, G., Porta, A., Galimberti, M. Elastomery (submitted)

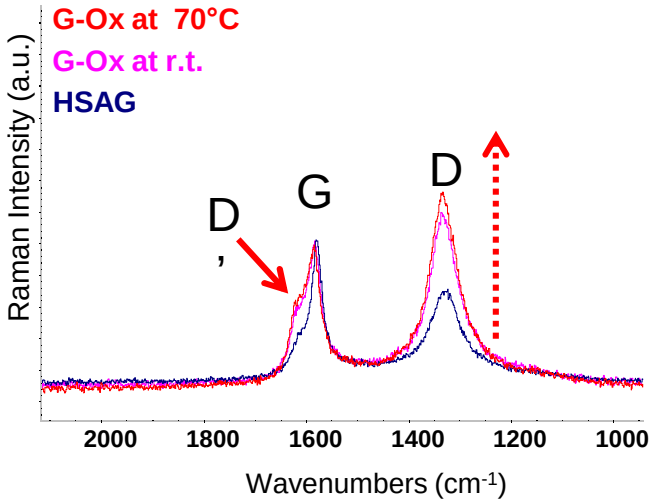
Oxidation of HSAG with H_2O_2

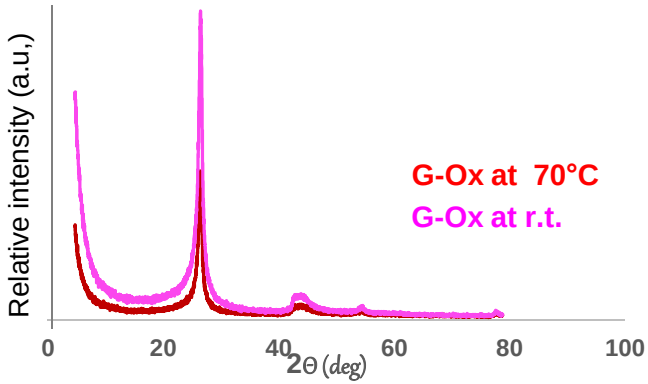


Barbera, V., Bernardi, A., Torrisi, G., Porta, A., Galimberti, M. Elastomery (submitted)

Oxidation of HSAG with H_2O_2



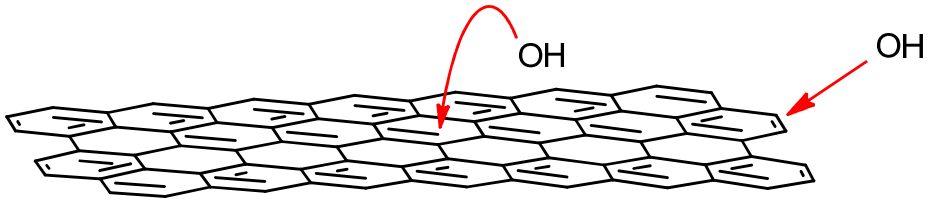




Barbera, V., Bernardi, A., Torrisi, G., Porta, A., Galimberti, M. Elastomery (submitted)

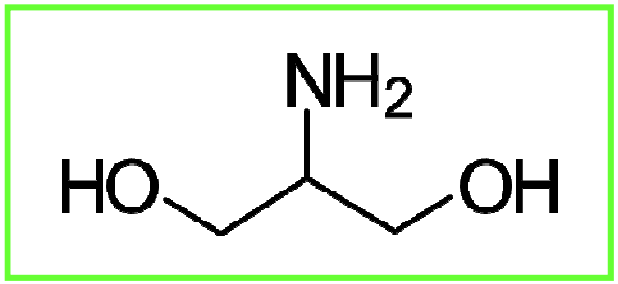
Oxidation of HSAG with H_2O_2

- Selective introduction of OH groups at room temperature
- In plane order substantially unaltered
- No expansion of interlayer distance

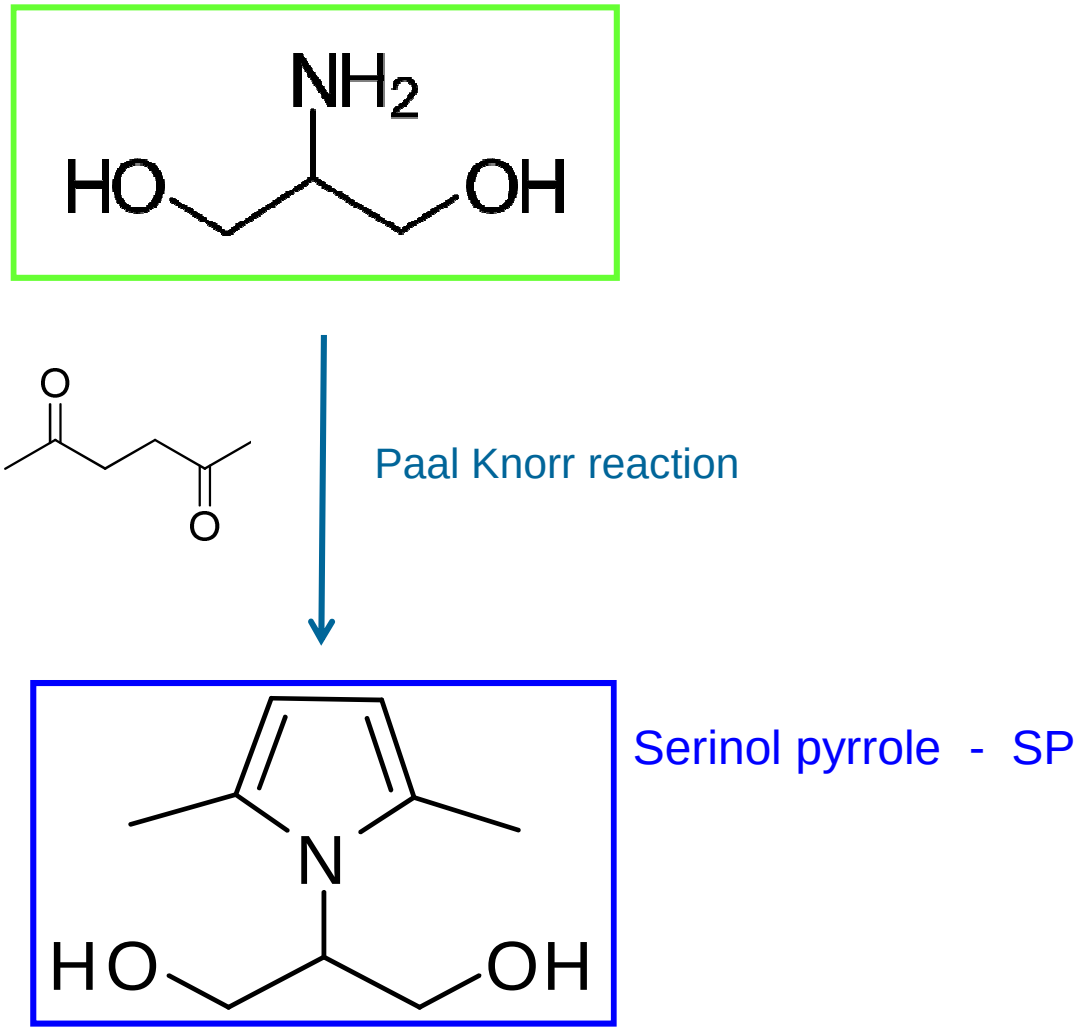


sustainable oxidation

Oxidation of CA with serinol derivative



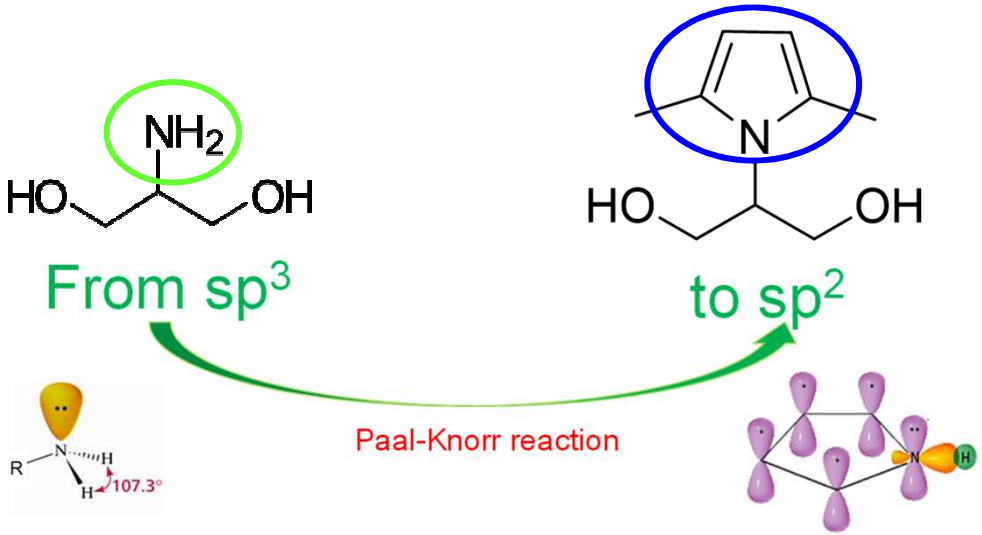
Oxidation of CA with serinol derivative



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

Barbera, V., Citterio, A., Galimberti, M., Leonardi, G., Sebastiano, R., Shisodia, S.U., Valerio A.M. WO 2015 189411 A1

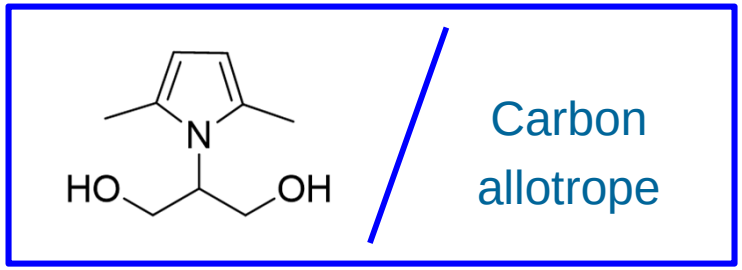
Neat synthesis of Serinol pyrrole



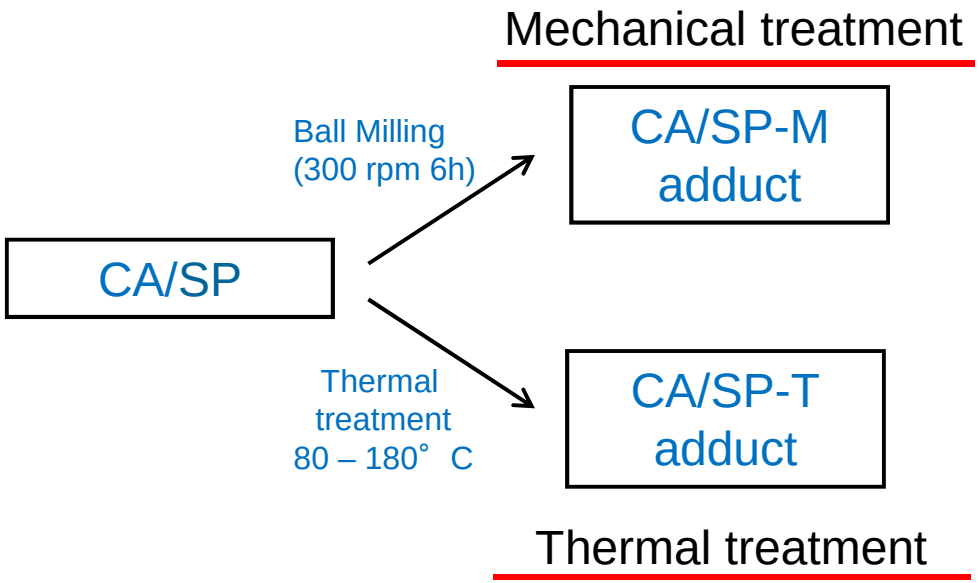
- Yield: at least 96%
- Atom efficiency: 85%
- Easy procedure
- No solvent
- By product: H_2O

Barbera, V., Citterio, A., Galimberti, M., Leonardi, G., Sebastiano, R., Shisodia, S.U., Valerio A.M. WO 2015 189411 A1
Galimberti, M., Barbera, V., Guerra, S., Conzatti, L., Castiglioni, C., Brambilla, L., A. Serafini, RSC Advances, 5(99), (2015) 81142-81152

Adducts of SP with CA - Preparation

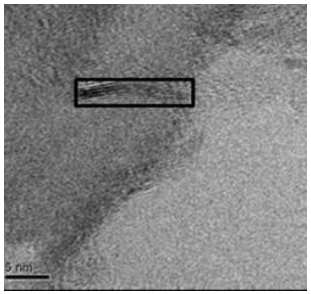
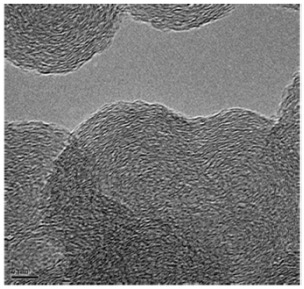
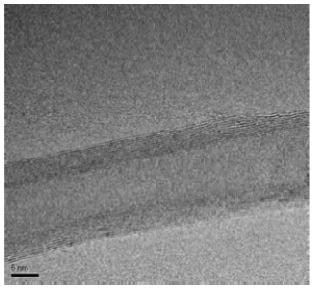


CA-SP



Barbera, V., Citterio, A., Galimberti, M., Leonardi, G., Sebastiano, R., Shisodia, S.U., Valerio A.M. WO 2015 189411 A1
Galimberti, M., Barbera, V., Guerra, S., Conzatti, L., Castiglioni, C., Brambilla, L., A. Serafini, RSC Advances, 5(99), (2015) 81142-81152

High yield functionalization!

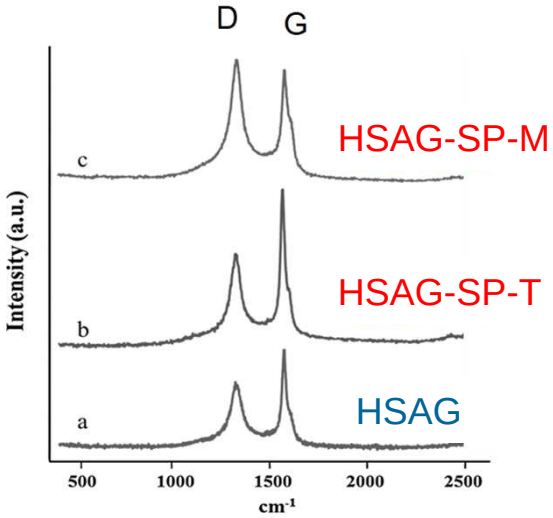
BET Surface area: [m^2/g]	**300**	**77**	**275**
Initial functional groups: [mmol/g]	**1.7**	**0.9**	**2.0**
Yields (%)*:	**96**	**82**	**92**

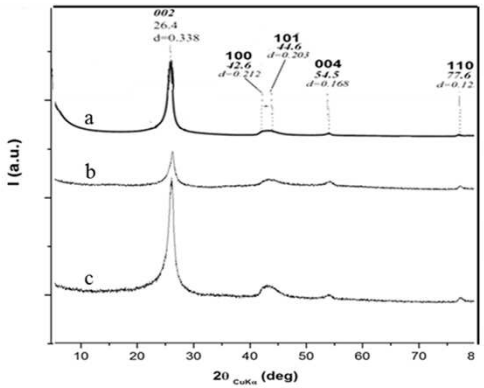
*was estimated through:

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

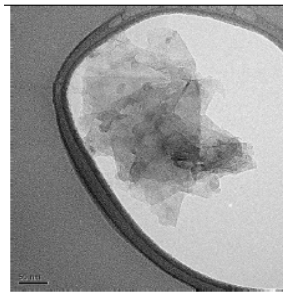
Galimberti, M., Barbera, V., Sebastiano, R., Citterio, A., Leonardi, G. WO/2016/050887 A1 (2016)

Adducts of SP with HSAG





Few layers graphene

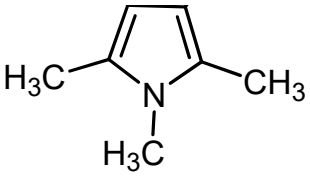


From water suspension

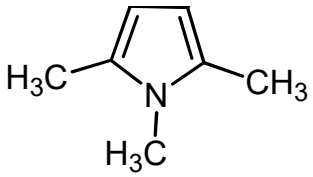
Results from elemental, TGA, IR, XPS, Raman, XRD, HRTEM analysis

Galimberti, M., Barbera, V., Sebastiano, R., Citterio, A., Leonardi, G. WO/2016/050887 A1 (2016)
Galimberti, M., Barbera, V., Guerra, S., Conzatti, L., Castiglioni, C., Brambilla, L., A. Serafini, RSC Advances, 5(99), (2015) 81142-81152

Mechanistic investigation



Model compound

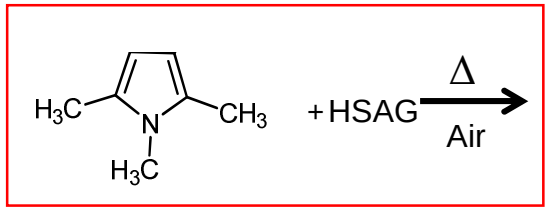


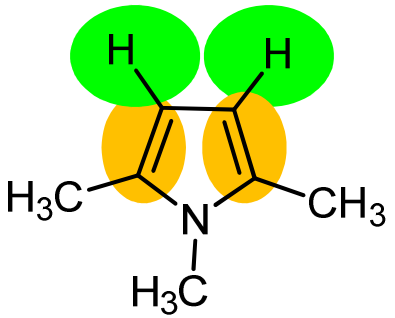
+ HSAG

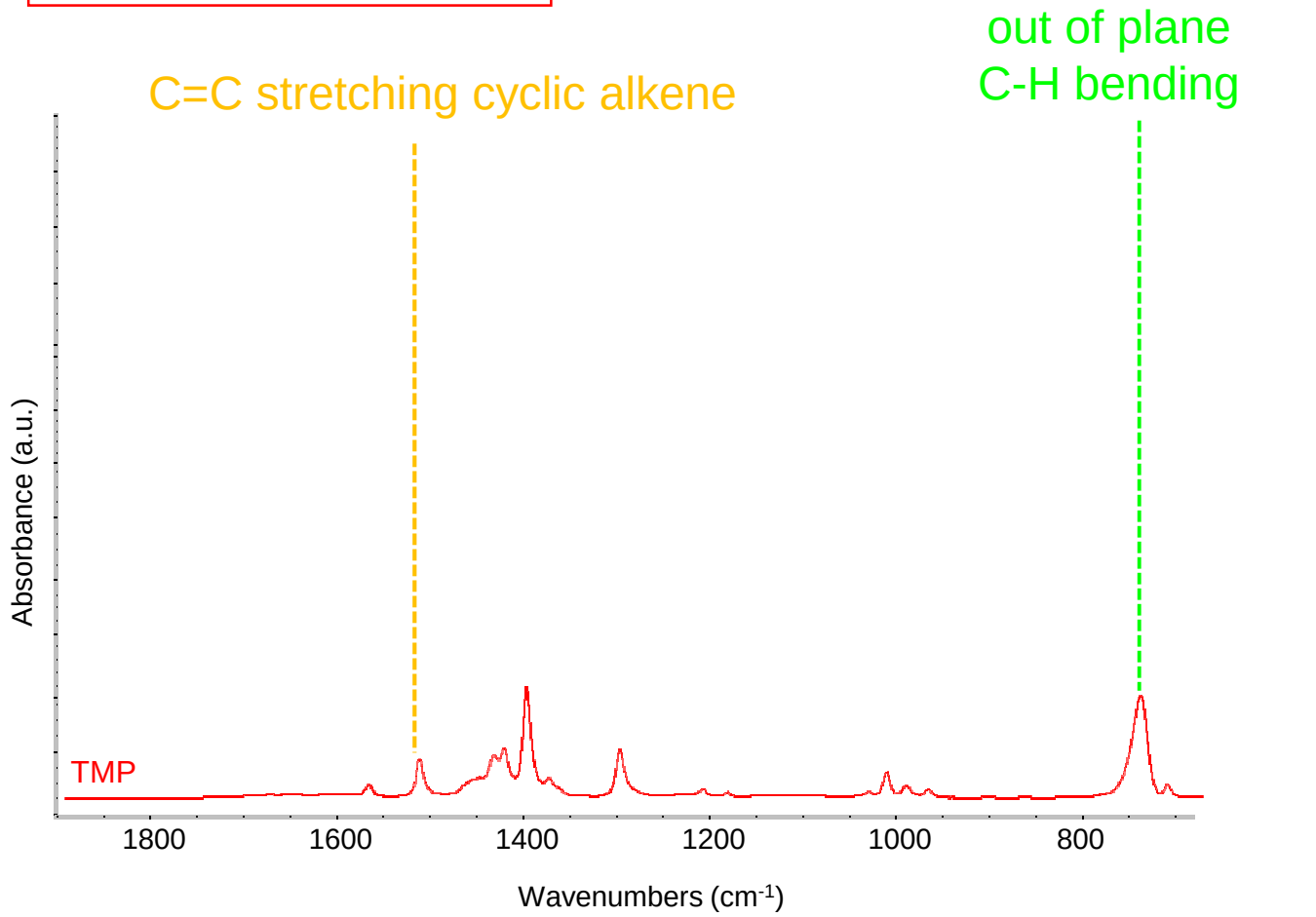
In air

Thermal energy

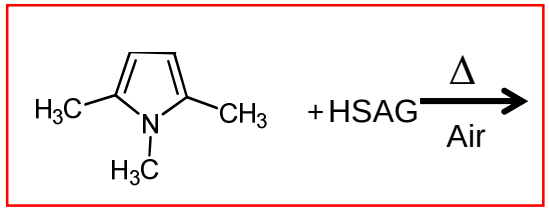
TMP + HSAG 1/1 - from 25 to 150°C

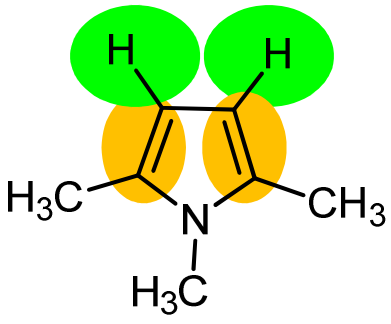


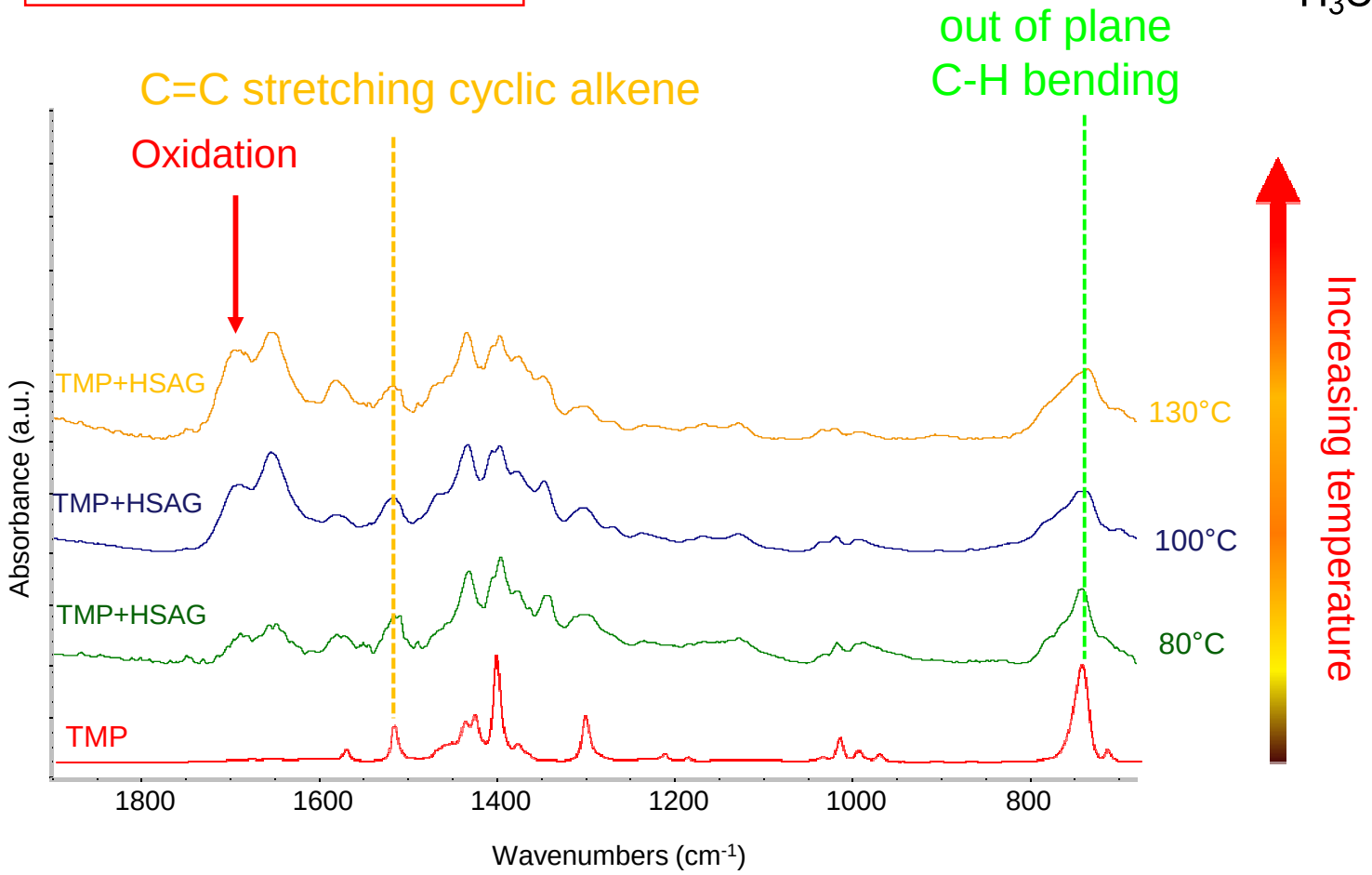




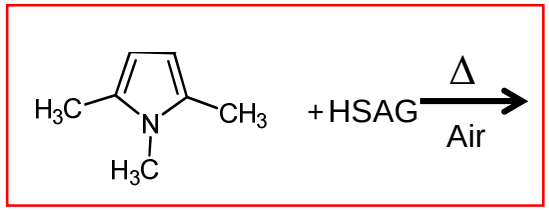
TMP + HSAG 1/1 - from 25 to 150°C

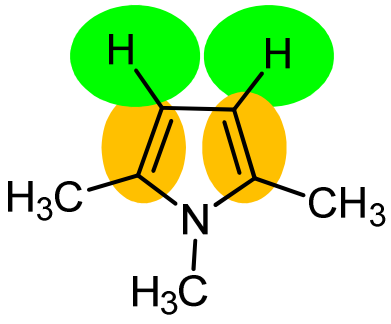


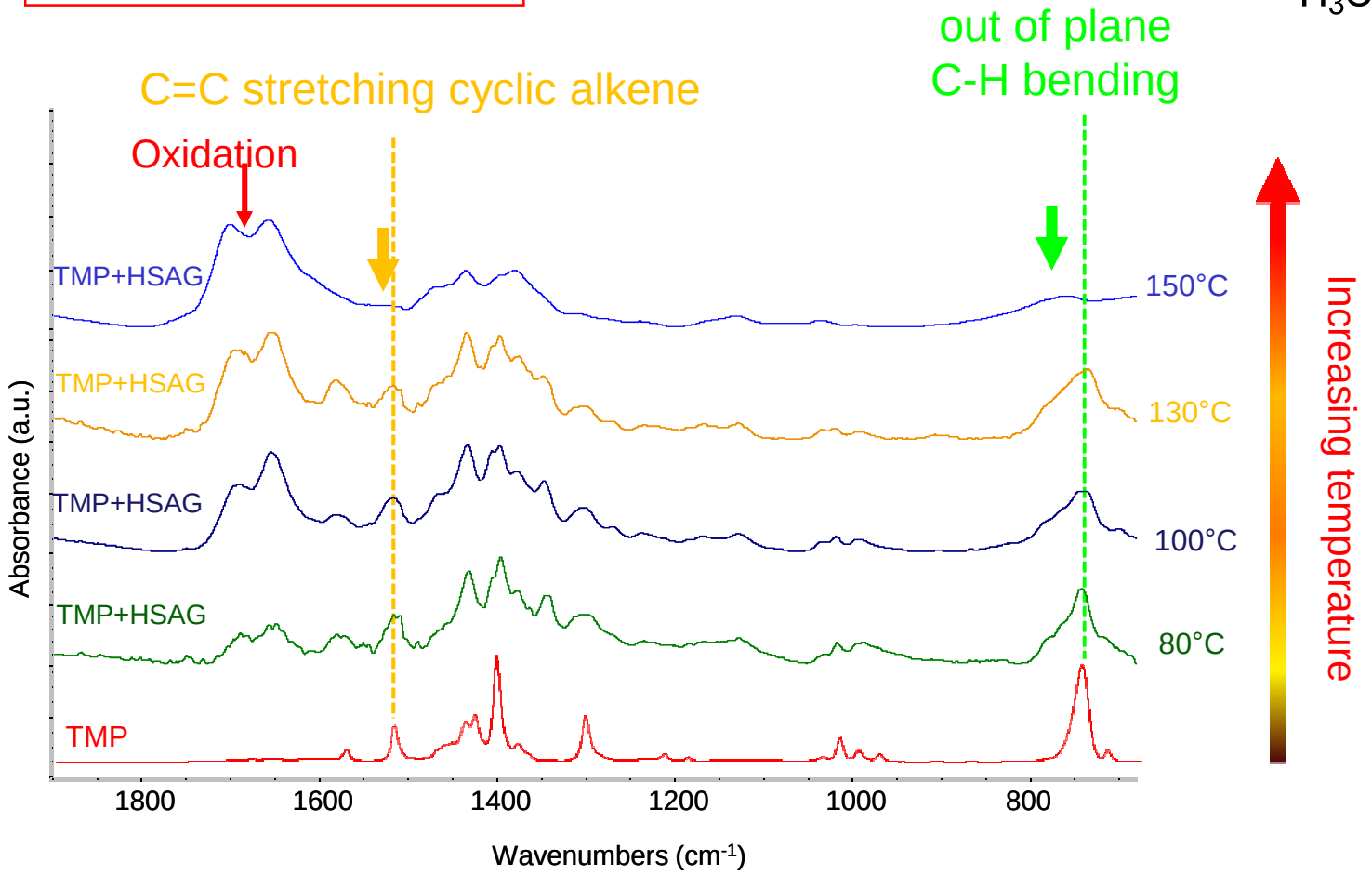




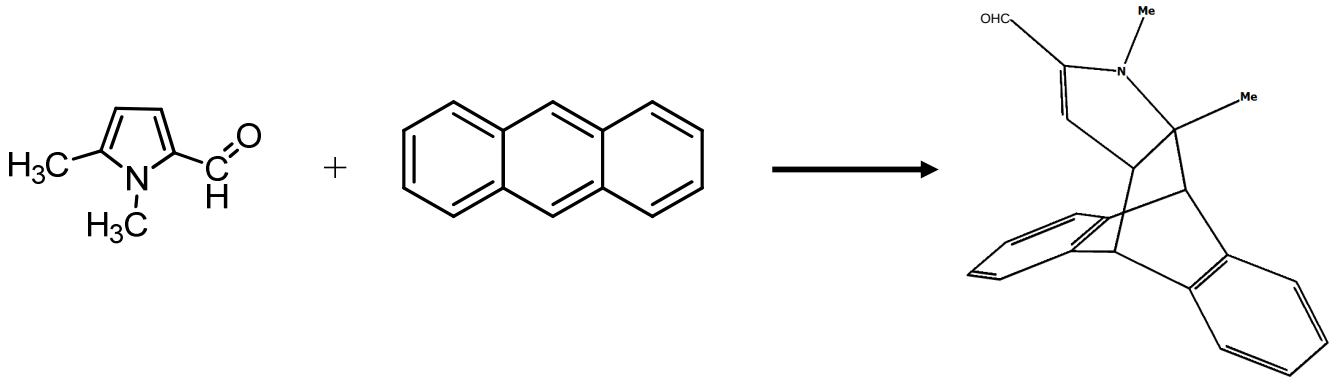
TMP + HSAG 1/1 - from 25 to 150°C







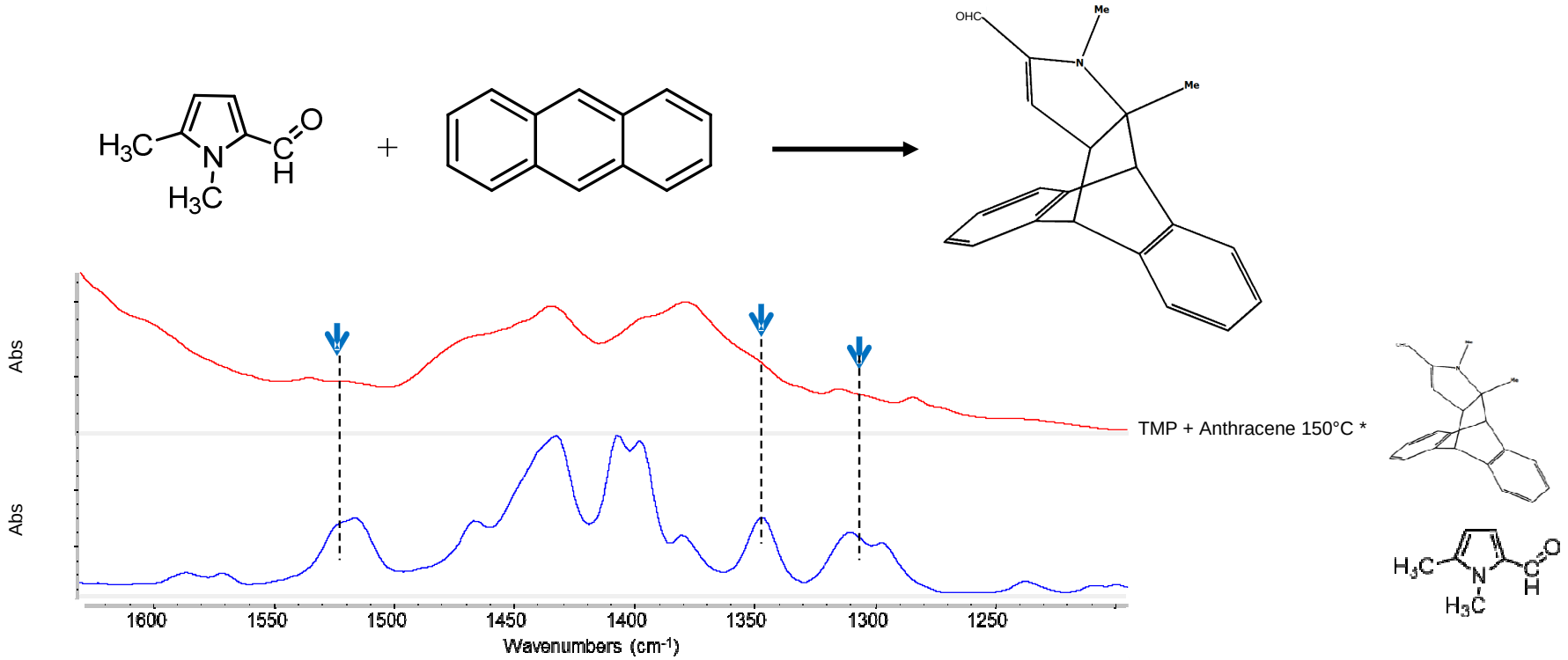
Model reaction and DFT calculation



* Structure confirmed by means of FT-IR and NMR spectroscopy

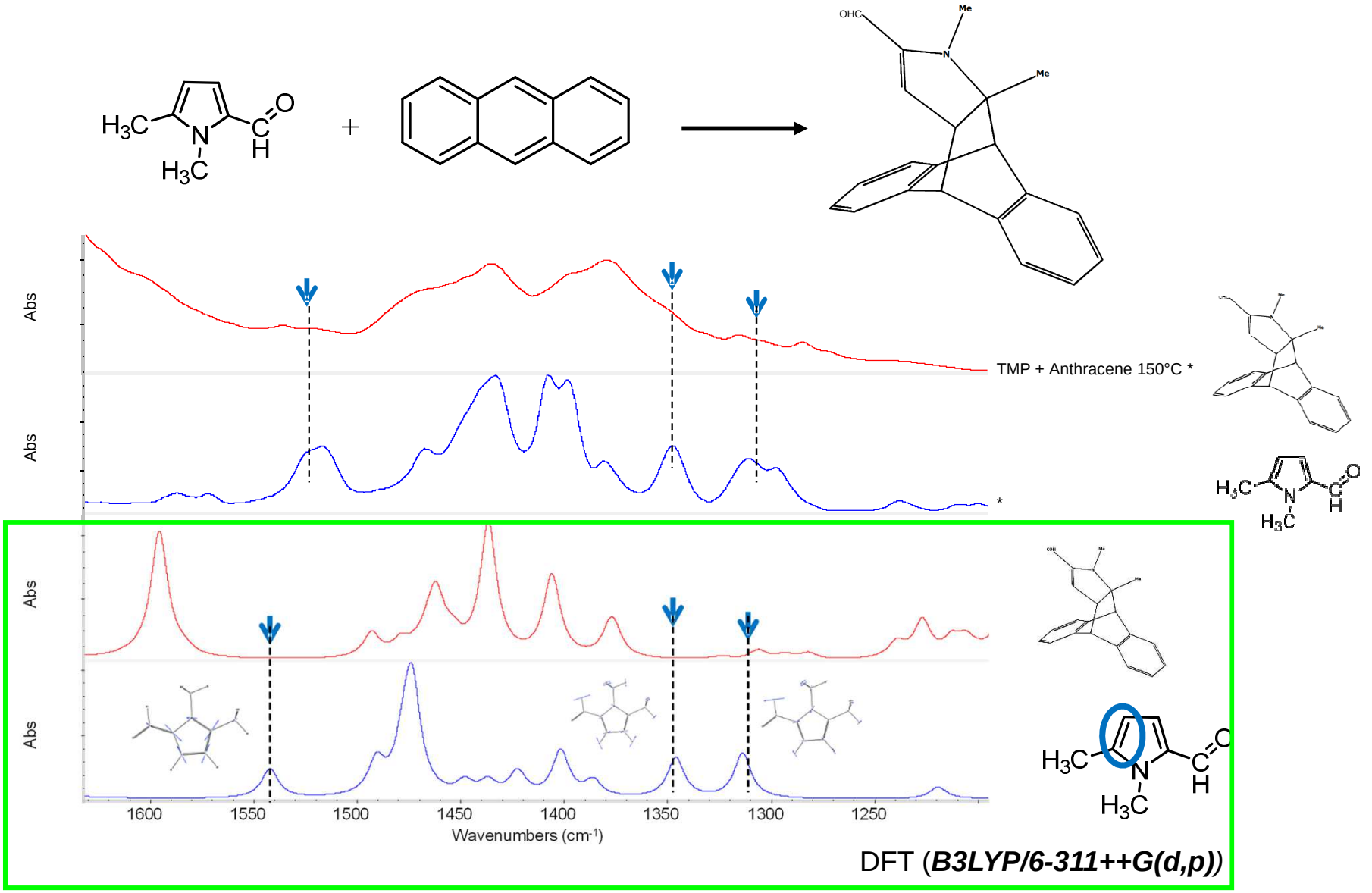
DFT (***B3LYP/6-311++G(d,p)***)

Model reaction and DFT calculation



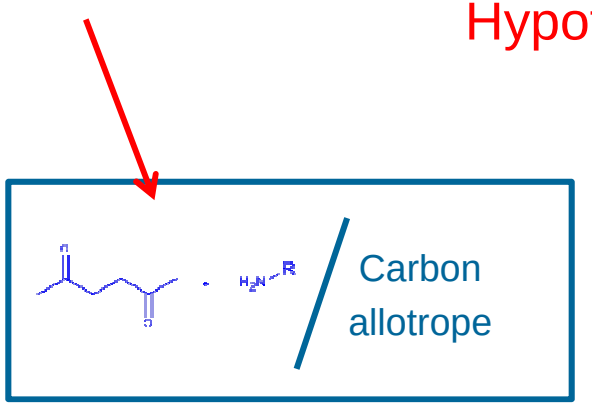
* Structure confirmed by means of FT-IR and NMR spectroscopy

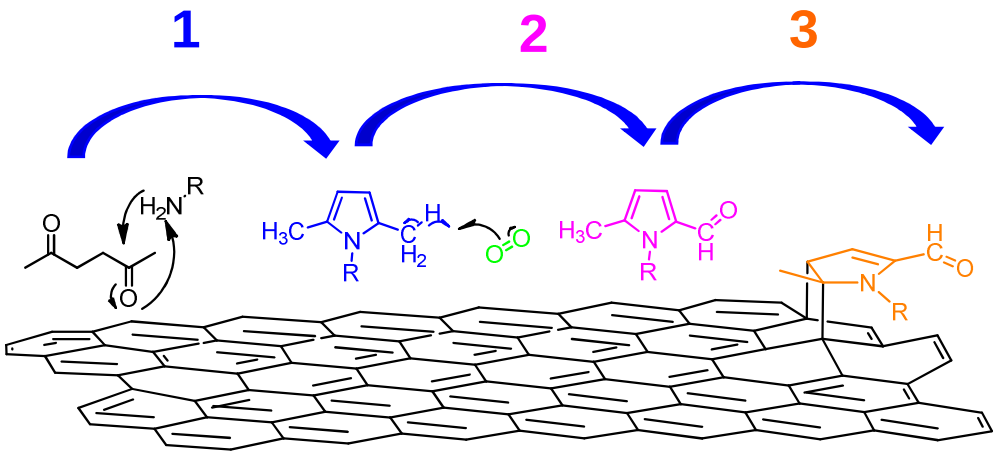
Model reaction and DFT calculation



Facile functionalization of graphene layers (carbon materials)

Hypothesis for the mechanism

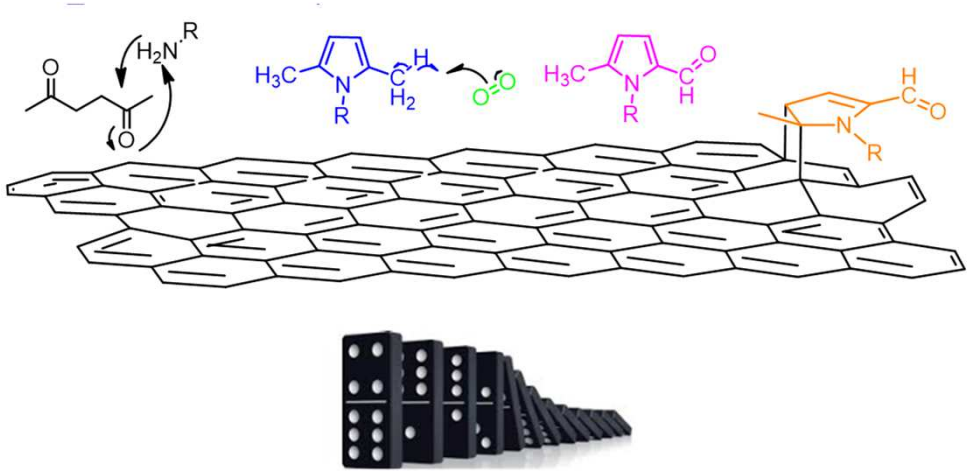




Barbera, V., Milani, A., Brambilla, I., Castiglioni, C., Palazzolo, A., Galimberti M., Presentation at AICING 2017, Milano June 2017; submitted for publication

Thanks to the carbon allotrope!

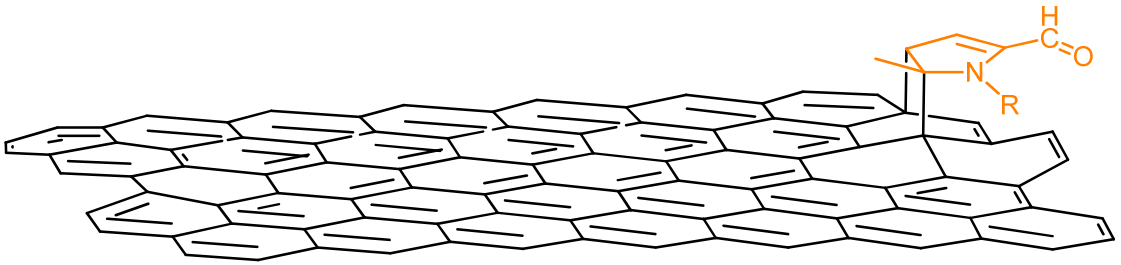
- Support: absorption of pyrrole ring thanks to π-π interaction
- Oxidation catalyst: protection of pyrrole ring and oxidation of lateral substituent
- Substrate for the cycloaddition reaction, i.e. for functionalization



Barbera, V., Milani, A., Brambilla, l., Castiglioni, C., Palazzolo, A., Galimberti M., Presentation at AICING 2017, Milano June 2017; submitted for publication

Adducts of SP with HSAG

- Functional groups up to 20%
- In plane order substantially unaltered
- No expansion of interlayer distance



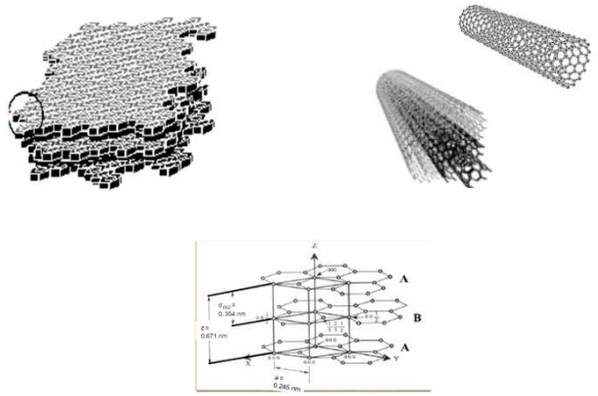
Galimberti, M., Barbera, V., Guerra, S., Conzatti, L., Castiglioni, C., Brambilla, L., A. Serafini, RSC Advances, 5(99), (2015) 81142-81152

Facile functionalization of carbon materials

- KOH
- H_2O_2
- Serinol derivative

+

sp^2 carbon allotropes (CA)



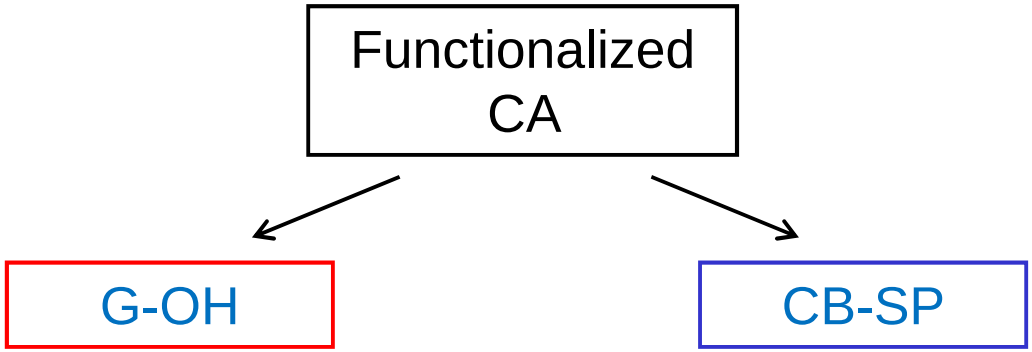
Functional groups on carbon allotrope surface

Bulk structure substantially unaltered

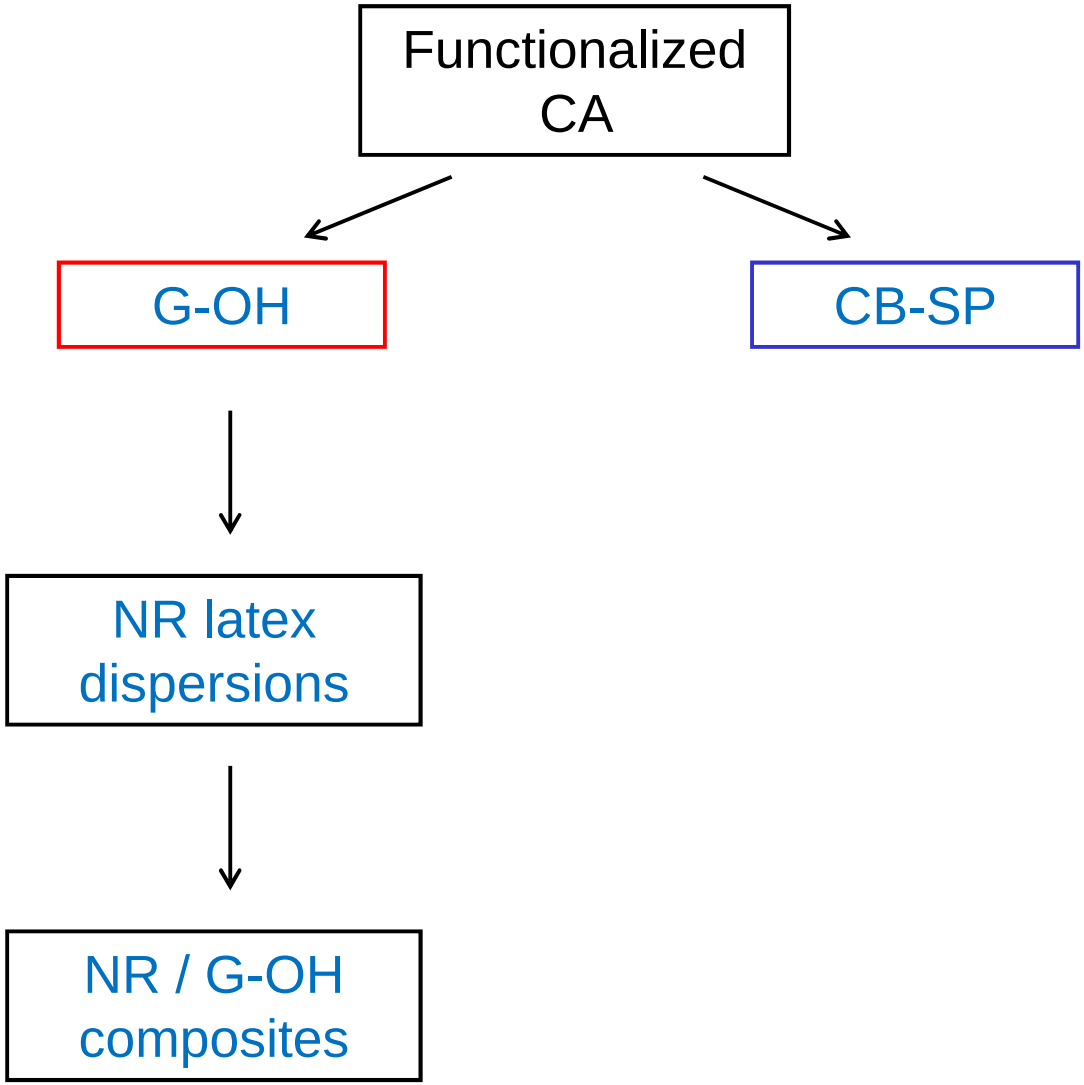
Barbera, V., Porta, A., Brambilla, L., Guerra, S., Serafini, A., Valerio, M.A., Vitale, A., Galimberti, M. RSC Adv., 2016, 6, 87767-87777
Barbera, V., Bernardi, A., Torrisi, G., Porta, A., Galimberti, M. Elastomery (submitted)
Galimberti, M., Barbera, V., Guerra, S., Conzatti, L., Castiglioni, C., Brambilla,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

Elastomers composites based on G-OH and CB-SP

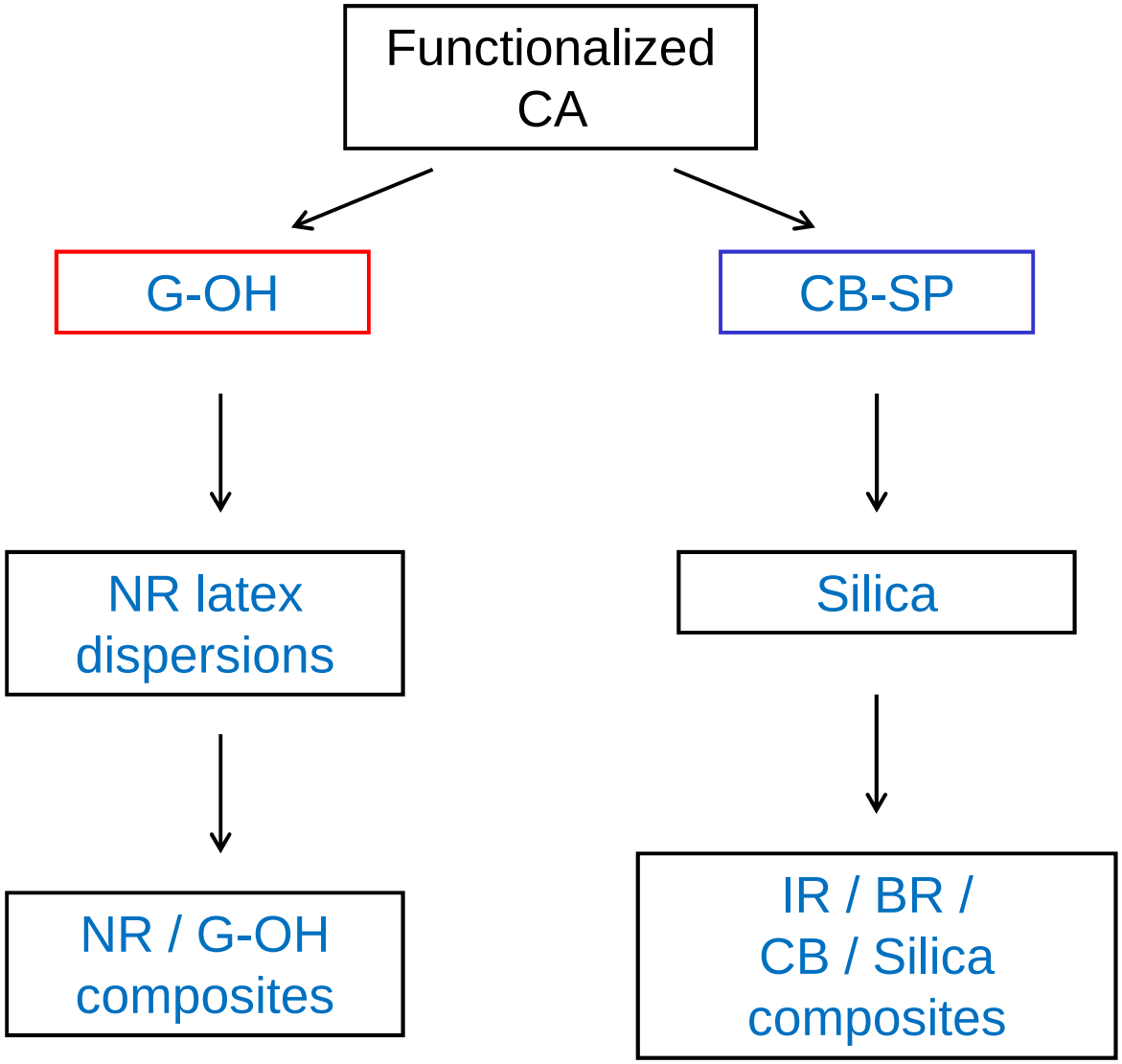
Elastomers composites based on G-OH and CB-SP



Elastomers composites based on G-OH and CB-SP



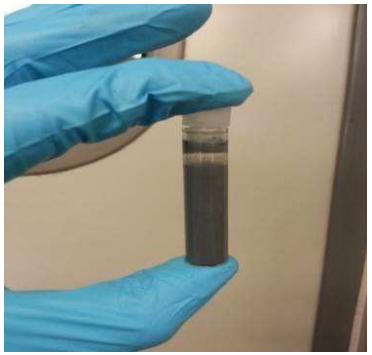
Elastomers composites based on G-OH and CB-SP

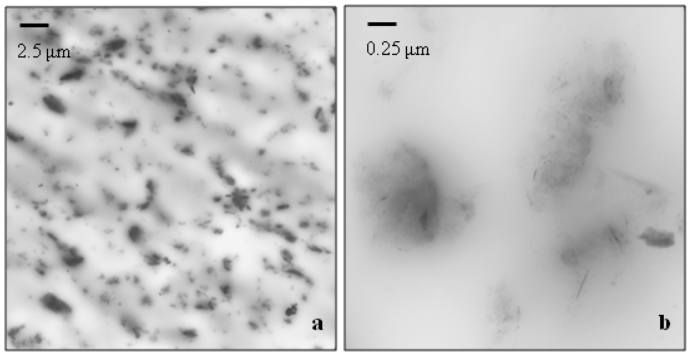


Composites based on NR and G-OH

Ingredient	G-OH_0	G-OH_4	G-OH_7	G-OH_10	G-OH_12	G-OH_15	G-OH_25
NR	100	100	100	100	100	100	100
G-OH	0	3.7	6.5	9.5	12.3	15.1	25

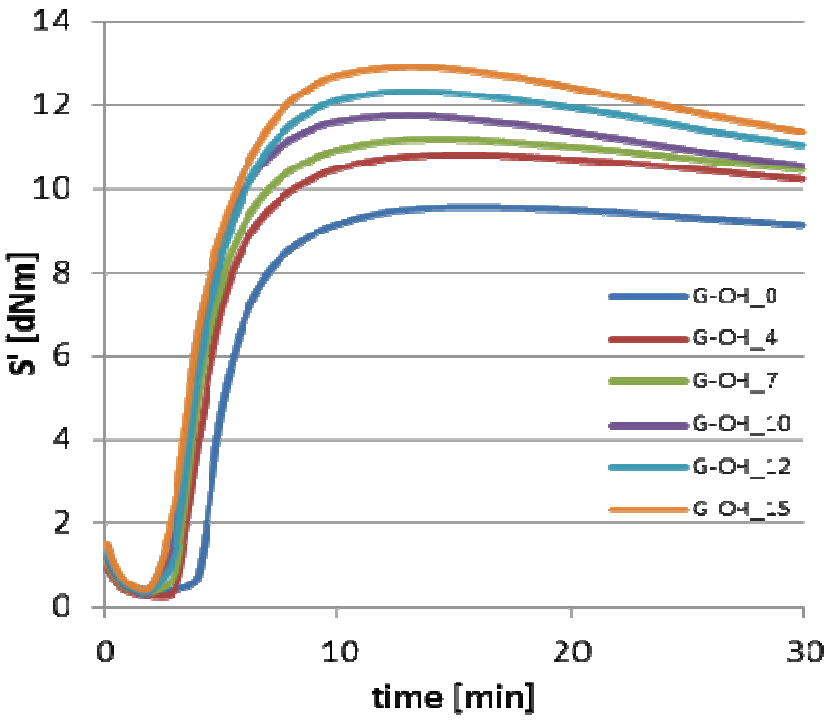
Silane TESPT 2, Stearic acid 2, ZnO 4, 6PPD 2,
Sulphur 3, TBBS 1.8

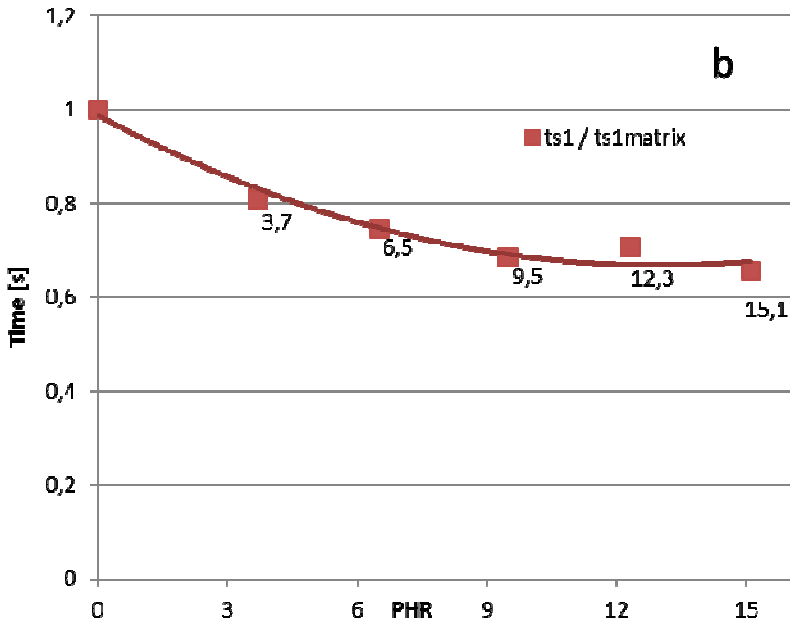




TEM micrographs
NR-GOH-9 composite
(precipitated from the latex)

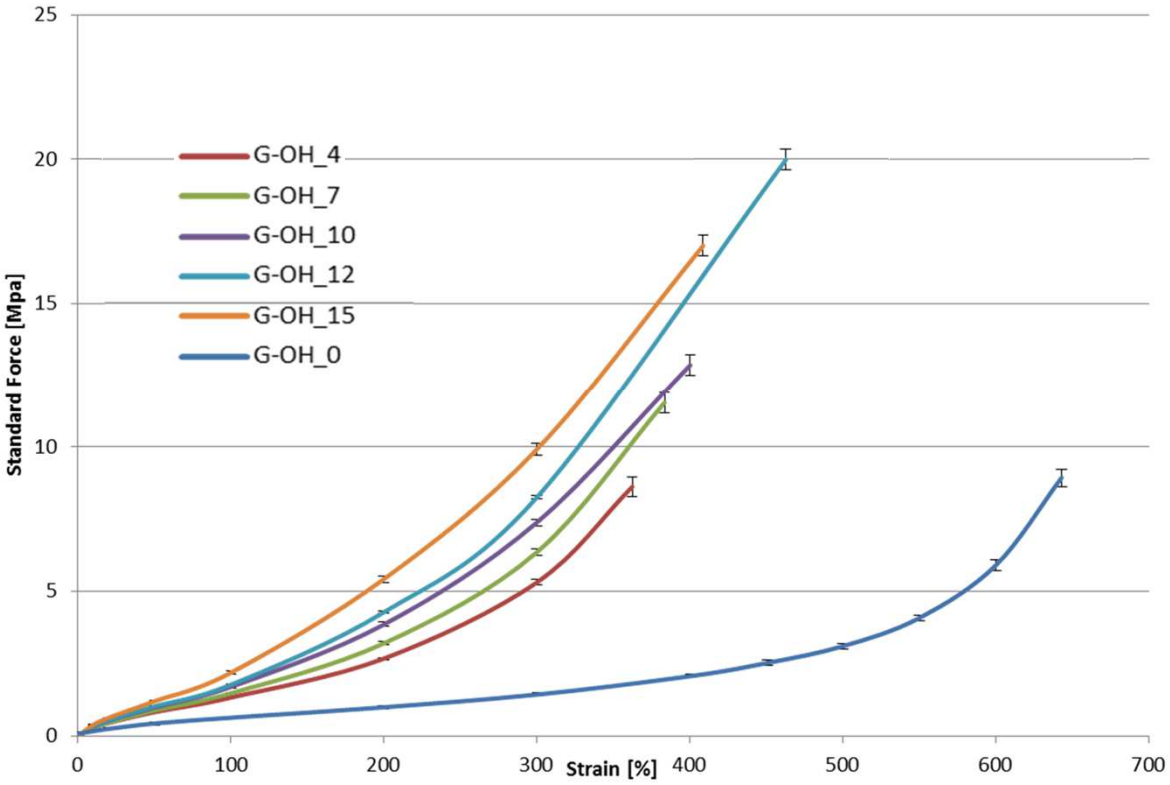
Vulcanization reaction





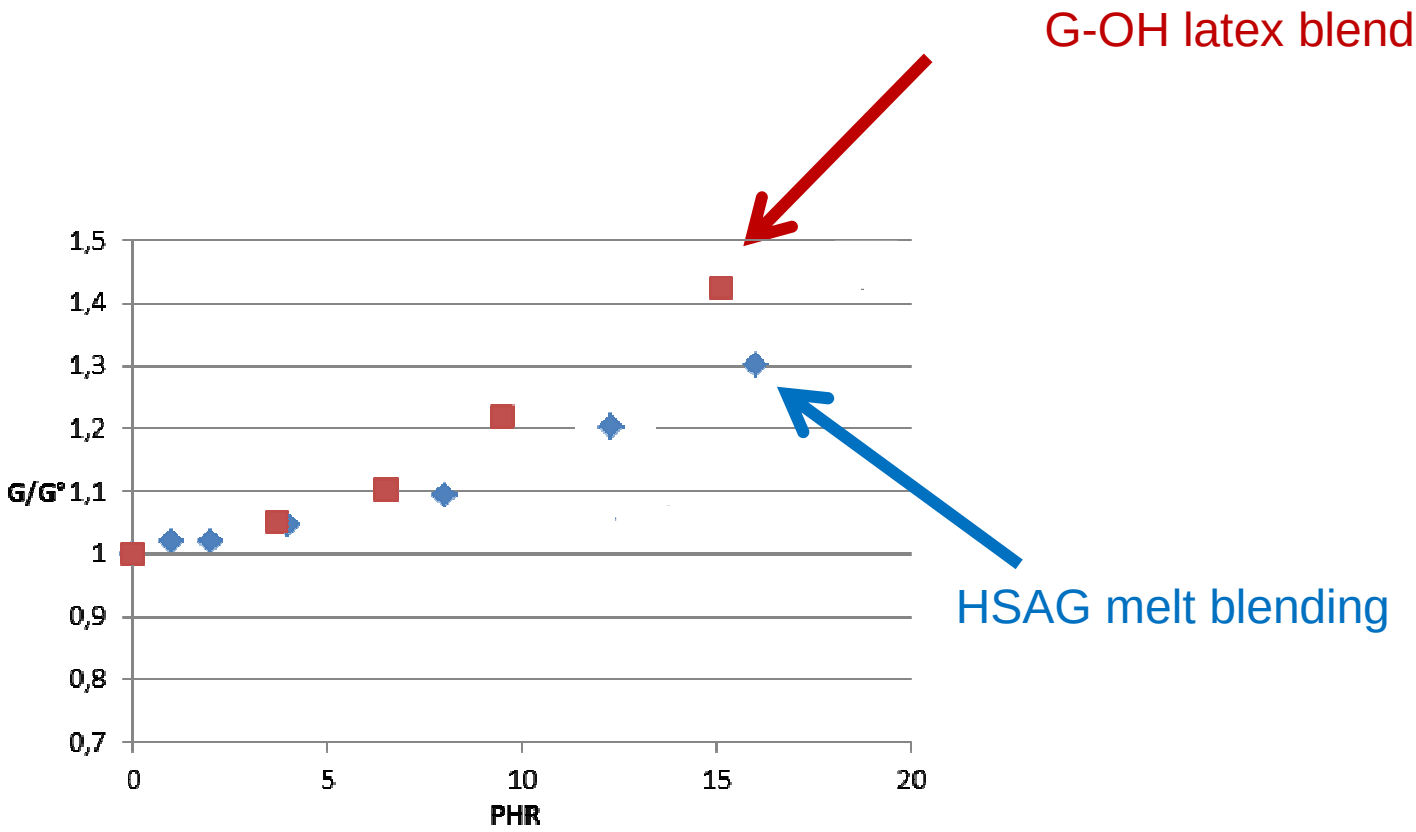
☞ Vulcanization reaction becomes faster as G-OH content increases

Tensile properties



☞ Stresses at all elongations increase with G-OH content

G/G^0 ratios vs G-OH content



☞ Higher G' moduli with G-OH: better dispersion

CB-SP in CB/Silica based composite

Recipes

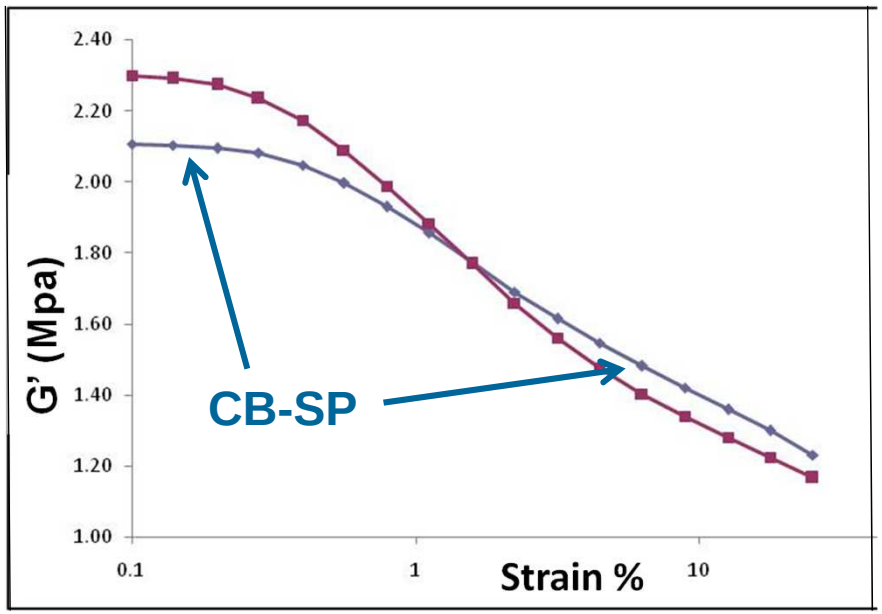
Ingredient	With CB	With CB-SP
IR	50	50
BR	50	50
Silica	25	25
CB N326	25	0
CB N326-SP	0	27
CB N326	0	25
SP	0	2

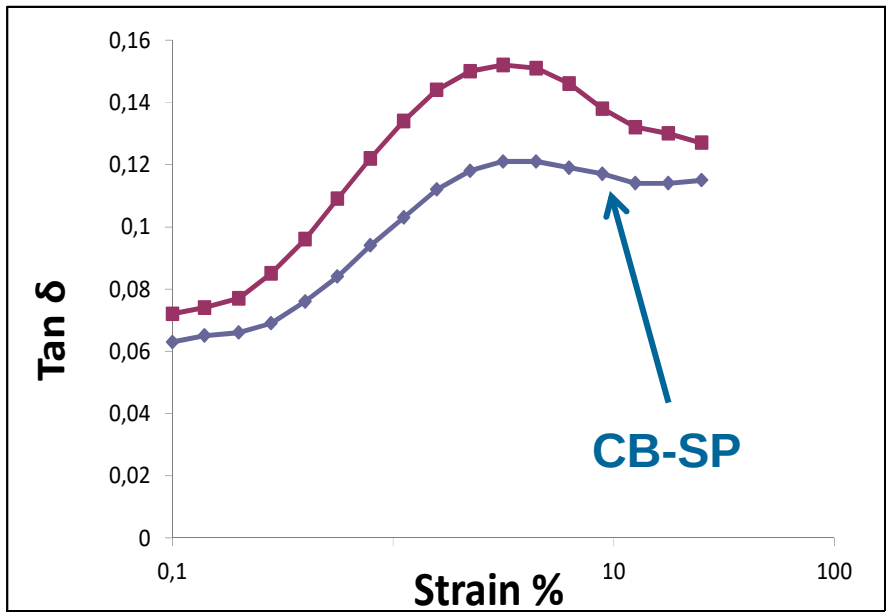
Silane TESPT 2, Stearic acid 2, ZnO 4, 6PPD 2,

Sulphur 1.5, TBBS 1.8

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

Dynamic-mechanical properties





With CB-SP

- ☞ Lower Payne Effect and crossover of the curves
- ☞ Lower Tan delta

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Conclusions

- Sustainable oxidation of sp^2 carbon allotropes

  was developed with: KOH, H_2O_2, serinolpyrrole

- Serinol pyrrole: very high functionalization yield

- Unaltered structure of carbon allotropes

- Functionalized carbon allotropes:

  better mechanical properties and lower Payne effect

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Thanks for the Attention

- Prof. Chiara Castiglioni, (Politecnico Milano)
- Dr. Luigi Brambilla, (Politecnico Milano)
- Dr. Andrea Serafini, (Politecnico Milano)