Facile and sustainable functionalization method for preparing graphene layers with different solubility parameters

Maurizio Galimberti,

Vincenzina Barbera, Andrea Bernardi, Alessandro Rosengart

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

ISCaMaP

Innovative Sustainable Chemistry and Materials and Proteomics Group

Thanks!

To the organizing Committee

To speakers and audience

For the attention

Objectives of the research activity

☞ To reduce the synthetic footprint in nanotechnology

in view of industrial applications

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- To reduce the synthetic footprint in nanotechnology in view of industrial applications

- To functionalize graphene and related materials with a sustainable, facile, versatile method, preserving the sp^2 hybridization of carbon atoms

- To prepare tailor made graphene materials, in view of the final application with 1 functionalization method

The starting point: sustainable oxidation

- KOH
- H_2O_2
- Serinol derivative

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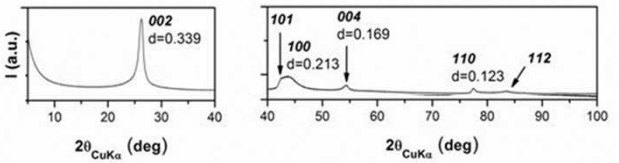
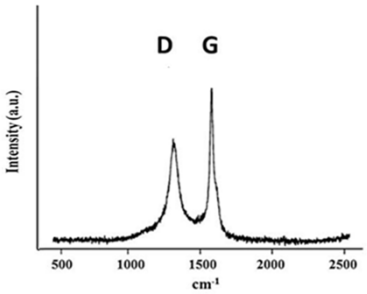
- Serinol derivative

+

High surface area graphite (HSAG)



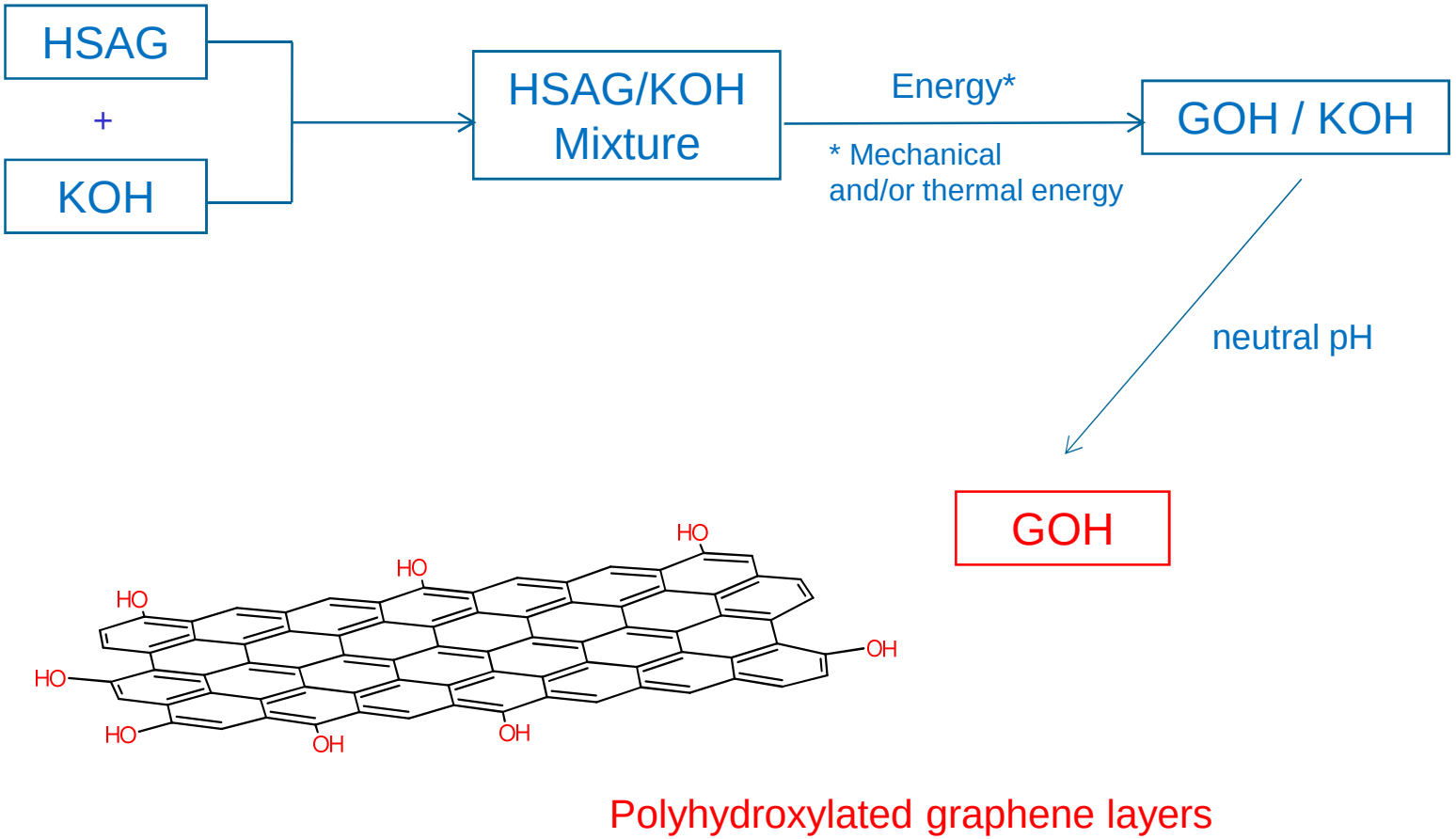
Surface area (m^2/g)	number of layers	$D_{\parallel} / D_{\perp}$
330	35	3.1



M. Mauro, V. Cipolletti, M. Galimberti, P. Longo, G. Guerra, *J. Phys. Chem. C* 116 (2012) 24809−24813

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

Oxidation of HSAG with KOH



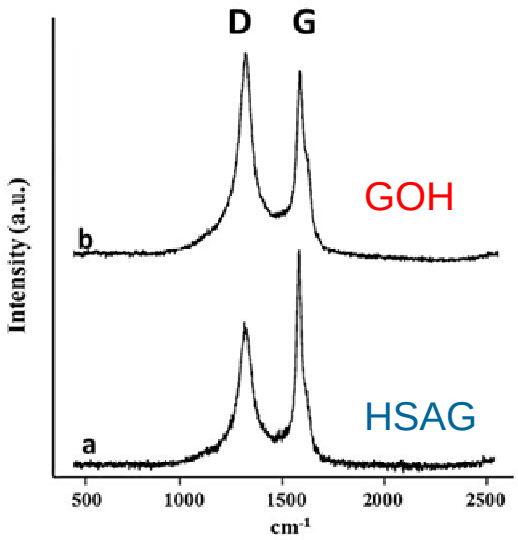
Polyhydroxylated graphene layers

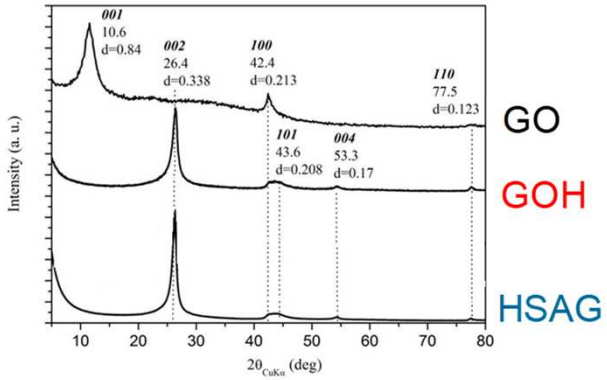
A. Porta, Thesis, Politecnico Milano, 2015

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

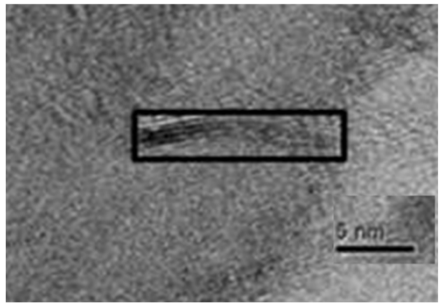
Polyhydroxylated graphene layers from HSAG + KOH

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





Few layers graphene



From water suspension

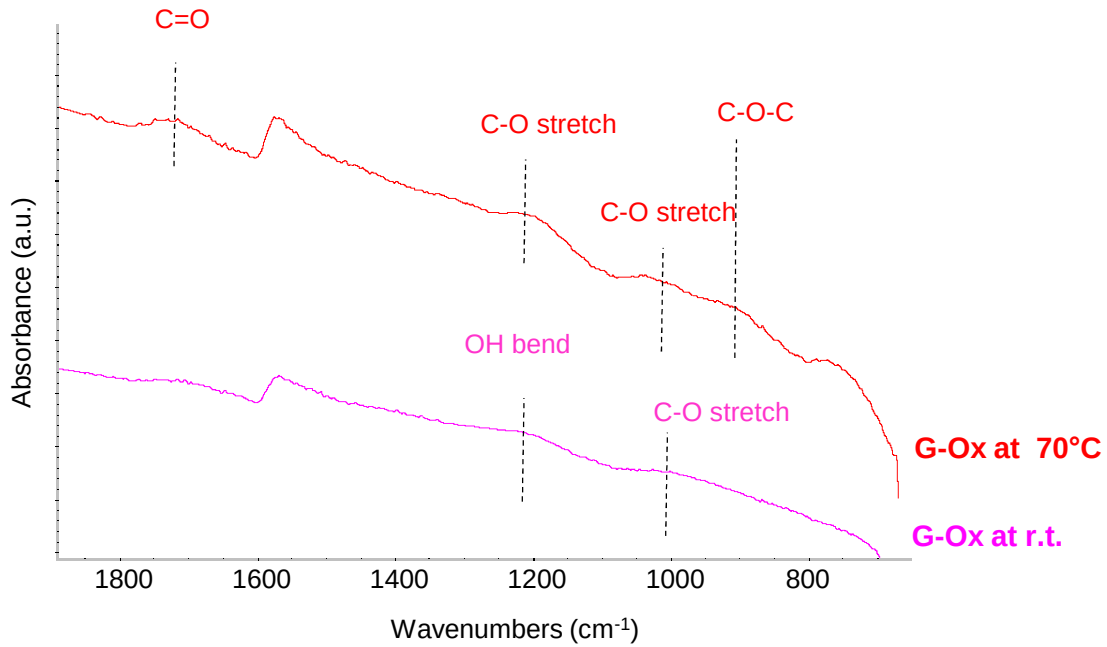
Results from elemental, TGA, IR, XPS, Raman, XRD, HRTEM analysis

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

Oxidation of HSAG with H_2O_2

HSAG + H_2O_2* → HSAG/H_2O_2 Mixture → (Thermal energy) G-Ox / H_2O → (filtration) G-Ox

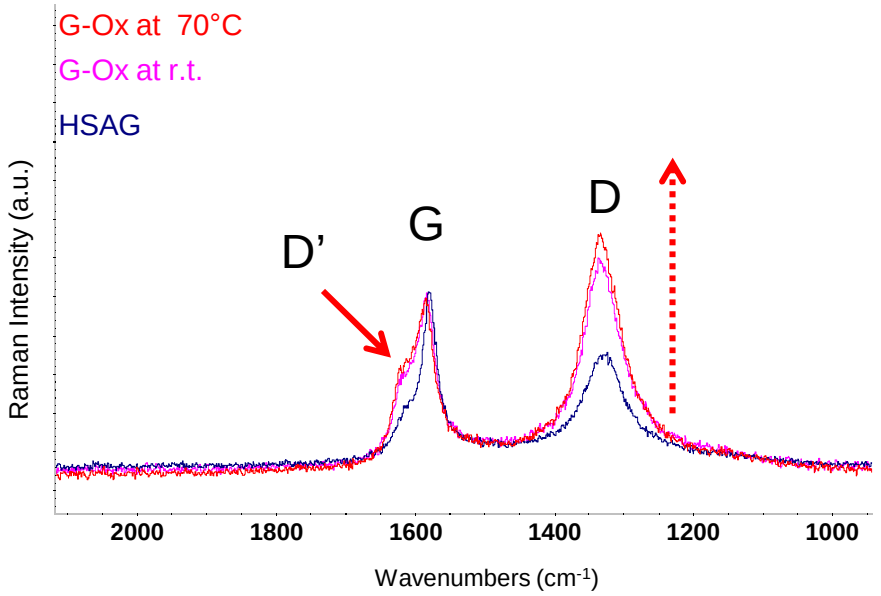
* 30 % (w/w) in H_2O

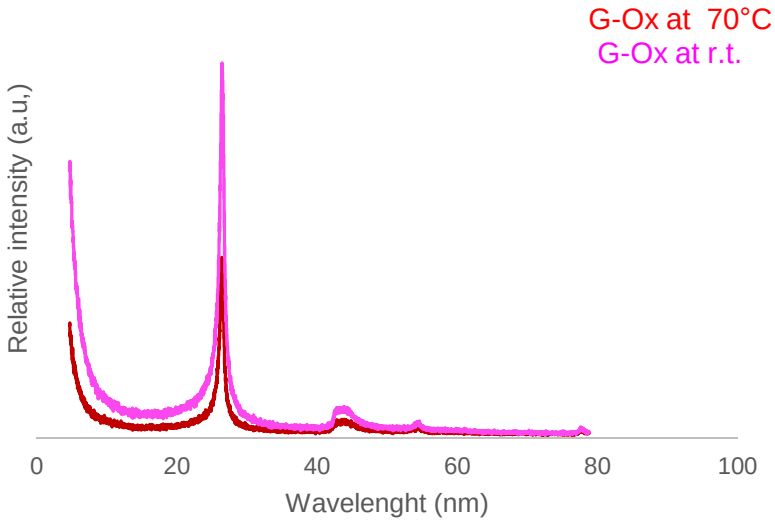


V. Barbera, L. Brambilla, M. Galimberti, submitted for pubblication

Oxidation of HSAG with H_2O_2

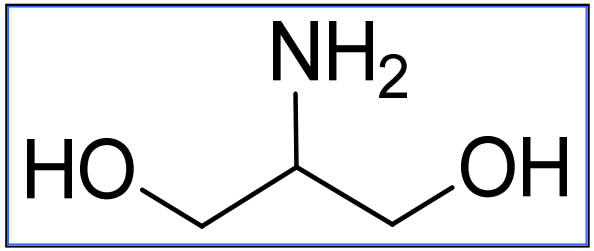
- Selective introduction of OH groups at room temperature
- In plane order substantially unaltered
- No expansion of interlayer distance





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

Oxidation of HSAG with serinol derivative



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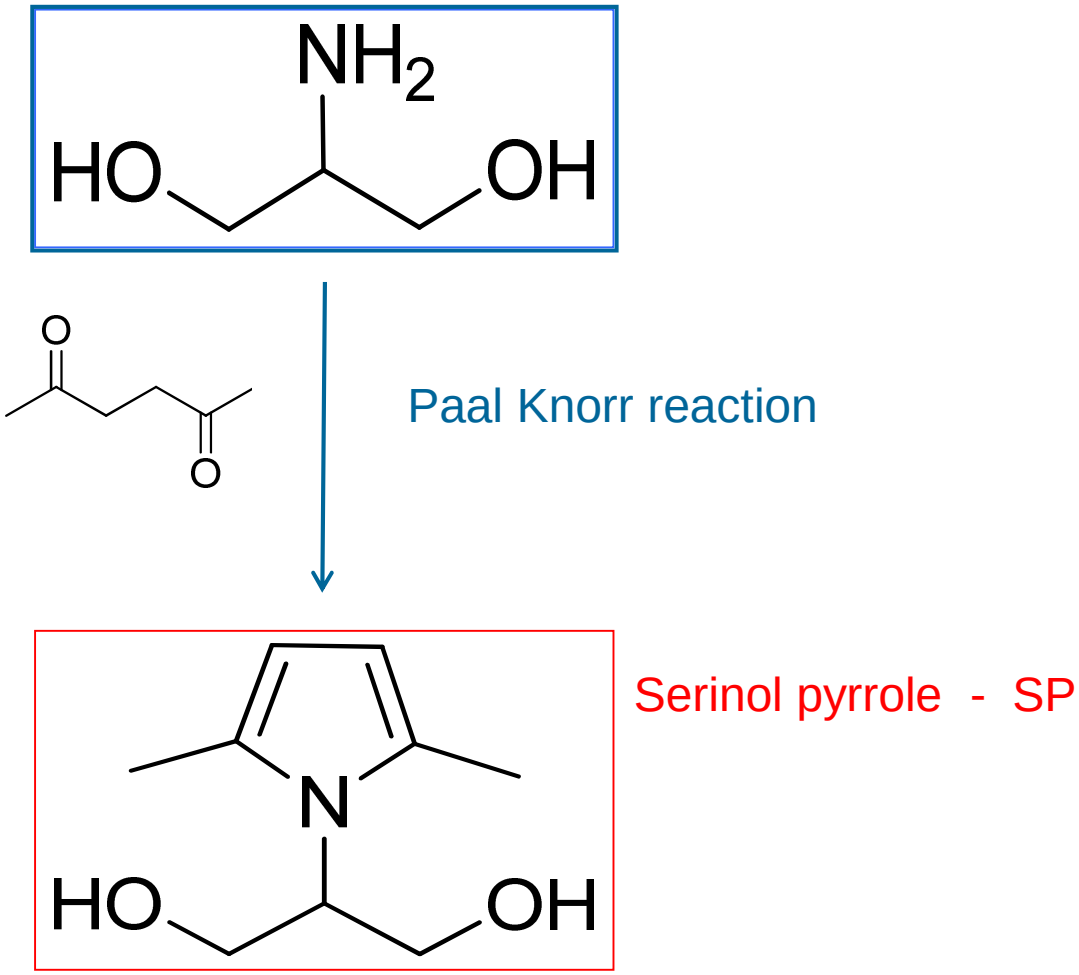
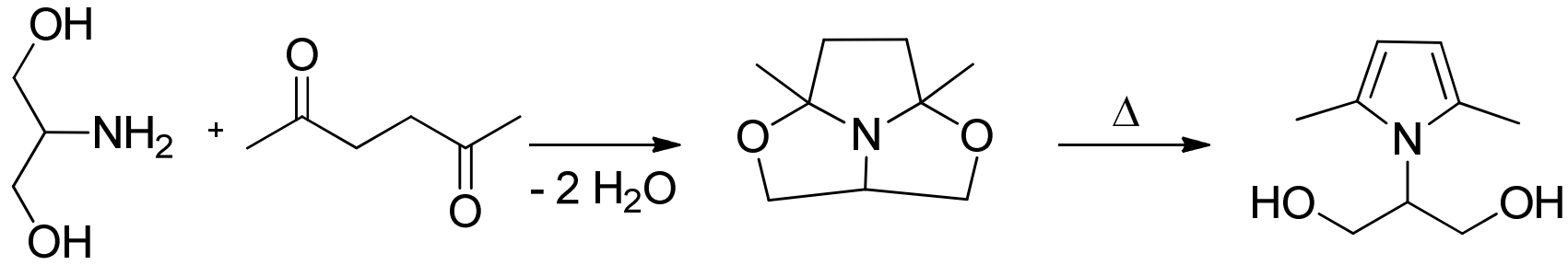


Serinol pyrrole - SP

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

Neat synthesis of Serinol pyrrole



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

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

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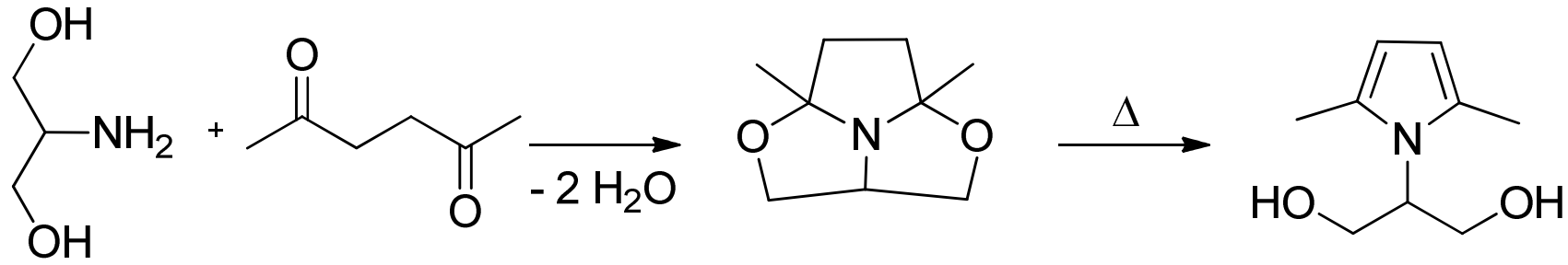

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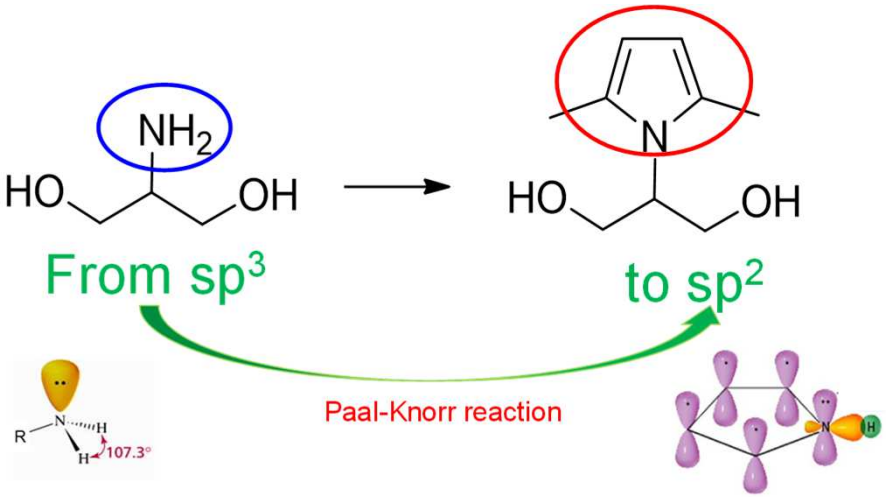

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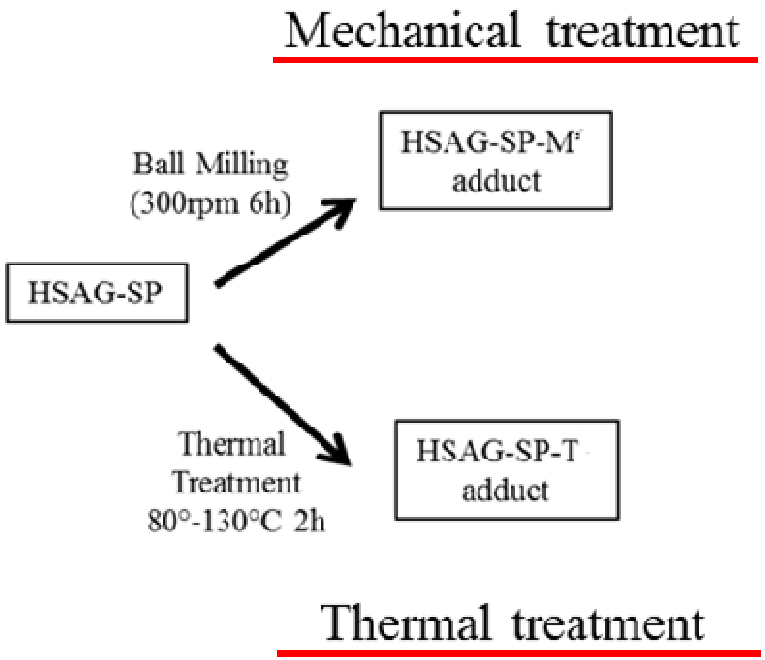
Adducts of SP with HSAG - Preparation



Functionalization Yield:

from 80 to 98%

Carbon allotropes: CNT: single and multiwalled,

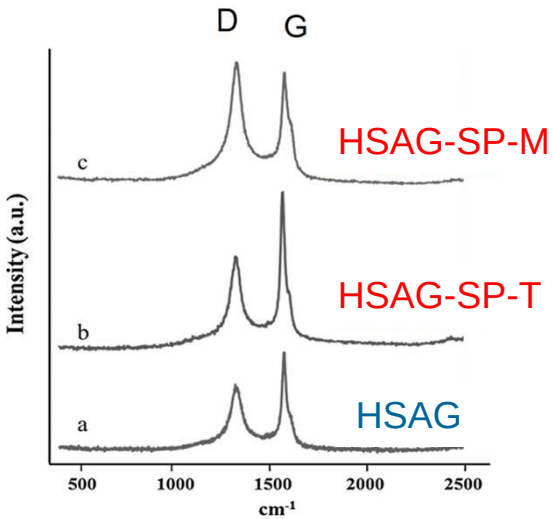
carbon black: various grades

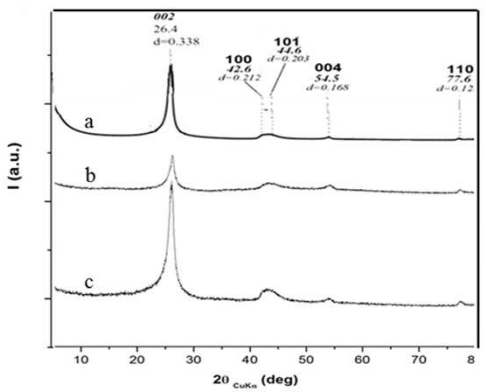
M. Galimberti, V. Barbera, R. Sebastiano, A. Citterio, G. Leonardi, A.M. Valerio WO 2016 050887 A1

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

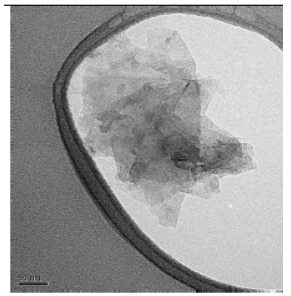
Adducts of SP with HSAG

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





Few layers graphene



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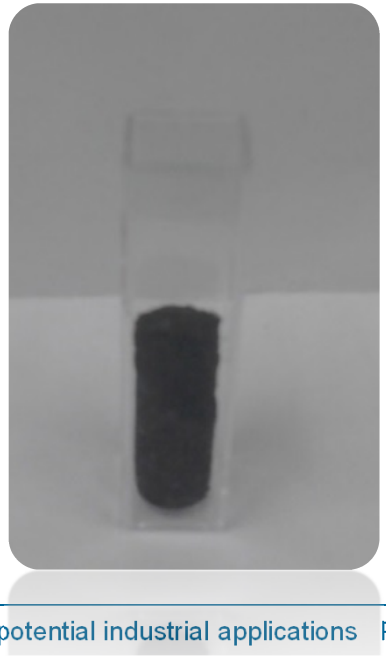
M. Galimberti, V. Barbera, S. Guerra, L. Conzatti, C. Castiglioni, L. Brambilla, A. Serafini, *RSC Adv.*, 2015, 5, 81142-81152

Development of Polyhydroxylated graphene layers

Flexible conductive

Carbon papers

Catalysis

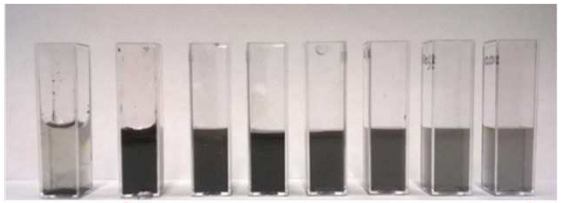


Monolithic

aerogels

Development of HSAG-SP adducts

Conductive inks



Graphite

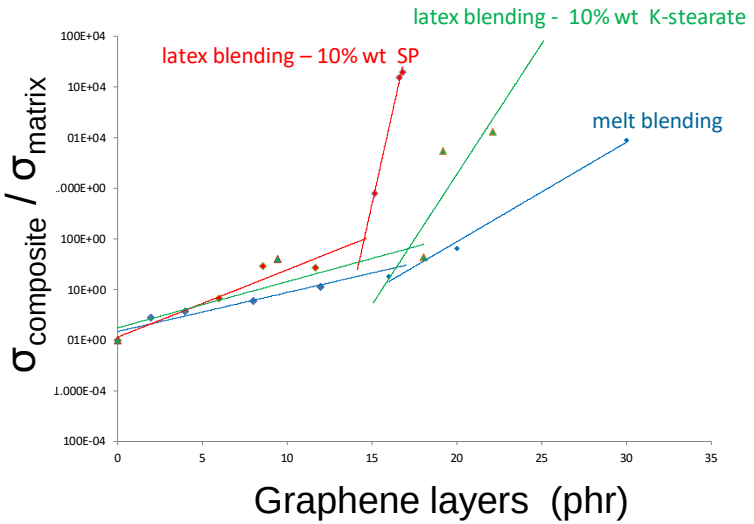
HSAG / SP

conc: from 10 to 0.1 mg/mL

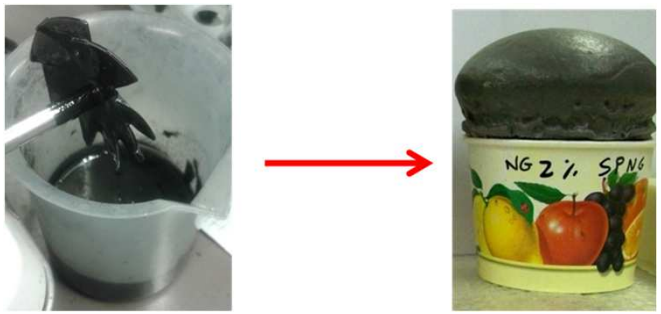
From 0.1 to 200 g/L

Poly(1,4-cis-isoprene) composites

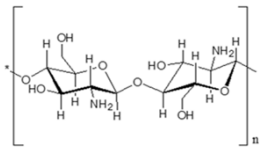
Electrical conductivity

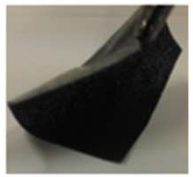


PU foams

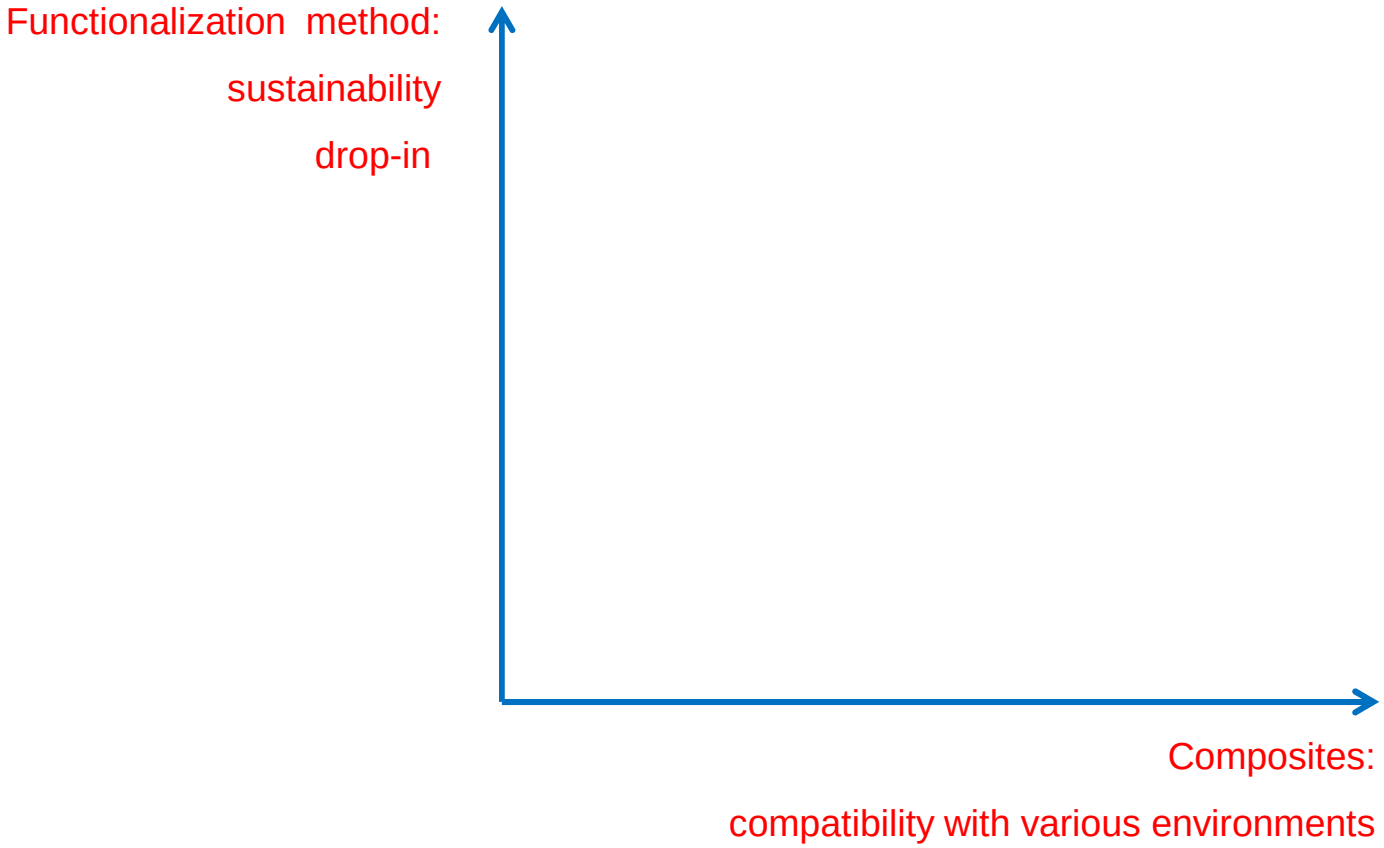


Carbon papers based on chitosan





Competition of functionalization methods

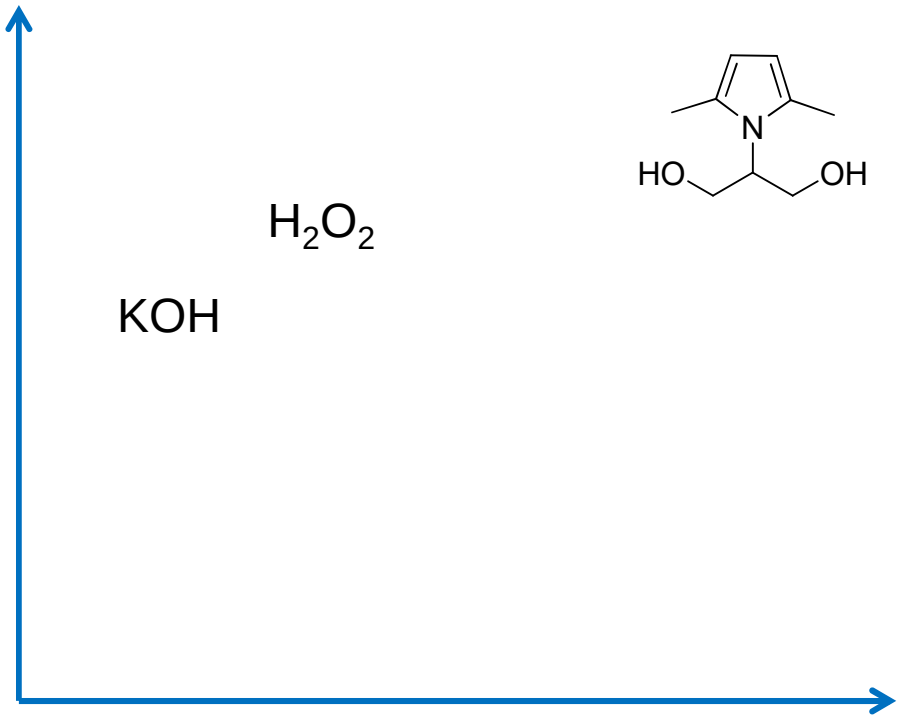


Competition of functionalization methods

Functionalization method:

sustainability

drop-in



Composites:

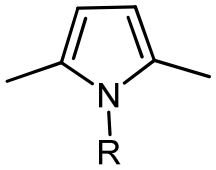
compatibility with various environments

Competition of functionalization methods

Functionalization method:

sustainability

drop-in



H_2O_2

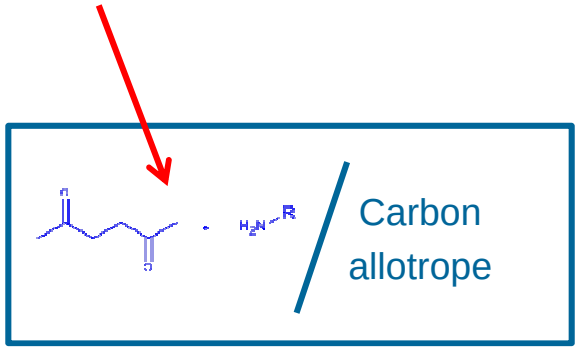
KOH

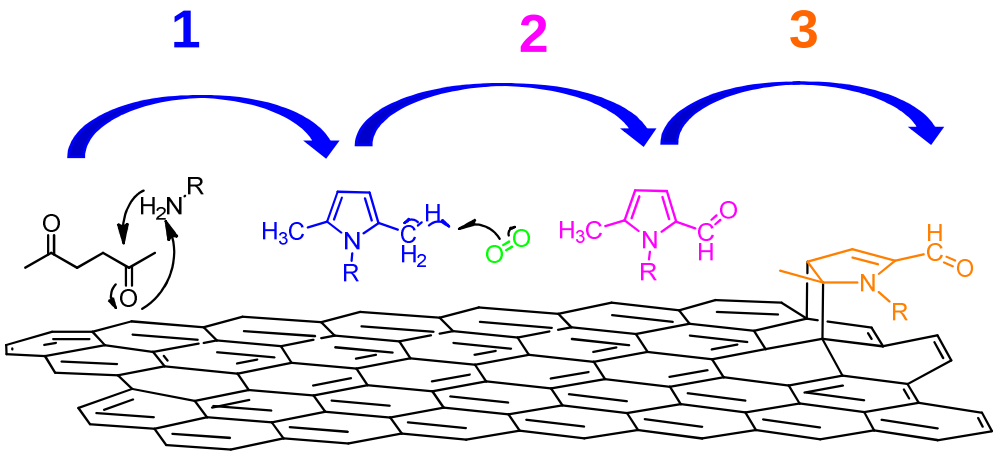
Composites:

compatibility with various environments

Facile functionalization of graphene layers (carbon materials)

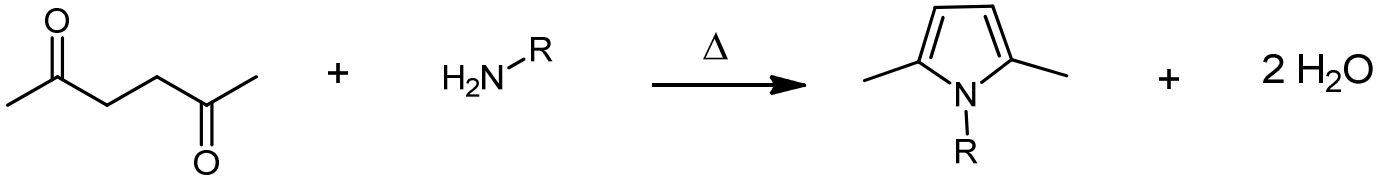
Hypothesis for the mechanism





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

Pyrrole compounds from neat Paal Knorr reaction



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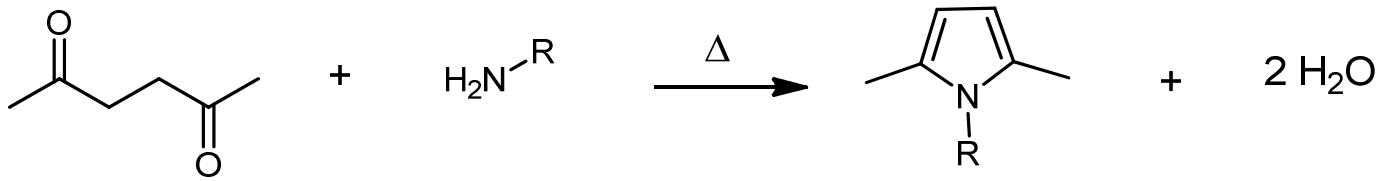

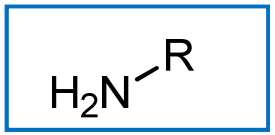

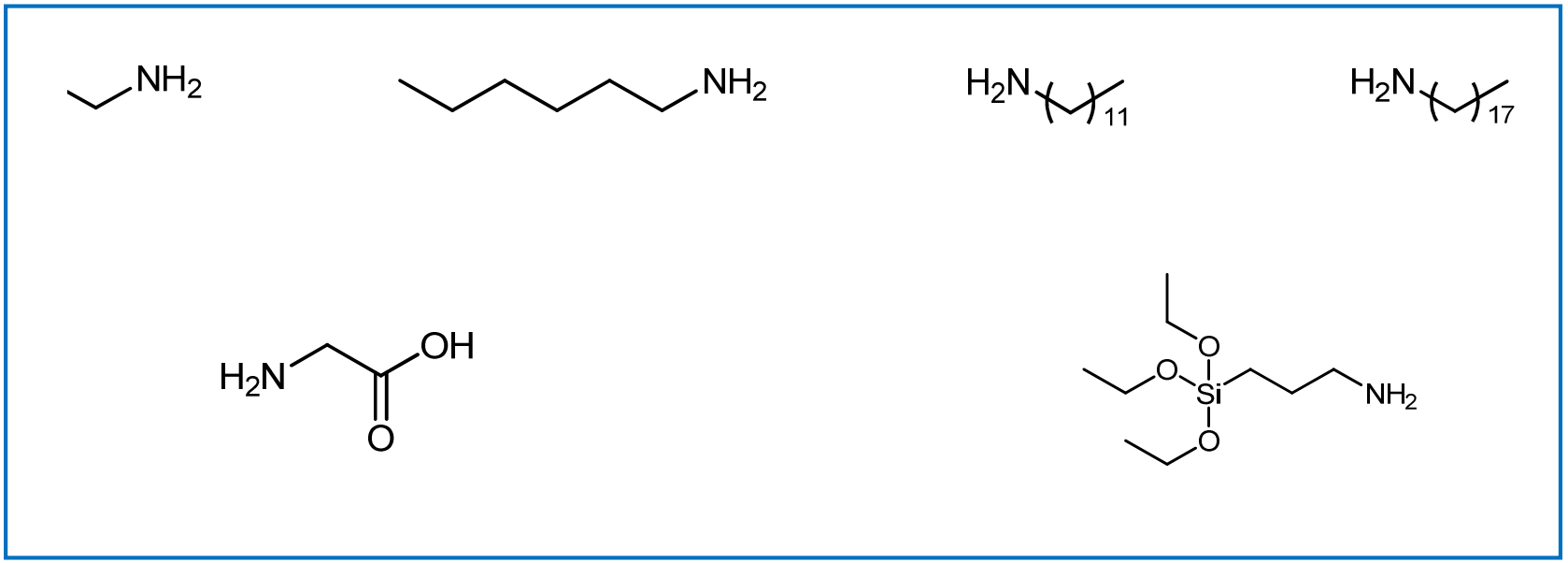

V. Barbera, A. Bernardi, A.Palazzolo, A. Rosengart, L. Brambilla, M. Galimberti Paper accepted for publication on Pure and Applied Chemistry

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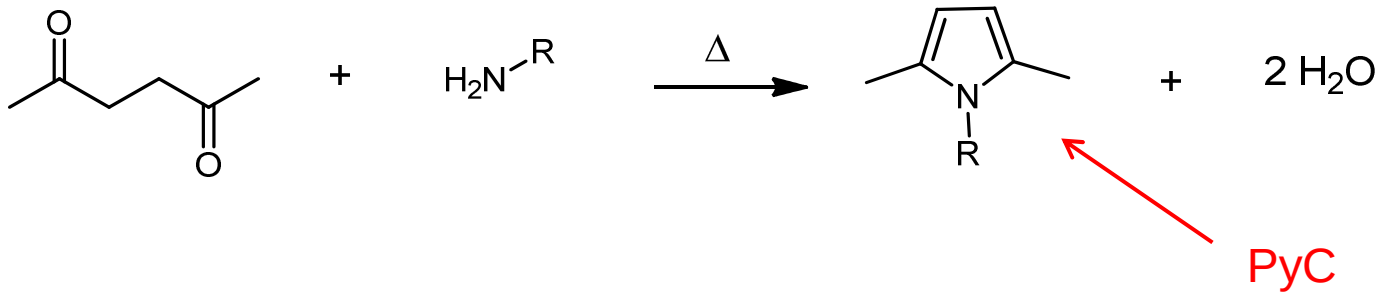
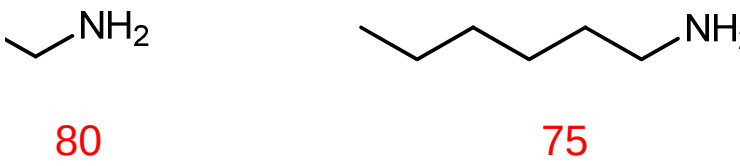


Yield %



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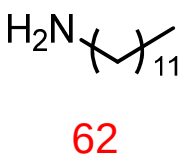
75



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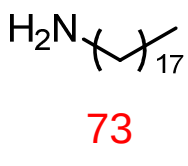

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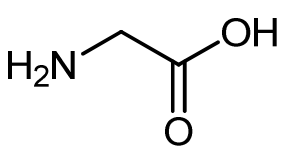

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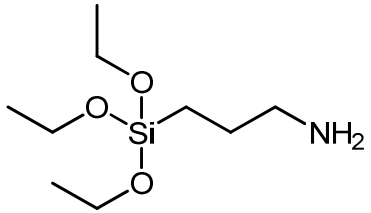

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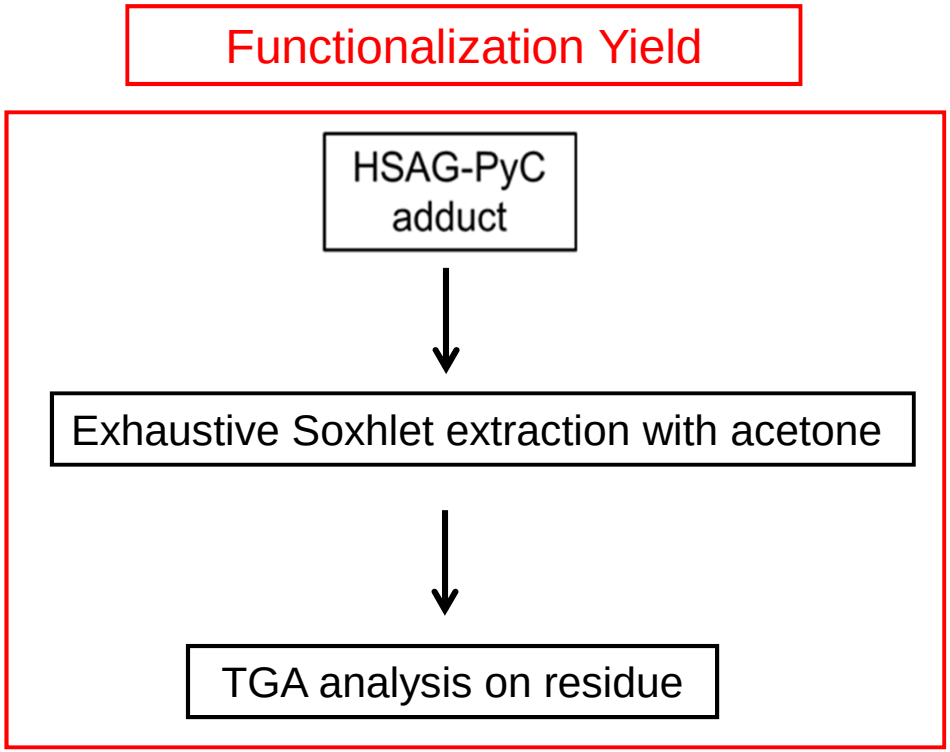
HSAG / PyC adducts



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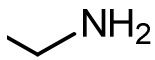
HSAG / PyC adducts

Functionalization Yield %



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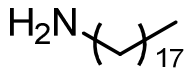
73



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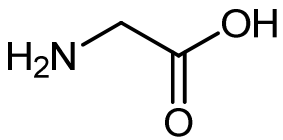

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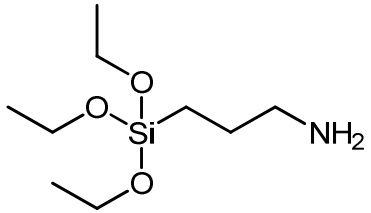

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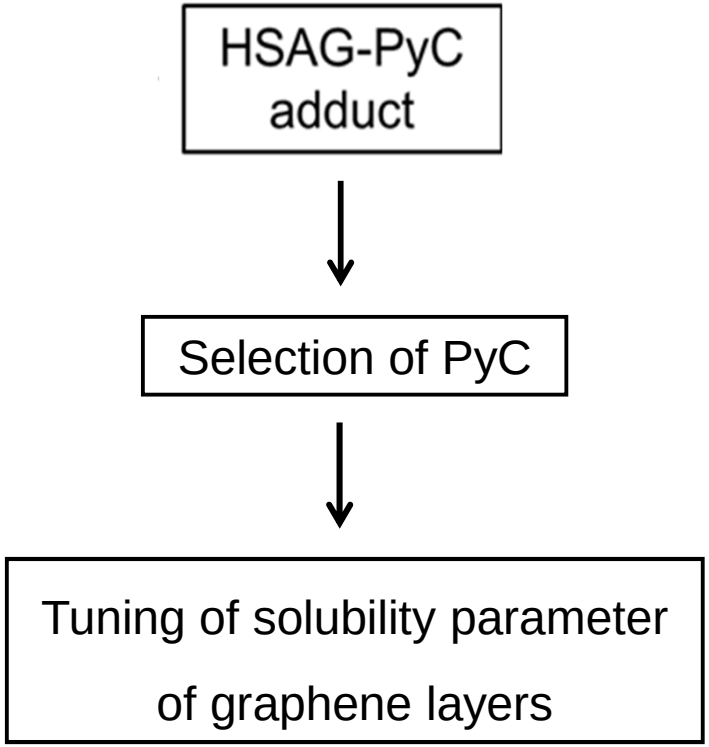
Tuning of solubility parameter of graphene layers



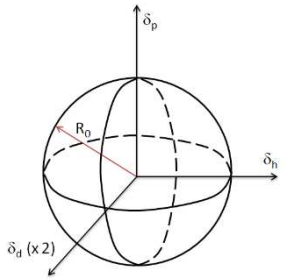
HSAG / PyC adducts - Tuning of solubility parameters

Experimental determination

Stable suspensions
in solvents
with different δ

Theoretical predictions

Computational model:
Hansen solubility parameters



Determination of solubility parameters of HSAG-PyC - Experiments

Adduct	solvents				
HSAG-	water	isopropanol	ethyl acetate	toluene	heptane
TMP	bad (↓)	good	good	good	good
HP	bad (↑)	bad (↓)	good	bad (↓)	good
DDcP	bad (↑)	good	good	bad (↓)	bad (↓)
SP	good	good	good	bad (↓)	bad (↓)
Gly	bad (↓)	good	good	good	bad (↓)
APTESP	bad (↑)	bad (↓)	bad (↓)	good	good

No suspension: **bad**

Unstable suspension: **bad**

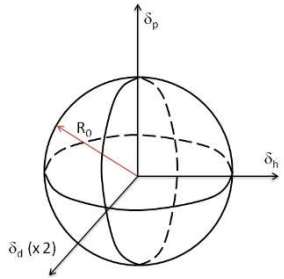
Stable suspension: **good**

V. Barbera, A. Bernardi, A.Palazzolo, A. Rosengart, L. Brambilla, M. Galimberti Paper accepted for publication on Pure and Applied Chemistry

Calculation of solubility parameters of HSAG / PyC adducts

By applying the Hansen Solubility Sphere representation of miscibility

Cohesive energy (Hildebrand model) of a substance:
sum of three contributions:
dispersion, polar, hydrogen bonding:
U_D, U_P, U_H



↓

The substance is identified by three coordinates (δ_D, δ_P and δ_H)
in the Hansen Parameters space

↓

The distance between two points (e.g. of a solute and a solvent)
is related to the cohesive energy difference

↓

Two points close to each other in the Hansen space
indicate miscible substances

Estimation of HSP of a solute *i*

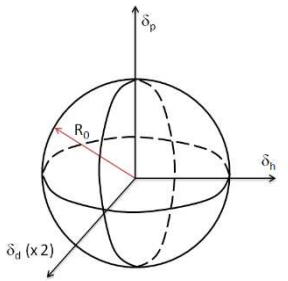
Dispersion tests are performed with different solvents *j*, distinguishing:
- good solvents, which provide stable solutions/dispersions
- bad solvents, which do not give stable dispersions.

↓

Minimization of the ratio * $\frac{\text{Distance between the solute and the solvent}}{R_0 \text{ radius of interaction}}$

↓

Calculation of the center coordinates of the Hansen solubility sphere

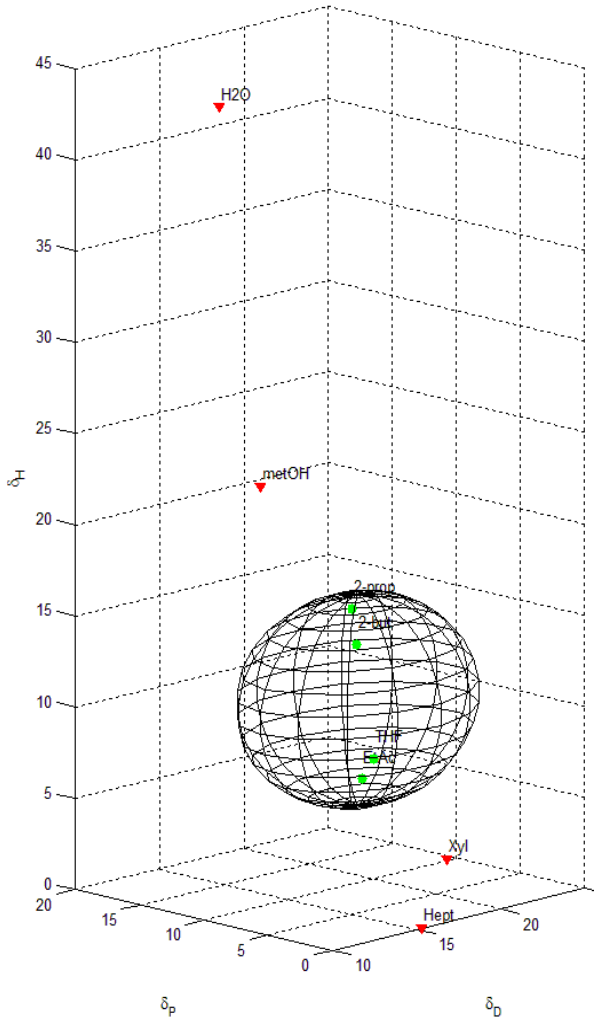


↓

The sphere center coordinates correspond to the three unknown HSP of the solute

* Fitting sphere program adapted from *J. Polym. Sci. Part B Polym. Phys* **47**(21), 2091 (2009) and solved in Matlab environment using the Nelder-Mead simplex algorithm.

Hansen solubility sphere calculated for HSAG-DDcP



Calculated HSP ($MPa^{0.5}$)

δ_D 16.5

δ_P 6.6

δ_H 11.2

green circles: good solvents

red triangles: bad solvents

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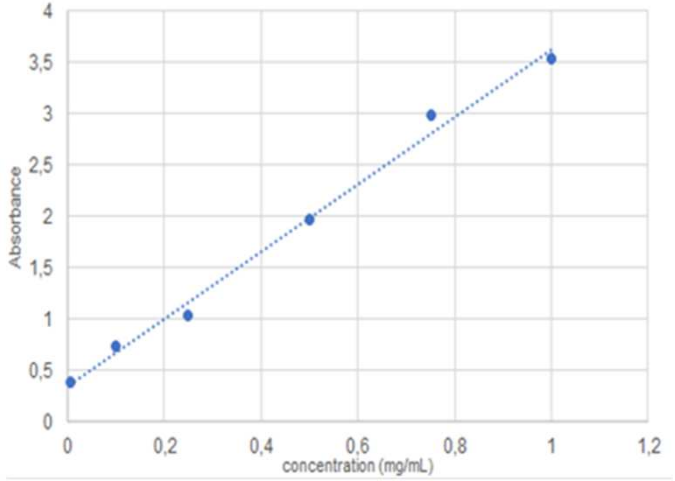
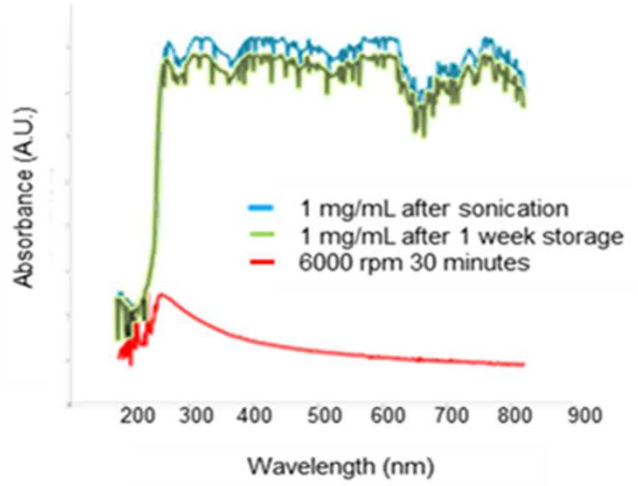
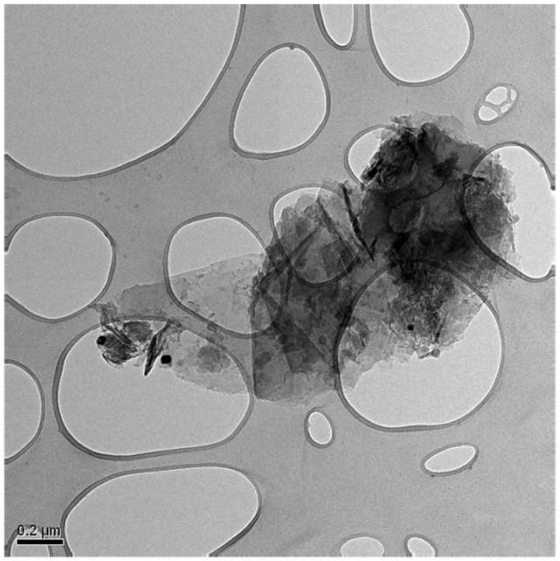
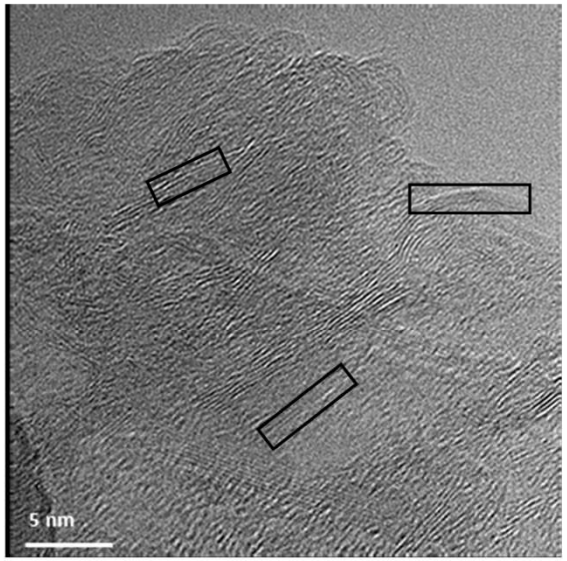
Ultimate dispersions and few layers graphene

By tuning the solubility parameter of graphene layers







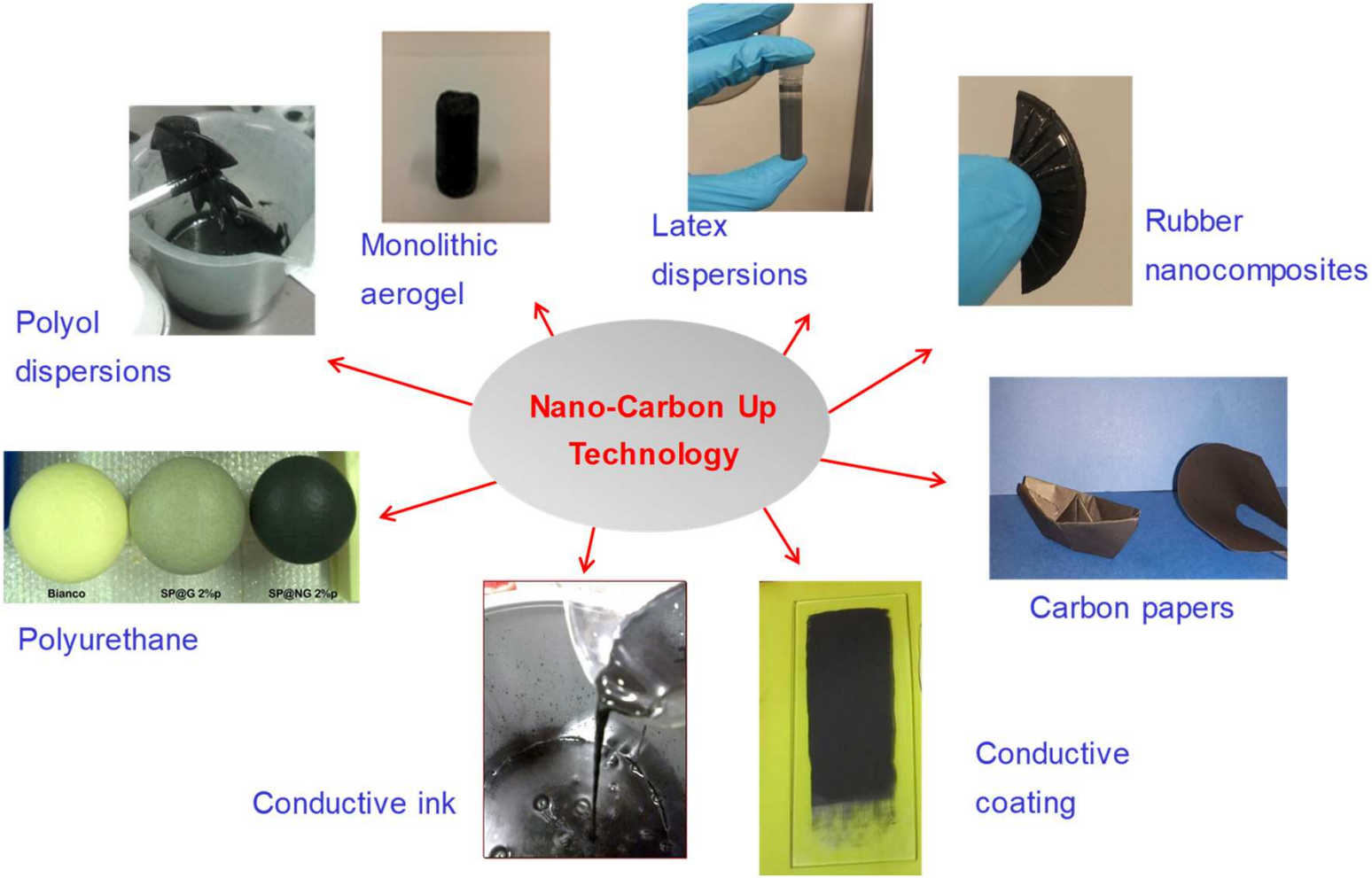


2-3 stacked layers

Conclusions

- Sustainable functionalization of graphene layers is indeed possible
- Functionalization with pyrrole compounds allows the tuning of solubility parameters of graphene layers
- Innovative technology was protected with families of patents
- Developments in progress in various fields

Nano-carbon Up Technology



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