Edge functionalization of graphene layers with a 2-pyrone

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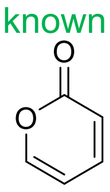
Introduction

2-pyrones are a class of unsaturated heterocyclic C-6 sugar derivatives with versatile chemical reactivity, intriguing building blocks in organic and polymer chemistry [1, 2]. A green and efficient procedure for the preparation of 2-pyrone is available, from galactaric acid [3], also known as mucic acid.

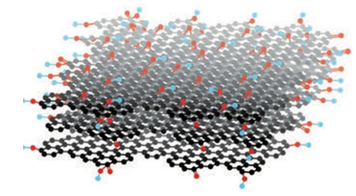


Chemical Structure of 2-pyrone.

Graphene is a cutting-edge material, with excellent mechanical, thermal, electrical and optical properties. [4] The Graphene Era has made available a large number of products with exceptional potential. Among them, Graphene Oxide (GO).

Nowadays, **two main families of GO** are available, with:

1) an extended oxidation of graphene layers;
2) a selective **edge oxidation** [5]



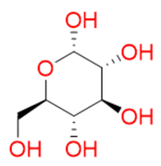
Objectives

➢ To prepare a new generation of **edge functionalized GO**, thanks to the use of a **biobased molecule, a 2-pyrone, PyrCOOEt**, through the functionalization of a nano-sized graphite with high surface area (HSAG) [6], without affecting the sp^2 hybridization of carbon atoms. [7]

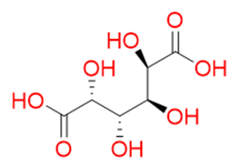
Preparation of PyrCOOEt and HSAG-PyrCOOEt adduct

Synthesis of Pyr-COOEt

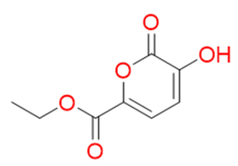
Arundo Donax



D- Glucose



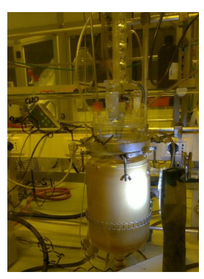
Mucic Acid



PyrCOOEt

+

HSAG

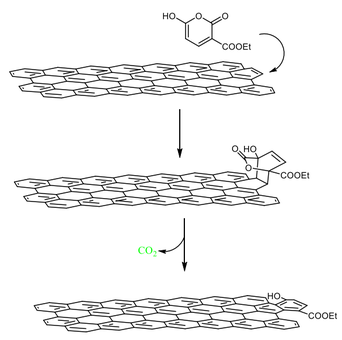


Scaled up @Materiali Sensibili, S. Giuliano Milanese (Mi)

- ☞ Easy procedure
- ☞ High Conversion
- ☞ No solvent
- ☞ Yield up to 73

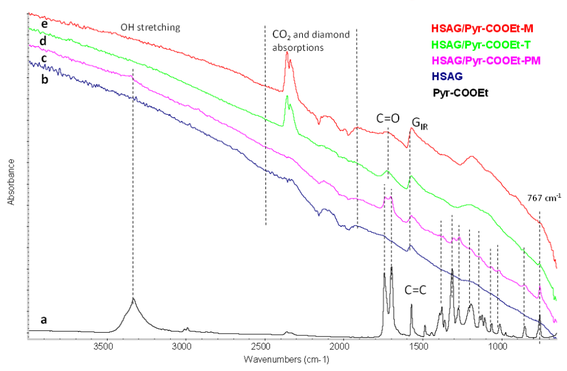
Preparation of HSAG-PyrCOOEt adduct

- ☞ Temperature = 150 °C
- ☞ Reaction time = 2 h
- ☞ Magnetic stirring = 300 rpm
- ☞ High yield of functionalization, up to 91%



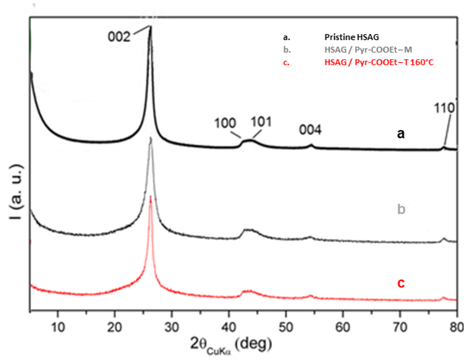
Properties of HSAG-PyrCOOEt adduct, edge functionalized nanosized graphite

FT-IR on diamond crystal



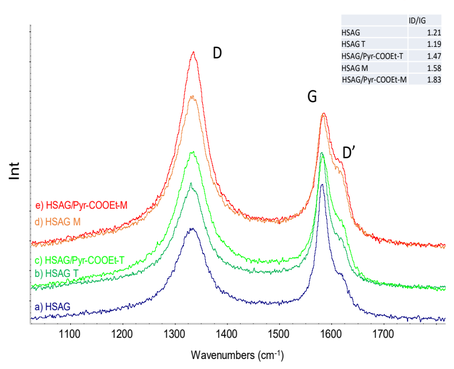
IR findings support the formation of the adduct

X-ray Diffraction Patterns



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

Raman Spectroscopy



Substantially unaltered bulk structure

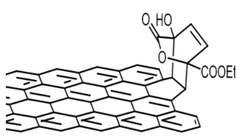
Hansen solubility parameters[a]

Sample	δ_D	δ_P	δ_H	Radius	δ_T[b]
HSAG	17.8	3.1	5.7	1.0	18,95
HSAG-Pyr-COOEt	8.36	12.46	13.59	16.05	20,64

[a]Measure unit: MPa $^{1/2}$; [b] $\delta_T^2 = \delta_D^2 + \delta_P^2 + \delta_H^2$

Modification of HSP after functionalization

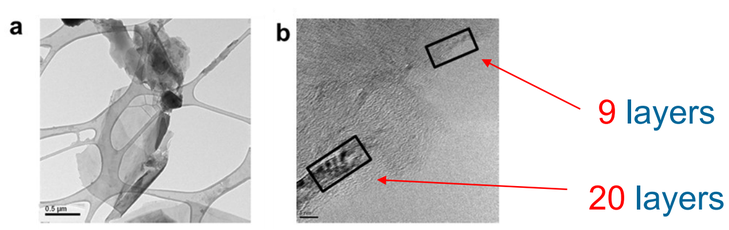
Conclusions



Edge functionalization of graphene layers was obtained using 2-pyrone, with high atom efficiency and low E factor.

Mild sonication and centrifugation of water dispersion of HSAG-PyrCOOEt allowed to isolate few layer graphene from the supernatant.

TEM (a) and HRTEM (b) micrographs



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