Edge functionalization of Graphene Nano-Plates: multi-step carboxylation and Friedel-Crafts reaction

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Introduction

Graphene is a material of recent discovery that shows excellent properties even if its preparation is rather difficult and complex. ***Graphene Nano-Plates*** *(GNPs), made by few tenths of graphene layers, have similar properties but their preaparation is easier. Nevertheless, their employment in the field of nanocomposite materials is not widely applied (diffuso) due to the difficulty to disperse their in solvent or polymeric matrix. The purpose of this work is the selective functionalization of the* ***edges*** *of the GNP, in order to preserve the internal aromatic structure of the plans, preserving the peculiar physical-chemical properties of the graphene materials.*
In this regard, ***two synthetic routes*** *have been applied: bromination, lithiation and subsequent carboxylation; Friedel-Crafts reaction, using succinic anhydride as an acylating agent.*

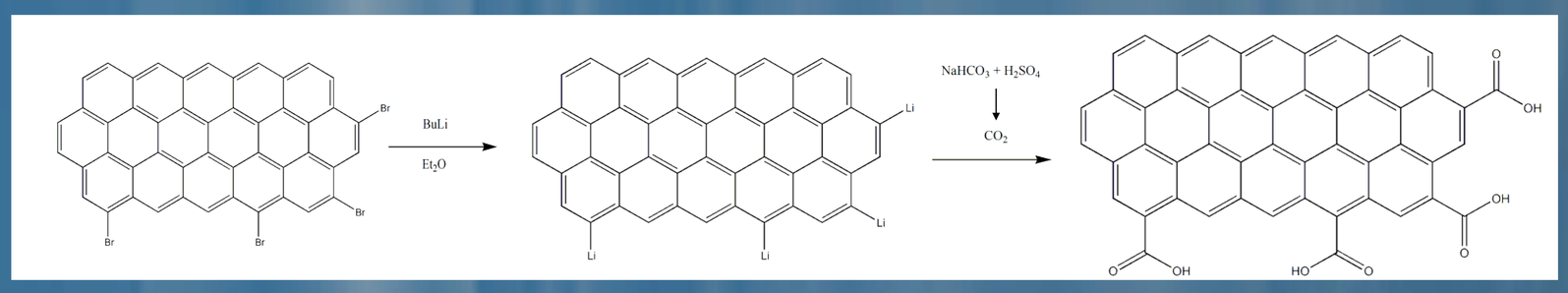
Preparation

Bromination of Graphene Nano-Plates [GNP-Br]

50 ml chloroform anhydrous (solvent) and 54 mg of GNP in an inert atmosphere with molecular nitrogen are placed in a 100 ml two-necked flask. Expected about 10 minutes under magnetic stirring, it is added excess aluminum trichloride and 1.5 ml of liquid molecular bromine.
Waiting 53 hours, the sample is filtered in vacuum and subsequent washed with dilute hydrochloric acid, water and acetone. the reaction product is dried in an oven at a temperature of 90 ° C and subsequently characterized.

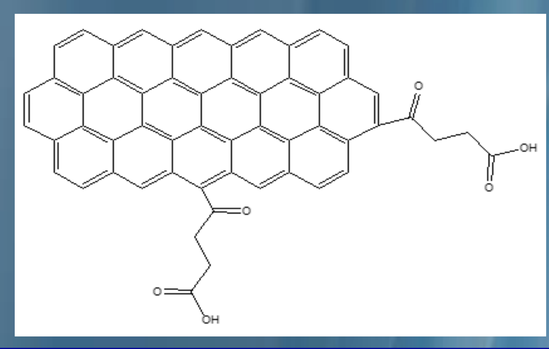
Litiation and carboxilation of brominated GNP [GNP-CO_2H]

20 ml of anhydrous ethyl ether (solvent) and 41 mg of GNP in an inert atmosphere (molecular nitrogen) and under magnetic stirring are placed in a 100 ml two-necked flask. With the help of a cryostat the reactor temperature is reduced to -45 ° C and 1 ml of 1.6 M butyl lithium (in hexane) is added. Subsequently carbon dioxide is introduced in the gaseous phase, it is produced in situ by means of a secondary flask (connected to the reactor by means of a canula) containing sulfuric acid and sodium bicarbonate.
After about 20 hours, the sample is filtered in vacuum and subsequent washed with dilute hydrochloric acid, water and acetone. The reaction product is dried in an oven at a temperature of 60 ° C and subsequently characterized.



Acylation of Friedel-Crafts on GNP with succinic anhydride [GNP F-C]

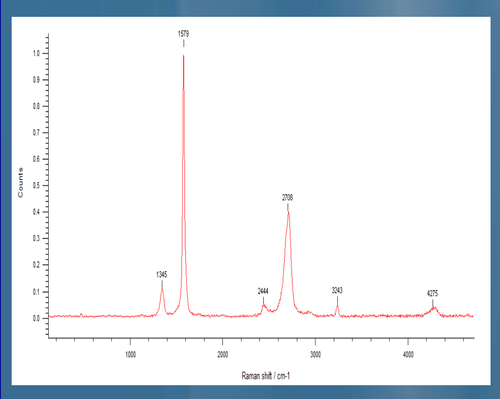
40 ml dichloromethane anhydrous (solvent), 52 mg of GNP and 2,26 g of succinic anhydrided in an inert atmosphere with molecular nitrogen are placed in a 100 ml two-necked flask. Expected about 10 minutes under magnetic stirring, it is added excess aluminum trichloride (4g).
After about 20 hours, the sample is filtered in vacuum (add methanol) and subsequent washed with plentiful water and acetone. The reaction product is dried in an oven at a temperature of 60 ° C and subsequently characterized.



Characterization

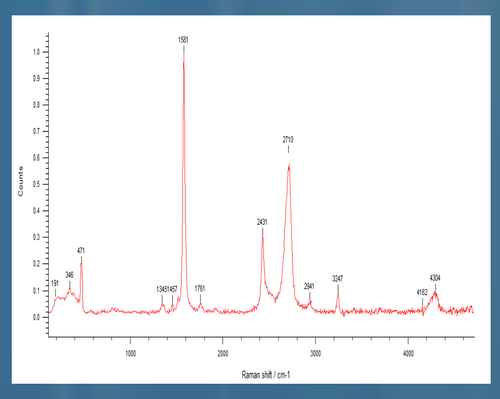
Characterization was carried out trough Thermogravimetric analysis (TGA), infrared spectroscopy (ATR-FTIR), Scannig Electron Microscope (SEM) ed Energy-Dispersive X Ray spectroscopy (EDX) and Raman Spectroscopy. Results are shown below.

Raman spectroscopy



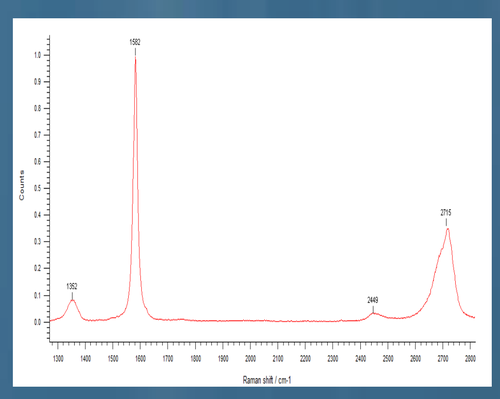
Raman spectrum of the sample GNP-Br

Note the increase in intensity of the D band, symptomatic of the defects of the material [1].



Raman spectrum of the sample GNP-CO_2H

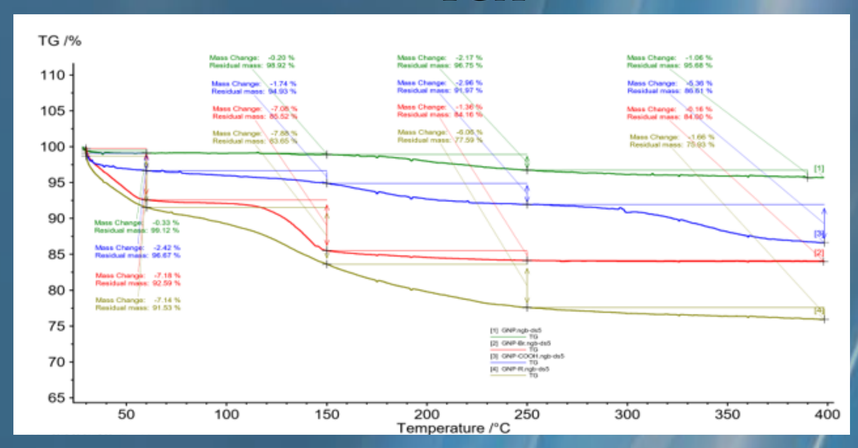
Note the presence of new peaks attributable to graphitic and graphene structures [1]. Of interest is the bands at low wave numbers.



Raman spectrum of the sample GNP F-C

Note the blue shift of the most important bands of graphene materials, which according to literature [2,3] can be attributed to carboxylic functional groups.

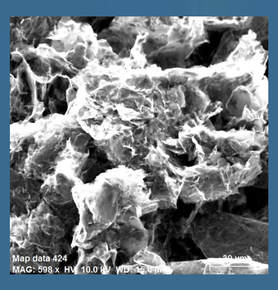
TGA



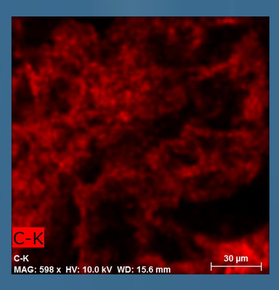
Sample	Region 1	Region 2	Region 3	Region 4
GNP	-0.33 %	-0.20 %	-2.17 %	-1.06 %
GNP-Br	-7.18 %	-7.06 %	-1.36%	-0.16 %
GNP-CO_2H	-2.42 %	-1.74 %	-2.96 %	-5.36 %
GNP F.C	-7.14 %	-7.88 %	-6.06 %	-1.66 %

The ATR-FTIR spectrum of the samples obtained is reported: GNP pristine (green); GNP-Br (red); GNP-CO_2H (blue) GNP F-C (yellow).

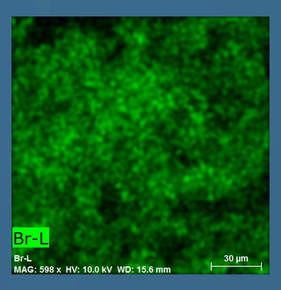
SEM-EDX



SEM morphological recostruction of GNP-Br

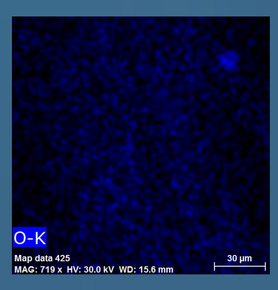


EDX morphological recostruction of the carbon in GNP-Br



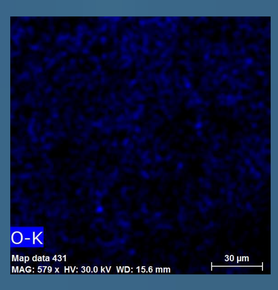
EDX morphological recostruction of the bromine in GNP-Br

Further EDX analyzes were performed on the morphology of the GNP-Br sample, in order to verify the degree of functionalization.
Bromo concentration was obtained: 5.21-21.25 % (weight); 0.82-4.23 % (atomic)



EDX morphological recostruction of the oxygen in GNP-CO_2H

The elemental analyzes carried out on the carboxylate sample showed the following results. Bromo concentration was obtained: 0-0,06 % (weight) and 0-0,01 % (atomic). Oxygen concentration obtained: 9,7-14.0 % (weight) and 6,99-10,89 % (atomic).

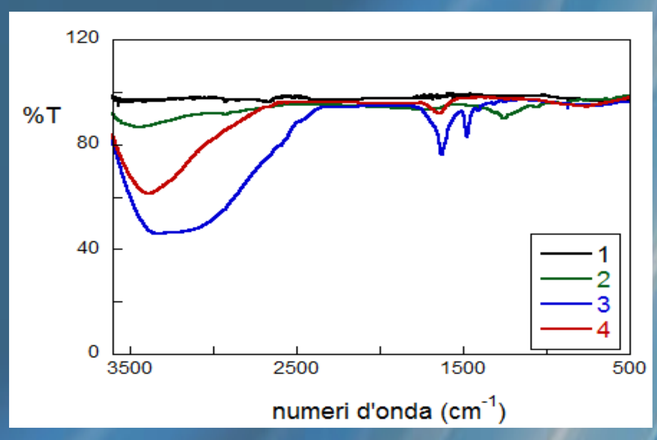


EDX morphological recostruction of the oxygen in GNP F-C

The research is based on the percentage increase in oxygen present in the material that reacted with succin anhydride. Oxygen concentration was obtained: 21,61-32,80 % (weight); 17,15-26,82 % (atomic)

Element	Unn.C [wt.%]	Norm.C [wt.%]	Atom.C [at.%]	Sigma [wt %]
Carbon	25.83	57.23	74.89	3.16
Oxigen	9.59	21.25	20.87	1.35
Bromo	9.71	21.52	4.23	0.48

ATR-FTIR



The ATR-FTIR spectrum of the samples obtained is reported, registered with a diamond cell : GNP pristine (1 black); GNP-Br (4 red); GNP-CO_2H (2 green) GNP F-C (3 blue).

The **GNP-Br** sample shows in addition to the water bands (3400-1640 cm^{-1}) a furher relatively intense and widened absorption band between 900-550 cm^{-1}, attributable to the stretching of the C-Br bond [4]. In addition to the water absorption bands, the **GNP-CO_2H** sample shows a not very intense band between 1730-1650 cm^{-1}, due to stretching C=O [4]. Finally the **GNP F-C** sample shows a very intense band between 1600-1700 cm^{-1}, indicating the presence of carbonyl and carboxylic groups. We also note the presence of a very intense and enlarged band set at 3400 cm^{-1}, suggesting that O-H stretching of the carboxylic group is also present at the water coordinated O-H [4].

Conclusions

The characterizations carried out on the functionalized materials have shown satisfactory results.
Having obtained functional groups on the material it is now possible to chemically modify the GNP at will in order to apply the modified material to new technologies in various fields of science.

[1] A. C. Ferrari e J. Robertson, «Interpretation of Raman spectra of disordered and amorphous carbon», 2000.
[2] X. Fan, D. W. Chang, X. Chen, J.-B. Baek, e L. Dai, «Functionalized graphene nanoplatelets from ball milling for energy applications»,2016.
[3] J. H. Lee, «Graphene in Edge-Carboxylated Graphite by Ball Milling and Analyses Using Finite Element Method», 2013.
[4] R. M. Silverstein, F. X. Webster, e D. J. Kiemle, *Spectrometric Identification of Organic Compounds*, 2005

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