

Sustainable and versatile functionalization of graphene layers

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ABSTRACT

Graphene layers were functionalized by using a sustainable, versatile, easily scalable method. Functionalizing agents were prepared through the reaction of a dicarbonyl compound with a variety of primary amines and were mixed and heated in air with a high surface area graphite. Functionalization occurred with high/very high yield, without producing wastes, thanks to a domino reaction which leads to the formation of covalent bonds in peripheral positions. The structure of the graphitic substrate remained substantially unaltered. The solubility parameter of the graphene layers was modified in a broad range of values and this allowed to develop many different applications: for inks and varnishes, rubber composites, bionanocomposites. The technology, named NanoCarbon Up is based on international granted patents.

Keywords: graphene layers, domino reaction, functionalization, solubility parameter, inks, bionanocomposite

1 INTRODUCTION

Nanosized carbon allotropes are the subject of huge research activity: carbon nanotubes (CNT) [1,2] graphene (G) [3] and graphene related materials (GRM) [4] are extensively investigated due to their outstanding properties.

Great interest is in particular on graphene (and GRM), in consideration of the very large surface area, exceptional mechanical strength, with elastic modulus theoretically over 1TPa and Young modulus of about 1060 MPa [5], high charge-carrier mobilities [6]. Impressive research is performed on nanocomposites based on G and GRM [7], as composites can bring the properties of graphene to the macroscopic scale.

To have ultimate distribution and dispersion of G and GRM in various matrices, of low or high molar masses, it would be highly desirable to modify the solubility parameters of the carbon materials. Hence, functionalization of graphene layers has to be performed. Much interest is on graphene oxide (GO), prepared from the oxidation of graphite [8]. GO is also a preferred intermediate to prepare graphene layers or, to say better, chemically reduced graphene oxide. However, some drawbacks characterize the preparation of GO and graphene layers through the oxidation-reduction pathway. Harsh reaction conditions and in some case toxic reagents are used. The structure of GO is substantially not completely

known. Moreover, only oxygenated groups are introduced, without any selectivity on their position on the graphitic layers. After the reduction, the bulk structure of graphitic material is not completely restored. Most functionalization methods reported in the literature share the same drawbacks, essentially: the complexity of chemical reactions, the poor versatility in the type of functional groups.

In this contribution, a sustainable, versatile, easy functionalization method is presented [8-13]. Graphene layers were functionalized with pyrrole compounds (PyC) obtained from the reaction of 2,5-hexanedione with various primary amines. Yield and atom efficiency of PyC synthesis are reported. The functionalization of graphene layers is described, from the procedure to the functionalization yield. Structure of functionalized layers is presented. Mechanism of functionalization is illustrated. Applications for inks and varnishes, rubber and thermoset composites and bionanocomposites are discussed.

2 EXPERIMENTAL

2.1 Materials

Reagents and solvents

Details on chemicals used for the present work are reported elsewhere [9].

High surface area graphite

Synthetic Graphite 8427® from Asbury Graphite Mills Inc was used. Main characteristics have been already reported [8,9].

2.2 Synthesis of pyrrole compounds (PyC)

General procedure

The selected primary amine and 2,5-hexanedione were poured in equimolar ratio in a 50 mL round bottom flask equipped with magnetic stirrer. The mixture was left to stir at 130 ° C for 3 hours. After this time the reaction mixture was cooled to room temperature and the water was removed at reduced pressure.

Details on the synthesis of PyC have been already reported [9].

2.3 Preparation of HSAG-PyC adducts

Synthesis of HSAG-PyC - General procedure

In a 50 mL round bottom flask were put in sequence HSAG (200 mg) and acetone (15 mL). The suspension was sonicated for 15 min, using a 2 L ultrasonic bath. After this time, a solution of pyrrole derivative (20 mg, 1:10 in mass) in acetone (5 mL) was added. The resulting suspension was sonicated for 15 min. The solvent was removed under reduced pressure. The black powder of HSAG/PyC was poured into a 25 mL round bottomed flask equipped with magnetic stirrer and was heated at 180°C for 2 h. After this time, the mixture was placed in a Büchner funnel with a sintered glass disc, washed and then recovered and weighted.

2.4 Characterization of HSAG adducts

Characterization was performed by means of: Thermogravimetric analysis (TGA), Fourier Transform-Infra Red spectroscopy (FT-IR), Raman spectroscopy, High-resolution transmission electron microscopy (HRTEM). Experimental details are reported elsewhere [9].

3 RESULTS AND DISCUSSION

Preparation

Pyrrole compounds were prepared through the Paal-Knorr reaction between a primary amine and 2,5-hexanedione [8-12], as described in Fig. 1.

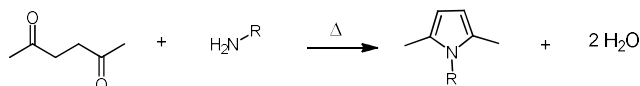


Figure 1. Schematic synthesis of pyrrole based compounds

The structures of primary amines used for the reactions and of pyrrole compounds obtained therefrom are shown in Table 1.

All the reactions of Table 1 are characterized by very good atom economy (from 81 % to 90 %), the only byproduct being water. All the syntheses were carried out in the absence of solvents and catalyst: neat reactions were at 130 °C for 3 h. High/very high yield was obtained and thus high atom efficiency. For example, the preparation of 2-(2,5-dimethyl-1H-pyrrol-1-yl)-1,3-propanediol (serinolpyrrole, SP) from 2-amino-1,3-propanediol (also known as serinol) as the primary amine has an atom economy (AE) of 83 % and gave a yield of 96 %, with and a reaction mass efficiency (RME) of 80 %. Most of the reaction of Table 1, with primary amine other than serinol, had a yield of at least 70 % and some of them of at least 80 %. The pyrrole compounds of Table 1 were thus obtained with a process that can be defined “sustainable”, characterized by reaction mass efficiency from 55 % to 80 %.

Amine	Yield (%)	AE ^a (%)	ID ^b	Product
	73	84	HP	

	62	88	DDcP	
	73	90	ODcP	
	80	81	GlyP	
	96	83	SP	
	80	89	APTESP	

Table 1: Primary amines used for preparation of PyC.

^aAE: atom economy, ^bID: acronym

All the pyrrole compounds of Table 1 were used for the functionalization of graphene layers. The functionalization procedure is shown in Figure 2 below.

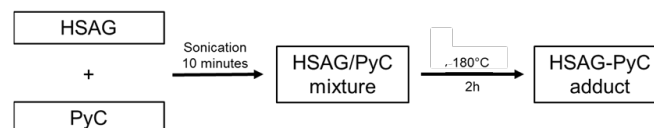


Figure 2. Block diagram for the preparation of HSAG-PyC adducts

In brief, PyC and HSAG were simply mixed and heated. The mass ratio between HSAG and PyC was 10:1. Adducts were thoroughly extracted with acetone and functionalization yield (%Y) was calculated by means of equation (1):

$$\%Y = 100 * \frac{\text{PyC mass \% in (HSAG-PyC adduct) after acetone washing}}{\text{PyC mass \% in (HSAG-PyC adduct) before acetone washing}} \quad (1)$$

Mass% of PyC in the adduct was determined through TGA analysis. PyC was detected in a temperature range between 150°C and 700°C, after subtracting the mass loss attributed to impurities on HSAG (equal to 0.5 mass%, as assessed through TGA analysis of pristine HSAG).

Functionalization yields are in Table 2.

Entry	Adduct	Yield *
1	HSAG-DDcP	80%
2	HSAG-ODcP	98%
3	HSAG-GlyP	82%
4	HSAG-SP	97%
5	HSAG-TMP	73%
6	HSAG-HP	87%

7	HSAG-APTESP	78%
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Table 2: Functionalization yields (%) of HSAG-PyC

Values in Table 2 allow to comment that stable adducts were obtained with all PyC.

It was demonstrated that such stability is due to the formation of covalent bonds between the graphene layer and the pyrrole compound [11]. Experimental findings (FT-IR, Raman, XPS) and DFT calculations led to hypothesize the following mechanism, based on a domino reaction. The pyrrole compound undergoes oxidation in the presence of air, catalyzed by the carbon substrate. 1,5-dimethyl-2-pyrrolcarbaldehyde (DMP-CHO) was isolated as oxidized product. DMP-CHO gives rise to cycloaddition reaction with dienes of the graphene layers. Structure of DMP-CHO and hypothesized reaction mechanism are in Figure 3

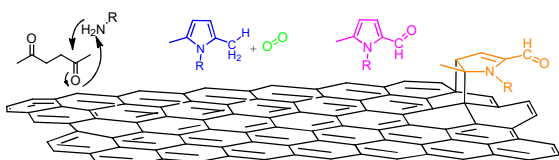


Figure 3. Domino reaction for the functionalization of graphene layers

It is indeed worth underlining that the synthesis of PyC can be performed *in situ*, on the graphene layers, as it can be seen in Figure 3.

Characterization

All the adducts were characterized by means of different analytical techniques. Results from Infrared (IR) and Raman spectroscopy are here commented. In Figures 4 and 5 samples analyzed are: HSAG (black), HSAG-SP (red), HSAG-Gly (blue), HSAG-HP (cyan), HSAG-DDcP (green) and HSAG-APTESP (violet)

Qualitative information on the functional groups on the graphene layers was obtained from Infrared spectroscopy: Spectra of HSAG and HSAG-PyC adducts, in the 700 cm^{-1} – 1800 cm^{-1} fingerprint region, are shown in Figure 4.

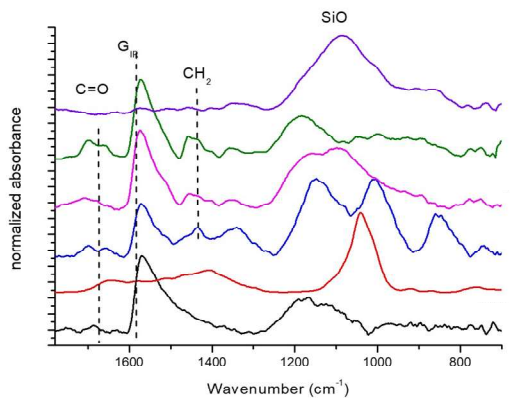


Figure 4. FT-IR spectra (between 700 and 1800 cm^{-1})

Baseline correction allowed to enhance the weak spectroscopic features of functional groups. Detailed comments are elsewhere [9]. The strong signal at 1590 cm^{-1} is typical of graphitic materials and it is assigned to the collective C=C stretching vibration. Absorptions close to 1700 cm^{-1} , common for all the spectra, are compatible with the presence of C=O stretching vibrations, and in the 1100-1200 cm^{-1} range, most likely due to the stretching vibrations of C-O-C and C-OH functional groups. In HSAG-SP and HSAG-APTESP spectra, there is the strong absorption of typical functional groups: at 1040 cm^{-1} (stretching of C-O-R groups) and at about 1100 cm^{-1} , typical of Si-O stretching vibration, respectively. Characteristic signals of HSAG-HP and HSAG-DDcP are close to 1450 cm^{-1} (CH_3 and CH_2 bending vibrations).

Raman spectra in Figure 5 reveal two main peaks located at 1580 cm^{-1} and 1350 cm^{-1} , attributed respectively to G and D bands. The high intensity of the D band has been attributed [8,9] to different types of molecular disorder. However, the relative amount of G and D bands is similar in all the spectra.

X-ray investigation brought to conclude that functionalizing molecules were not intercalated in the interlayer space and that the same crystalline order was maintained inside the layers.

All the findings from characterization of G-PyC adducts allow to conclude that the structure of graphene layers is not altered by the functionalization with pyrrole compound, which occurs in peripheral positions, essentially on the edges.

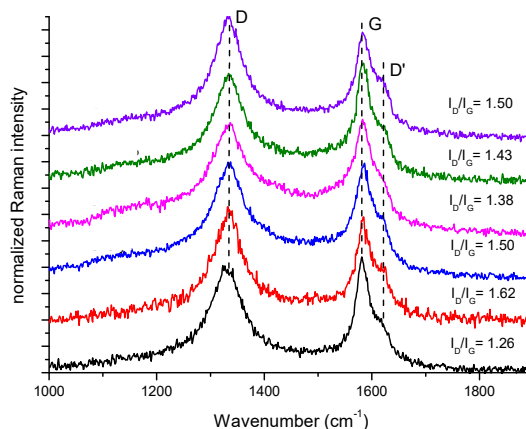


Figure 5. Normalized Raman spectra recorded at 632.8nm, with ID/IG values reported.

Solubility parameters of adducts of graphene layers with PyC were estimated, as reported elsewhere [9]. Stability of suspensions in solvents with different solubility parameters were investigated and elaboration was performed with the method of the Hansen solubility parameters. In Table 3 are reported values of the radius of the Hansen sphere. It can be observed that functionalization increases the value of the radius, and thus, enlarges the compatibility of HSAG with different environments.

Sample	Radius
HSAG	1.0
HSAG-TMP	11.6
HSAG-DDcP	12.3
HSAG-APTESP	8.3
HSAG-SP	13.8
HSAG-GlyP	15.3

Table 3. Radius of Hansen sphere

Applications

Few selected examples are reported

Isolation of graphene layers

Few layers graphene were isolated by preparing water dispersions of HSAG-SP, sonicating and centrifugating. Pictures in Figure 6 show that the size of graphene layers is the same as in pristine HSAG (a) and that few layers are in the stack.

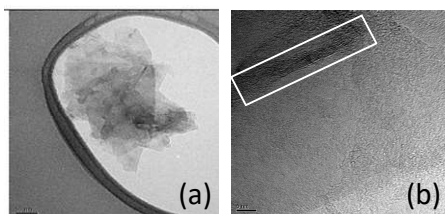


Figure 6. Few layers graphene from HSAG-SP

With this functionalization technique FLG can be isolated without using critical solvents, such as aromatic and chlorinated chemicals.

Inks

Electrically conductive coatings were prepared with water based inks based on HSAG functionalized with SP. Figure 6(a) shows water dispersions (2-8) of HSAG-SP, stable for months, with concentration from 1.0 to 0.1 mg/L. It was even possible to prepare dispersions with 200 g/L of HSAG-SP Fig. 6(b).

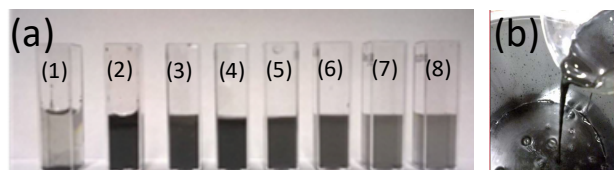


Figure 6. Inks based on HSAG-SP

Bionanocomposites

Electrically conductive bionanocomposites, with good mechanical properties, were prepared from a water dispersion of chitosan and HSAG-SP. They are shown in Figure 7: carbon papers (a) and aerogels (b).



Figure 7. Bionanocomposites from chitosan and HSAG-SP

4 CONCLUSIONS

A domino reaction generated by simply mixing and heating a dicarbonyl compound and a primary amine on graphene layers leads to the functionalization of the layers. The structure of the graphitic substrate remains substantially unaltered. Solubility parameters of the carbon nanomaterial can be modulated in a broad range of values and thus can be achieved the compatibility of graphene layers with different environments. Such functionalization method is sustainable and easily scalable. Many applications are in progress and can be envisaged. The technology, named NanoCarbon Up is based on families of patents [12-14].

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