Effect of different coupling agents in the doping of graphite oxide with 3–3′ diaminobenzidine: textural, structural and electrical properties

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Abstract

The doping reactions of graphite oxide (GO) with 3-3′-diaminobenzidine (DAB) were studied using N, N′-dicyclohexylcarbodiimide (DCC), cyanuric chloride (CC) and hexafluorophosphate (HATU) as coupling agents. The bifunctionality of the coupling agents aid to interact GO functional groups with amino groups of DAB without being part of the final product. The doped materials (d-GO) and GO were characterized by thermogravimetric analysis, x-ray diffraction, FTIR/Raman spectroscopy, x-ray photoelectron, high-resolution electron microscopy and cyclic voltammetry. The GO-HATU material was more thermally stable than other graphitic material, with at 10% weight loss at 300 °C, this thermal stability is related to a more difficult intramolecular physisorbed water removal process than the other d-GO materials. GO-CC and GO-HATU materials presented 8.2 and 8.0 Å of interlayer spacing, which was associated with a good oxidation-doping process. Besides, these two materials showed modifications in the vibrations by FTIR technique, corresponding to epoxy and hydroxyl groups of the GO being more susceptible to react with the amino groups. Moreover, $I_D/I_G$ ratio calculated by Raman Spectroscopy presents the following trend 0.70, 0.94, 0.97 and 1.04 for GO, GO-CC, GO-DCC and GO-HATU, respectively, this increase is related with a major disorder during the doping process. XPS analysis shows C–N and N=C bands for high resolution of C 1s and N 1s, respectively, for d-GO materials. This possibly suggests the formation of benzimidazoles during the oxidation-doping process, this generates a similar -non-lattice and -lattice oxygen amount for O 1s related to crosslinking between the functional groups of GO and DAB which improve the electronic mobility between the surface and the bulk of the final graphitic material. Finally, the obtained d-GO materials were investigated as a working electrode for electrochemical capacitors and all of them showed typical capacitive behaviour.

1. Introduction

Graphite oxide (GO) was first synthesized in 1855 by Benjamin C. Brodie since then it has attracted interest in the scientific community [1]. GO is a non-traditional compound obtained from graphite oxidation, like nanoplatelets, it acts as an important precursor of graphene after the chemical reduction and an exfoliation process. Industrial production of GO is used in the development of graphene-like structures with different...
applications, including conductive polymer composites [2] supercapacitors [3], molecular, electrochemical, or biochemical sensors [4], antigen biosensors [5], lithium storage materials [6], amongst others.

GO’s diverse physicochemical properties are due to the synthesis method and the degree of oxidation generating disorganization of the structure. The oxidation exhibits lamellar structure with randomly distributed unoxidized aromatic regions (sp²-carbon atoms), six-membered aliphatic regions (sp³-carbon atoms), GO’s interlayer spacing is about two times larger at ~0.7 nm than that of graphite [7]. The space between layers results in different hydration capacities with intermolecular attraction type Van der Waals forces. The interlayer spacing caused by the oxidation process generates ortho-quinone, ketone, para-quinone, carboxyl, hydroxyl and epoxy functional groups, which are capable of facilitating a broad range of synthetic transformations. Popular synthesis methods are Brodie, Staudenmaier, Staudenmaier-Hofmann-Hamdi and Hummer, this last method being one of the best graphite oxidation processes with elementary analysis C/O values from 2.44 to 2.7 [8]. These methods are commonly used to modify the structure, generating greater disorder and therefore different distances between layers related with irregular packaging.

The spacing of layered graphitic materials in organic molecules is a reaction that permits a facile control over the physicochemical characteristics. Coupling agents and ions enter the galleries that separate the layers, usually with an expansion of the lattice along the stacking axis.

The expansion between layers can be generated by the addition of nitrogen-containing compounds, these reactions are carried out with the functional groups of the GO. Particularly compounds with functional groups such as NH₃ providing an alkaline environment that favour the nucleophilic substitution reaction between the amine groups and the epoxy groups [9], generating combinations of oxygen, hydrogen, carbon, and itself than any other element which are modifiers of the mentioned functional groups. Its several valences enable it to unite with these other elements to form a variety of nitrogen-containing functional groups [10]. The mechanism begins with the attack of the amine on carbonyl carbon. Acid-base equilibria allow protonation of the -OH leaving the molecule aided by the cession of the electronic pair of the second hydroxyl group. The reaction mechanism is reversible and can be reversed with hot acids or bases, again obtaining the acid and the amine. The formation of amide bonds is one of the most prevalent transformations in the pharmaceutical industry [11].

 Particularly, Xue et al 2014 functionalized graphite oxide and graphene oxide composite membranes with 3,3′-diaminobenzidine (DAB) and 5-tert-butyl isophthalic acid (BuIPBI) to obtain polybenzimidazoles by microwave [12]. Benzimidazole and its derivatives are regarded as an important heterocyclic motif, exhibiting a wide range of pharmaceutical applications, including anti-cancer-, anti-hypertensive, antivirals, antifungals, anti-HIVs, anti-convulsant, and anti-diabetics. In view of their wide-ranging of applications, the synthesis of benzimidazoles and its derivatives to improve the solubility in organic solvents remain a primary focus. For example, it was used as the substrate in horseradish peroxidase catalysis reaction as a voltammetric enzyme immunoassay system for the detection of the carcinoembryonic antigen in human serum [13].

The formation of amide, imidazoles, benzimidazoles and polybenzimidazoles bonds has been investigated by various authors due to the importance in the pharmaceutical industry. In particular, the coupling agents used in the large-scale condensation of acids and amines for medicament synthesis. Amide bonds are incorporated very frequently in assets pharmaceutical grade active ingredients. In fact, the formation of the amide bond is one of the most frequent transformations in the pharmaceutical industry (16% of all reactions) [14].

The chemical complexity of the coupling agents derives in the bi-functionality that characterizes them. As a result, in the activation of carboxyl group that helps promote coupling with an amine and the generation of high value-added products on an industrial scale.

There are many considerations when selecting an amide coupling reagent for plant production. The ideal reagent is economical, readily available, non-toxic, safe, easy to handle, easy to purge from reaction mixtures and only contribute minimally to waste streams.

In this work three complexing agents CC, DCC and HATU were used in the doping graphite oxide with 3-3′-diaminobenzidine (DAB) using cyanuric chloride (CC), N,N′-dicyclohexylcarbodiimide (DCC), and hexafluorophosphate N-oxide (HATU) as coupling agents. The three complexing agents used are representative reagents of several groups commonly used in the amide bond formation as reagents. The doped GO materials were used in several research areas due to the mechanism of intercalation during the oxidation-doping process in which the oxygen concentration available superficially and degree of functional groups. The changes in textural, structural and morphology properties of the d-GO were followed by thermogravimetric analysis, x-ray diffraction, x-ray photoelectron, FTIR/Raman spectroscopy, high-resolution electron microscopy and linked with their electric properties through the use of cyclic voltammetry.
2. Experimental section

2.1. Materials

All materials were used as received. Graphite (∼325 mesh [<44 μm, ≥99%] particle size), potassium permanganate (KMnO₄, 99% from Aldrich) were purchased from Merck, sulphuric acid (H₂SO₄ 95%, from Aldrich), hydrochloric acid (37%) were provided by J. T. Baker, hydrogen peroxide solution H₂O₂ (30 % w/w in H₂O), 3-3′-diaminobenzidine (DAB, 99%), cyanuric chloride (CC, 99%), N,N′-dicyclohexylcarbodiimide (DCC, 99%), 4-(dimethylamino) pyridine (DMAP, 99%), N-[((dimethylamino)-1H-1,2,3-triazolo[4,5-b] pyridin-1-ylmethylene]-N-methylmethanaminium hexafluorophosphate N-oxide) (HATU, 97%) N,N-dimethylformamide (DMF, 99.8%), sodium borohydride (NaBH₄, 98%), L-ascorbic acid (C₆H₈O₆, 99%), butyl acetate (C₈H₁₈O₂, 99.5%), and N-methylmorpholine (C₅H₁₃NO, 99.5%) were provided by Aldrich, ethanol (C₂H₅OH, 99.5%) and acetone (C₃H₆O, 99.6%) were provided by Meyer.

2.2. Synthesis of graphite oxide

Graphite oxide was synthesized by a modified Hummers’ method [15]. Natural graphite flake (3.0 g) was oxidized in a solution with 80 ml of concentrated sulfuric acid under stirring with on ice bath. Potassium permanganate (11.5 g) was slowly added to the suspension and the temperature remained constant with reaction temperature at ∼20 °C and stirred for about 18 h. After this, the ice bath was removed, and the mixture was stirred at 30 °C for 1 h. Subsequently, deionized water (0.3 l) was slowly added under vigorous stirring at ∼30 °C for 3 h, the diluted suspension was further stirred at ∼90 °C for 1 h. Afterward deionized water (300 ml) with hydrogen peroxide solution H₂O₂ (8 ml, 50 wt% in H₂O, from Aldrich) was added. The product was collected and purified by washing with a 5% solution of hydrochloric acid (HCl, 37 wt% in H₂O, from Aldrich) in order to remove the sulphates. The product was then washed with deionized water (1 l), ethanol (0.5 l, 99.45%, from Aldrich) and acetone (0.3 l, 99.9%, from Aldrich). The final product was centrifuged for about 1 h, and the resulted graphite oxide was dried for 48 h at 60 °C.

2.3. Synthesis of doped graphite oxide materials (d-GO)

The synthesis of doped graphite oxides (d-GO) covalently were carried out by 3-3′-diaminobenzidine (DAB) and one of the coupling agents: cyanuric chloride (CC), N,N′-dicyclohexylcarbodiimide (DCC), and 2-(1H-7-azabenzo[1,2-c;3,4-c′]triazol-1-yl)-1,1,3,3-tetramethyl uronium hexafluorophosphate methanaminium (HATU), the resulting products were named GO-CC, GO-DCC and GO-HATU, respectively.

2.3.1. Synthesis of GO-CC

The doping process of GO-CC initially part of 0.2 g of GO dispersed into 30 ml of butyl acetate and sonicated by 1 h, then 0.192 g of CC and 0.35 ml of N-methylmorpholine (NMM) were added, the mixture was vigorously stirred by 1 h, then 0.25 g of DAB was added and stirred at room temperature for 3 h. The final product was collected and purified by three centrifuged cycles with deionized water finally, the product was washed and centrifuged with ethanol and acetone and dried at 60 °C by 12 h, the yield obtained 0.130 g.

2.3.2. Synthesis of GO-DCC

A dispersion was made of 0.20 g of GO with 30 mL of butyl acetate was sonicated by 45 min, then 0.25 g of DAB, 2.30 g of DCC and 0.23 g of DMAP were added and refluxed and stirred for 29 h, resulted orange dispersion was washed and centrifuged by cycles of deionized water, ethanol and acetone. The bright black solid was dried at 60 °C by 12 h, with a performance at 0.16 g.

2.3.3. Synthesis of GO-HATU

Finally, doping GO-HATU started with 0.20 g of GO dispersed in 30 ml of anhydrous DMF and sonicated for 1 h, then 0.25 g of DAB and 0.25 g of HATU were added and stirred vigorously for 45 min at RT, then the suspension was heated at 100 °C for 5 h. Resulted product was washed and centrifuged with deionized water several times. Finally, ethanol and acetone washings were made until an uncolored solution was seeing, resulting solid was dried at 60 °C by 12 h, with a performance at 0.19 g.

2.3.4. General reduction for doped materials

After doping reactions, the d-GO material followed by a reduction reaction. In a 0.5 l round-bottomed flask were added and dispersed 0.10 g of d-GO material in 300 ml of deionized water, under vigorous stirring 0.50 g of L-ascorbic acid was added and heated at 80 °C for 1.5 h, then was added sodium carbonate until reach pH approximately at 9.0 and 0.6 g of NaBH₄ was added stirred and heated at 80 °C for 1.5 h. The product was
collected and washed with deionized water and centrifuged until residual washing water had pH ~5.0. The final solid was dried at 60 °C for 12 h.

2.4. Materials characterizations
The thermal decomposition of GO and of the d-GO was analyzed in a TGA-DTA in a TA Instruments Q600 equipment, in an inert atmosphere with a heating rate of 10 °C · min⁻¹ from room temperature to 950 °C. The x-ray diffraction spectra were taken in a PXRD D8 Advance Bruker AXS using CuKα radiation, the spectra were acquired in a 2θ angle geometry in a domain 5 to 50° with a 0.019° step and the spectra were checked against the previous sited crystallographic tables. FTIR analysis of GO and the d-GO were performed with an infrared spectrophotometer (Bruker, Luftin, TX, USA) where the materials were cast on diamond crystal top-plate of attenuated total reflectance (ATR) accessory and scanned in the range 500–4000 cm⁻¹. Raman Spectra were carried out by Thermo Scientific DXR Raman Microscope equipment with a 50x objective, at 2 mW with He-Ne laser 532 nm laser excitation, and at 1800 lines/nm grating monochromator with a charge-coupled-device (CCD) detector, where the materials were loaded over glass slide, 3 different points were taken per sample, then an average was performed and scanned in the range 90–1800 cm⁻¹. The chemical analysis was obtained using X-ray photoelectron spectroscopy (XPS). The analysis was carried out using a VG Microtech ESCA2000 Multilab UHV system, with an AlKα X-ray source (hν=1483.6 eV), operated at 12.5 kV and 22 mA beam, and a CLAM4MCD analyzer, where the surface of materials etched for 2 min with 3.0 kV Ar⁺ at 0.06 μA mm⁻². XPS spectra were obtained at 55° to the normal surface in the constant pass energy mode (CAE), E₀ = 50 and 20 eV for the survey and high-resolution narrow scan, respectively. The peak positions were referenced to the background silver 3d₅/₂ photopake at 368.20 eV, having a FWHM at 1.10 eV, Au 4f₇/₂ in 84.00 eV and C 1s hydrocarbon groups in 284.45 eV central peak position. XPS spectra of the GO and d-GO materials were measured at room temperature using a VG Escalab 200 R - x-ray photoelectron spectroscopy was carried out using a K-alpha Thermo Fischer Scientific spectrometer with a monochromatic Al Kα radiation (1486.6 eV) as an x-ray source and were micro-focused at the source to give a spot size on the sample of 400 microns in diameter. XPS high-resolution spectra were collected using analyzer pass energies of 20 eV, respectively, the recorded spectra were fitted through a Gaussian–Lorentzian combination based on an Offset Shirley background type. High-Resolution Electron Microscopy (HREM) images were performed in JEM2010 FEG equipment, the JEOL 2010 FE-TEM provides conventional and high resolution TEM scanning with a point-to-point resolution at 0.25 nm.

2.5. Electrode fabrication and electric tests
The electrochemical behaviour of GO and of the d-GO materials was investigated using cyclic voltammetry, with AUTOLAB potentiostat/galvanostat (model PGSTAT 30) equipment. The GO/paste and d-GO/paste work electrodes were made for this purpose. The GO and the d-GO carbon paste electrodes were prepared using each d-GO (0.10 g) with graphite powder (0.40 g of 99.99%, Alfa Aesar 2–15 μm) and 0.18 ml silicon oil (Sigma, ρ = 0.96 g ml⁻¹) as a binder. To prepare the carbon paste electrode, the two solids (graphite and d-GO) were thoroughly mixed with the silicon oil in an agate mortar until a homogeneous paste was formed; this was introduced into a polyethylene syringe (10 cm long × 0.2 cm diameter) and compacted. The system was constituted by three electrodes in an electrochemical cell with the d-GO/paste as the working electrode, a saturated mercury sulfate as the reference electrode (Hg/HgSO₄/K₂SO₄)(Radiometer Analytical) and a graphite bar (99.99%, Alfa Aesar) as the counter-electrode. A platinum wire was joined to copper using silver solder in order to establish electrical contact with the graphitic-material-paste. The baseline medium was 50 ml at 1.0 M of H₂SO₄. All measurements were performed at room temperature and repeated three times to verify its reproducibility.

3. Results and discussion

3.1. Electrochemical analysis
The direct electrochemical performances of GO and the d-GO with different coupling agents at different scan rates from 5, 10, 20, 50, 100 and 150 mV · s⁻¹ were investigated by cyclic voltammetry (CV) and are shown in figure 1. The CV provides the capability for generating a species during the forward and backward scan and then provide information about the behaviour with the reverse subsequent cycles and peak current increased as a function of scan rate. The GO and the d-GO curves presented quasi-rectangular shape curves attributed to the combination of electric double layer and pseudocapacitance properties occasioned by the components of the working electrode surface, also can be related with poor reversible oxidation-reduction process caused by the passivation of the working electrode [16]. Pumera et al, 2013, found inherent reduction peaks in the cathodic region of about ~700 mV (versus Ag/AgCl) due to the reduction of presumably epoxy, peroxide and aldehyde.
groups present at graphite and graphene oxides [17]. The inherent reduction peaks of our graphitic materials pose potential constraints on the usage of these materials in electrochemical devices as the cathodic window is limited to less than $-300$ mV. For each hysteresis curve with a rectangular-like shape event at a potential window up to $2.0$ V, a clear relaxation due to water molecule reorientation is seen by broadband dielectric spectroscopy (BDS). The rotational water dynamics are dependent on the hydration level during the oxidation process of graphite. At high water concentration ($c_w > 15$ wt%), water-water interactions seem to dominate the dielectric response [18]. In our case, the CV hysteresis curves of the d-GO materials were larger than GO material, as a function of scan rate during the oxidation-reduction process. The increment in hysteresis curves in cathodic and anodic peaks height, which in turn are associated with the injection and extraction of charges in GO and the DAB.

CV profiles of GO between $-0.3$ and $+0.7$ V window potential are shown in figure 1(a). The curves present a maximum current at $-0.659$ μA for $150$ mV·s$^{-1}$, with two oxidation peaks at $-0.038$ and $0.328$ V and one reduction peak at $0.21$ V associated with the oxidation-reduction of the epoxy, carboxyl and hydroxyl functional groups and the electrolyte.

Otherwise CV profiles of GO-CC (figure 1(b)) presented one remarkable oxidation peak at $0.385$ V and one reduction peak at $0.222$ V associated to adsorption-desorption process between CC and GO-CC and irreversible oxidation of cyanate anions can be detected in the explored potential region [19] also DAB is partial oxidized to a rather stable cation (DAB$^+$) in a one-electron transfer process [20].

GO-DCC CV profiles (figure 1(c)) presented a maximum current at $-1.879$ μA for $150$ mV·s$^{-1}$, this represents an increase in the maximum current of $2.8$ times more than GO with the same voltage sweep. CV curves present a weak reversible process and the anodic peak corresponding to the oxidation of the parent amino groups of DAB to the corresponding cation radicals as reported for aniline and polynuclear aromatic compounds with NH$_2$ groups [21].

Finally, the GO-HATU CV profiles (figure 1(d)) presented a maximum current at $-0.05$ μA and hysteresis quasi-square associated with an irreversible reduction at $-0.05$ and $+0.27$ V (versus SCE) of potential, confirming the incomplete reduction of GO. The GO-HATU cross-linked degree was higher than other coupling agents, possibly due to provide faster couplings with less epimerization. It is also particularly efficient for sterically hindered couplings formed during the synthesis [22]. Free ions associate with ions of opposite charge to make electrically neutral ion pairs that do not contribute to the conductivity. Ion pairing differs for weak electrolytes because the bonding in an ion pair is entirely electrostatic, whereas that in weakest electrolytes.

Figure 1. Cyclic voltammetry profiles of (a) GO, (b) GO-CC, (c) GO-DCC and (d) GO-HATU in H$_2$SO$_4$ at 1.0 M, with scan rate at 5, 10, 20, 50, 100 and 150 mV·s$^{-1}$ respectively.
involves the formation of covalent molecular bonds between DAB and GO. Ion pairing may be understood as a competition between the energies of electrostatic attraction.

When the scan is reversed, the complementary cathodic peak is not observed, indicating the fast consumption of the electrogenerated cation radicals by follow-up chemical reactions to produce electroactive products (PDAB) on the surface of the working electrode. Another possibility is the electron transfer domain the test where the final product could be reduced through a two-electron transfer process.

The use of various scans shows an indication of the specific capacitance ($C_s$) of the as-prepared graphitic materials, this was calculated from the CV curve using equation (1):

$$C_s = \frac{\int I dV}{m \times v \times \Delta V}$$

where $I$ represent the response current (A), $\Delta V$ is the potential window (V), $v$ is the scan rate (V·s$^{-1}$), and $m$ is the mass of active material in the working electrode (g). The specific capacitance curves are shown in figure 2.

The values of as-prepared graphitic materials GO, GO-CC, GO-DCC and GO-HATU are 75.0, 74.7, 91.9 and 133.9 F·g$^{-1}$, respectively, at a scan rate of 5 mV·s$^{-1}$. GO-HATU exhibits superior specific capacitance when compared to the other materials, which is attributed to the uniform morphology and distribution of DAB in the GO configuration occasioned by a slow current accumulating process during the CV test.

The specific capacitance calculated here can present the same tendency as a function of the current density obtained with galvanostatic charge-discharge measurements as a result of electrolyte ions not being able to enter the internal structure of DAB and GO a high current density and following the surface redox reaction. The decay of specific capacitance was observed at higher scan rate, whereas a low scan rate contributes to the relatively slow current accumulating process which facilitates the access of active sites on the working electrode, thereby resulting in high specific capacitance, which was also confirmed from the relationship between specific capacitance and current density.

In the electrical measurements of the graphitic materials presented above, as well as in the subsequent characterization results of our materials certain behaviour or tendencies, these behaviour can be attributed to the different coupling agents, since during doping process they could remain in small quantities because they did not be completely removed during the synthesis.

### 3.2. Thermogravimetric analysis (TGA-DTA)

Thermogravimetric analysis (TGA-DTA) is an analytical technique used to determine a material’s thermal stability and its fraction of volatile components by monitoring the weight change that occurs as a sample is heated at a constant rate. The TGA curves of GO and the d-GO show multi-step decomposition due to different gravimetric effects. Figures 3(a)–(d) shows TGA-DTA curves for GO, GO-CC, GO-DCC and GO-HATU materials, respectively. Raw graphite did not have any significant weight loss until 600 °C because of its high thermal stability (curve no presented).

The GO has hydrophilic behaviour because of its high concentration of polar functional groups, exhibiting three regions of weight loss.

The first weight loss region at 0 °C–200 °C of the materials follows as 7, 15, 20 and 25% for GO-CC, GO-DCC, GO-HATU, and GO materials, respectively. These thermograms were associated with an endothermic process at 108 °C could be attributed to the removal of both physisorbed water and the solvent on the solid surface in DTA curves. In this region the GO-CC material was more thermal stability than GO due to the
endothermic process for GO was at 30°C more than GO-CC. These phenomena are possibly due to the d-GO materials have a lower total content of oxygen and fewer C=O and −COO− groups than GO, as indicated by the XPS results.

The second region at 200°C–400°C is associated to CO, CO₂ and water loss, resulted from pyrolysis associated with a curve of the exothermic process [28, 29]. GO exothermic peak was presented at 232°C and for d-GO material were at 321, 279 and 335°C for GO-CC, GO-DCC and GO-HATU, respectively. This increment in temperature was related to a modification in the order of the final structure of the graphitic material, which could be intermolecular trapped water from of the oxygen-containing derived from functional groups interactions between internal groups of graphite and condensed water with higher intermolecular bonding than GO material.

Finally, for the third at 400°C–700°C region was attributed to the sublimation of organic compounds precursors, the weight loss of graphitic materials follows as: 55, 60, 95 and 100% for GO-CC, GO-DCC, GO and GO-HATU materials, respectively. The elimination of coupling agent precursor for GO and GO-HATU was total, where de GO-CC presented major thermal stability possibly due to major order regions and possibly graphite pre-expansion phenomenon occurred during the intercalation process [30].

In general, all TGA-DTA curves of GO and the d-GO materials showed a gradual weight loss over the entire temperature range applied, indicating that only a partial interaction between the functional groups of the GO and the DAB as a function of various coupling agents where the DAB can be bridged adjacent layers and then cross-links the oxide graphite layer and resist swelling by solvents employed during the synthesis [31]. Other explanations of this behaviour can be an offer by different types of bonds formed during GO doping, in which the amount of surface water and trapped in the internal planes of GO is indirectly related to a degree of ordering of graphitic materials [32].

3.3. X-ray diffraction (XRD)

The XRD patterns of GO and of the d-GO are shown in figure 4. The GO showed a reflection peak (001) at 11.39° with planar distance d₀₀₁ value at 7.8 Å for GO. The d-GO materials presented two weak reflection peaks (001) and (002) associated to graphite oxide pure and graphite raw and/or interlayer peak of graphitic carbon which is corroborated with ICDD 041-1487 (graphite). Calculating the interplanar distance with Bragg’s Law and λ = 1.54 Å (Cu Kα radiation), where the GO-CC exhibited two peaks approximately at 10.81 and 24.83° in 2θ, associated to interplanar distances d₀₀₁ and d₀₀₂ with values at 8.2 and 3.6 Å, respectively. The GO-DCC only presented one width peak at 25.29° with d₀₀₂ value at 3.6 Å associated to graphite raw. Finally, the GO-HATU material showed two peak at 10.92 and 25.67° with d₀₀₁ and d₀₀₂ values at 8.0 and 3.5 Å. In general, all d-GO presented a small shift in 2-Theta (10.81 to 11.39°) due to less amount of residual water intercalated between basal planes in GO layer. The interlayer distance during the doping process increase with CC and HATU as
coupling agents respect to GO from 7.7 to 8.2 Å. This growth in the spacing is an indication that water is intercalated between the galleries of the GO as observed also by other authors [33, 34]. It also can correspond to the uptake of a water monolayer in the interlayer space of GO due to reorientation and rotational intramolecular water behaviour [35]. However, the presence of CC or HATU could not completely prevent the formation of aggregated structural and staking GO layers, resulting in these weak peaks.

3.4. FTIR spectroscopy
Fourier-transform infrared (FTIR) spectroscopic study was employed for analyzing the diverse functional groups of GO doping with DAB using different coupling agents, each spectrum shows with vertical dashed lines indicating one or more symmetrical or asymmetrical stretching, bending or rotational vibrations. The minor unassigned peaks, specifically for GO-CC, GO-DCC and GO-HATU materials are consistent with a buildup of water vapor in the samples chamber during data collection and have been ignored. The figure 5(a) presents the spectrum of GO with indicative peaks of C–H bending vibrations derivate from epoxy group (970 cm\(^{-1}\)), C–O stretching of alkoxy group (1040 cm\(^{-1}\)), C–O stretching of the epoxy group (1225 cm\(^{-1}\)), –OH stretching vibration (1375 cm\(^{-1}\)), C=O stretching or can be assigned to the adsorbed water molecules H–O–H bending (1610 cm\(^{-1}\)), C=C stretching or can be assigned to the adsorbed water molecules H–O–H bending (1610 cm\(^{-1}\)), –C=O stretching from the carboxyl group (1710 cm\(^{-1}\)), symmetric and asymmetric stretching vibration of -CH\(_2\) (2800 cm\(^{-1}\)), –OH stretch from graphite oxide (3745 cm\(^{-1}\)), where the peak assignation is consistent with previously reported in literature [36].

The GO-CC spectrum (figure 5(b)) exhibits eleven major peaks are clearly formed in the region at 500–4000 cm\(^{-1}\). The first peak is assigned to C-Cl stretch (610 cm\(^{-1}\)) from the CC coupling agent compound, imidazole C-H out-of-plane bending overlapped by benzene aromatic skeletal absorptions [37] (795 cm\(^{-1}\)), C–O stretching of alkoxy group (1040 cm\(^{-1}\)), C–N stretch (1150 cm\(^{-1}\)), CH\(_2\) bend (1420 cm\(^{-1}\)), the stretching frequencies due to the triazine rings [38] (1550 cm\(^{-1}\)), C=O stretch (1850 cm\(^{-1}\)), C≡C– stretching (2080 cm\(^{-1}\)), –COOH stretch (2325 cm\(^{-1}\)), –NH stretch (3400 cm\(^{-1}\)), and –OH stretch from graphite oxide (3745 cm\(^{-1}\)).

The GO-DCC spectrum (figure 5(c)) shows at least fifteen indicative peaks of vibrations of various types assigned as follows: -NCN- stretch (670 cm\(^{-1}\)), –CH of ring-1 stretching (800 cm\(^{-1}\)), –CH of ring-5 very weak (870 cm\(^{-1}\)), C–O stretching of alkoxy group (1040 cm\(^{-1}\)), NH the ring of imidazole group (1200 cm\(^{-1}\)), C–N stretching (1440 cm\(^{-1}\)), C–H asymmetrical bending (1490 cm\(^{-1}\)), N–H bending (1560 cm\(^{-1}\)), C=O stretching

![Figure 4. XRD patterns of (a) GO, (b) GO-CC, (c) GO-DCC and (d) GO-HATU samples.](image-url)
The doping reactions between GO and DAB occur mainly via a nucleophilic ring-opening reaction on the epoxy groups located on the graphitic framework of GO, which plays an increasing role in the basal interlayer distance and in the hydrophilicity [43] as documented for reactions between GO and amino molecules [44]. Furthermore, the signal C–N no presented peaks characteristic indicating that additional bonds are formed between the GO and DAB derive from the reaction between C–O and amino groups, where the N–H associated to is presented in GO-CC and GO-DCC the GO-HATU no presented signal of secondary amine possibly associated to major crosslinking or intercalation degree. The cross-linkers can be selected based not only on their reactivity but on their length and type of cross-bridge that they possess. Some heterobifunctional families differ solely in the length of their spacer. The nature of the cross-bridge may also govern the overall hydrophilicity of the reagent. For instance, GO and DAB cross-bridges create hydrophilic reagents that provide water solubility to the entire heterobifunctional compound which affected their reactivity [45].

Figure 5. FTIR spectra of (a) GO, (b) GO-CC, (c) GO-DCC and (d) GO-HATU samples.
3.5. Raman spectroscopy

Raman measurements provided insight into the structural order of graphitic materials. For observed disordered structural of the carbon during GO doping with DAB with various coupling agents. Raman spectra of GO and the d-GO (figure 6) exhibit two remarkable bands D- and G-band with different intensities are observed at 1350 and 1580 cm$^{-1}$ in Raman shift, respectively. D-band is associated to points of dislocation where heteroatoms suffer from disturbances due to the vibration of carbon atoms with hanging bonds in the flat terminations of disordered graphite or glassy carbons [46]. It also represents the disorder caused by the graphite edges and finally an A$_{1g}$ zone-edge mode of vibration due to the defects of the graphitic material [47].

Otherwise, G-band corresponds to a disorder caused by graphite edges. The stretching vibrations C=\(\text{C}\) coming from the aromatic rings are present by sp$^2$ hybridization. The E$_{2g}$ vibration modes were due to a hexagonal geometry where the carbon atoms attached to sp$^2$ in a graphite layer and the high frequency of Raman allow the optical phonon mode [48].

The ratio \(I_D/I_G\) is often used as an indication of the degree of disorder in a carbon structure and where high values prevent agglomeration of the planes [49]. In our case, the ratio was increased from 0.70 for GO, to 0.94, 0.97 and 1.04 for GO-CC, GO-DCC and GO-HATU, respectively, where the coupling agents increased the \(I_D/I_G\) ratio due to the nucleophilic addition of DAB in GO and the subsequent formation of covalent bonds named Grafted-to species. This registered trend reflects the decrease in the average size of sp$^2$ domains creating a new graphite domain associated with a restructuring of the material [50].

All coupling agents affect the intensity of G-band, the decrement in the G-band represents a higher degree of oxidation particularly by HATU, possibly due during the doping process this coupling agent generated a cross-linked material with structural defects.

Table 1 presents the Raman peak positions, Full Width at Half Maximum and the intensity ratio \(I_D/I_G\). The intensity of the G-band with respect to the D-band was 0.5 times greater for the GO sample. However, with the use of coupling agents like HATU the intensity between both bands presented the same intensity. Additionally, the FWHM for D-band shows mayor values than G-band for all materials except for GO-DCC which the values for two bands presents the same FWHM possibly associated with an increment in disorder during the intercalation of GO with DCC. This can be attributed to structural defects and partially disordered structures of the sp$^2$ domains [51]. Raman spectra to the greater distance between each template of GO, corroborated by HREM micrographs of the GO-HATU displaying a view of packages attached to the GO layer [52].

![Figure 6. Raman spectra of (a) GO (b) GO-CC, (c) GO-DCC and (d) GO-HATU samples.](image-url)
3.6. X-ray photoelectron spectroscopy (XPS)

XPS technique was used to characterize GO and the d-GO graphitic materials. In figure 7(a) the high resolution of C 1s XPS spectrum of GO presents five peaks at 284.24, 285.14, 286.44, 288.14 and 290.64 eV associated to C–C, C–O, C–O–C, C=O, and π–π, respectively. For the samples d-GO (figures 7(b)–(d)) the spectra show five peaks with binding energies, bond assignments, FWHM and relative concentration, summarized in table 2. All d-GO samples present decrement in C–O band respect to GO samples, revealing the formation of C–N bond possibly associated to formation of benzimidazole by carboxyl and amine interaction during the doping process [53]. The effectiveness of the oxidation method can be judged by the proportion of graphite oxide in the product or by its carbon to oxygen ratio. C/O ratio was 1.47, 2.75, 3.21 and 3.37 for GO, GO-HATU, GO-CC, and GO-DCC, respectively. DCC presented high values of oxidation over the other coupling agents, revealing that most oxygen-containing functional groups with the use of these coupling agents were partially removed after the oxidation-doping process.

In the other case, figure 8 presents the high-resolution XPS of O 1s in the left and N 1s in the right for GO, GO-CC, GO-DCC, and GO-HATU, respectively. The spectrum of O 1s by GO presented three bands at 534.87, 532.67 and 531.05 eV associated to trapped water interlayer non-lattice and lattice oxygen bands, respectively. For d-GO materials showed two bands non-lattice and lattice oxygen associated to surface oxygen and bulk oxygen. The ratio between these two band was 1.15, 1.63, 1.71 and 1.80 for GO, GO-CC, GO-DCC and GO-HATU, respectively. This behaviour is assigned with a major electronic mobility between the surface and the bulk. The mobility is substantially low compared to that of single crystals due to the formation of the lattice/structural defects [54].

Table 1. Raman Peak Positions (cm⁻¹), the Full Width of Half Maximum FWHM (cm⁻¹) and the intensity ratio of the D- and G-bands for GO and the d-GO materials.

| Sample      | Center D (cm⁻¹) | Center G (cm⁻¹) | FWHM D (cm⁻¹) | FWHM G (cm⁻¹) | I_D/I_G |
|-------------|----------------|----------------|---------------|---------------|--------|
| OG          | 1345           | 1588           | 104.4         | 72.4          | 0.70   |
| OG-CC       | 1348           | 1580           | 177.7         | 125.8         | 0.94   |
| OG-DCC      | 1346           | 1578           | 133.4         | 133.4         | 0.97   |
| OG-HATU     | 1349           | 1586           | 187.7         | 123.4         | 1.04   |

Figure 7. X-ray photoelectron spectra high resolution fitted model and peak deconvolution for GO and the d-GO materials. XPS C 1s high resolution for (a) GO, (b) GO-CC, (c) GO-DCC and (d) GO-HATU samples.
Table 2. Parameters showing binding energy (eV), chemical bonds, FWHM (eV) and relative percentage concentration of spectral components of the deconvoluted C 1s peaks for GO and the d-GO materials.

| Sample | Binding energy (eV) | Bond assignment | FWHM (eV) | Relative concentration (%) |
|--------|---------------------|-----------------|-----------|---------------------------|
| GO     | 284.24              | C–C             | 0.72      | 66.44                     |
|        | 285.14              | C–O             | 1.50      | 16.73                     |
|        | 286.44              | C–O=C           | 1.74      | 5.85                      |
|        | 288.14              | C=N             | 1.90      | 3.82                      |
|        | 290.64              | π–π             | 3.00      | 7.16                      |
| GO-CC  | 284.49              | C–C             | 1.42      | 65.99                     |
|        | 284.99              | C–N             | 1.30      | 8.11                      |
|        | 285.59              | C–O             | 1.00      | 8.37                      |
|        | 286.69              | C–O=C           | 1.66      | 10.83                     |
|        | 288.39              | C=O             | 1.90      | 6.70                      |
| GO-DCC | 284.24              | C–C             | 1.26      | 65.18                     |
|        | 284.74              | C–N             | 1.30      | 7.78                      |
|        | 285.34              | C–O             | 1.00      | 8.06                      |
|        | 286.44              | C–O=C           | 1.57      | 12.09                     |
|        | 288.14              | C=O             | 1.90      | 6.89                      |
| GO-HATU| 284.30              | C–C             | 1.44      | 65.04                     |
|        | 284.80              | C–N             | 1.30      | 8.05                      |
|        | 285.40              | C–O             | 1.00      | 8.16                      |
|        | 286.50              | C–O=C           | 1.64      | 12.23                     |
|        | 288.20              | C=O             | 1.90      | 6.52                      |

Otherwise, the two nitrogen atoms in benimidazole are indistinguishable N–C and N=C; several authors attributed to two shoulders one of them to benimidazole and other for benimidazole anion which generated a copper compound immersed in ethanol solution [55]. Other authors study the interaction between montmorillonite and thiabendazole and benimidazole and the high resolution N 1s spectra is decomposed in two components centred at 399 and 401 eV which have been attributed to non-protonated and protonated nitrogen [56, 57]. In our case the high resolution N 1s spectra for the d-GO materials resolved into three peaks at 401.88, 400.70 and 399.69 eV (figures 8d, f and h) as previously proposed. Tang et al 2003 employed benimidazole as corrosion inhibitors and XPS studies for N 1s spectra presented three peaks, where to the first component is assigned to the oxidized nitrogen resulting from the protonation of the nitrogen in the imidazole rings or amino group (N+H–), which leads to a positive polarization of the nitrogen atom and therefore an increase of the binding energy. The second component with the highest contribution to the N 1s signal is mainly assigned to the coordinate nitrogen in the imidazole rings with the steel surface (N–Fe), which causes, therefore, the peak shift to higher binding energy and finally, the third component is attributed to the un-protonated N atoms (=N-structure) in the imidazole rings [58]; bond assignments, FWHM and relative concentration.

Nonetheless Xu et al 2000 employed benzimidazole un carbamates with tribological performance and these author associated to presented three peaks to N 1s as follows N–C=N, N= and NOx, where only –N=C– is attributed to Benzimidazole group and that compound plays an important role in the formation of stable adsorption layer [59]. In our case, the XPS N 1s spectra indicate the presence of nitrogen atoms with at least three different binding energies, where the three peaks of d-GO with binding energy, FWHM, and relative concentrations were summarized in table 3. Indicating the higher relative concentration of the second peak for GO-CC than other d-GO materials associated to benzimidazole formation during the doping process. The oxygen-containing in functional groups were removed by N 1s assigned for three bonds, which confirms the covalent bonding between GO with DAB molecules. Furthermore, according to the result of the XPS spectra, the atomic ratio of C/N follow as 3.79, 3.48 and 4.69 for GO-DCC, GO-CC and GO-HATU respectively, which suggest that every 16.8 carbon atoms would share one DAB molecular [60, 61]. Additional information regarding the chemical environment of the GO doped with DAB poorly modified interlayer space as commented below.

In general, the doping reactions of GO and DAB with various bi-functional molecules as their reaction with the layered coupling agent could occur intra-molecularly (when the intercalated molecule reacts with two reactive sites at the same GO layer) forming benzimidazoles or inter-molecularly (when the reaction takes place between reactive sites located on two different GO layers) by formation of bridges which generates macromolecules well-defined with number of active functional groups distributed along their branches and ending groups.
3.7. High resolution electron microscopy (HREM)

The higher degree of crystallinity seen in the high-resolution electron microscope (HREM) images of the GO and the d-GO. Figures 9(a) and (b) show HREM images of the samples GO and GO-HATU, respectively, in which the electron incidence is along the (002) plane with zone-axis of the graphite crystals. The images show two possible arrangements: in one case: nanosized pores possibly caused by pristine Graphite similar morphological effects have been reported [62]. On the other case provided evidence (001) plane corresponding...
to oxidized graphite. In general, coupling agents no-showed an increment in their interplanar distance between slabs of GO and DAB.

The CC modifies the GO doping process because it is a nucleophilic agent that transfer its electrons so that the carboxyl and/or hydroxyl of the GO and the amino groups from the DAB could react \[63\]. This reactivity occasioned by coupling agent generating different crystalline regions. Within these crystalline regions, the CC

| Sample    | Binding energy (eV) | Bond assignment | FWHM (eV) | Relative concentration (%) |
|-----------|---------------------|-----------------|-----------|----------------------------|
| GO        | 534.87              | trapped water   | 2.30      | 6.92                       |
|           | 532.67              | \(O_{\text{non-lattice}}\) | 2.35      | 49.82                      |
|           | 531.05              | \(O_{\text{lattice}}\) | 2.00      | 43.26                      |
| GO–CC     | 532.27              | \(O_{\text{non-lattice}}\) | 2.26      | 61.92                      |
|           | 531.17              | \(O_{\text{lattice}}\) | 1.52      | 38.08                      |
|           | 401.88              | \(–N–C–N\)      | 1.90      | 22.09                      |
|           | 400.70              | \(–N = C–\)     | 1.62      | 53.81                      |
|           | 399.69              | \(NO_X\)        | 1.51      | 22.10                      |
| GO–DCC    | 532.32              | \(O_{\text{non-lattice}}\) | 2.52      | 63.12                      |
|           | 531.07              | \(O_{\text{lattice}}\) | 2.02      | 36.88                      |
|           | 402.00              | \(–N–C–N\)      | 1.83      | 8.76                       |
|           | 401.10              | \(–N = C–\)     | 1.70      | 51.44                      |
|           | 399.85              | \(NO_X\)        | 1.70      | 39.80                      |
| GO–HATU   | 532.23              | \(O_{\text{non-lattice}}\) | 2.54      | 64.31                      |
|           | 531.09              | \(O_{\text{lattice}}\) | 2.00      | 35.69                      |
|           | 401.70              | \(–N–C–N\)      | 1.90      | 25.73                      |
|           | 400.96              | \(–N = C–\)     | 1.6       | 48.26                      |
|           | 399.72              | \(NO_X\)        | 1.46      | 26.01                      |

Table 3. Parameters showing binding energy (eV), chemical bonds, FWHM (eV) and relative percentage concentration of spectral components of the deconvoluted O 1s and N 1s peaks, respectively, for GO and the d-GO materials.

Figure 9. HREM micrographs of (a) GO and (b) GO–HATU, with SAED (right upper corner).
and HATU increased the interlayer dispersion. The resulting structure may be increasing the crystallinity within coupling agents, it has been shown to enhance mechanical stiffness as well as thermal stability, compared to amorphous samples of the DCC doping samples.

The first coupling agent CC modifies the GO doping process because it is a nucleophilic agent giving up its electrons so that the carboxyl and/or hydroxyl from GO and the amino groups from the DAB react. This reactivity is due to its chlorine atoms towards the nucleophiles, and the displacement of the chlorine atom in the CC by several nucleophiles corresponds to substitution reactions between surface functional groups of the GO and the chemical grafting of the amine from DAB.

The DCC is used as a coupling agent for preparing carboxylic acid and derivatives as amines, esters and peptides. DCC improve the electrophilicity of the carboxyl groups, embedded in its carbon layers of GO, the negatively charged oxygen is activated by the DCC and generates a better leaving group. The negatively charged oxygen will act as a nucleophile, attacking the central carbon in DCC, where the coupling agent temporarily binds to the old carboxyl group forming an electrophilic intermediate, which causes the nucleophilic attack by the amino groups of the DAB being present a regular degree of intercalation.

Finally, the HATU is used as a coupling agent for its resistance against racemization HATU is a structurally very close analogy to (HBTU) by the formation of π-bridge, which are beneficial for enhancing the effective conjugation length and intermolecular π–π stacking. However, it provides faster couplings with less epimerization; this reagent has seen widespread use as a coupling reagent for amide bond formation due to the mild reaction conditions and the usually high yields of amide products that it provides. It is also particularly efficient for sterically hindered couplings. For these reasons, several process groups in pharmaceutical companies have reported HATU applications for the synthesis of drug candidates.

The modified surface of GO allows for covalent modification by reactions at carboxyl and hydroxyl groups. The cross-linked reaction of GO with DAB with different coupling agents proceeds by nucleophilic substitution (NS2) on the carboxyl groups, provided that the amines are in neutral form. It is possible then, that the intercalation of a dysfunctional amine could produce a pillared structure, as shown in figure 10. This substitution is repeated for the other amino group each of the coupling agents could generate the three possible representations of benzimidazole formation. In our case of figure 10(a), crosslinking or bridge conformation was generated between the GO layers called polybenzimidazole, in (b) a loop was generated.
between the same functional groups of one of the layers, probably this behaviour is less measured due to the steric hindrance of the interlayer functional groups of the GO and finally it is observed for (c) the tail conformation in which only one carboxyl group interacts with two amino groups of the DAB generating this type of covalent interactions.

4. Conclusions

The coupling agents during the doping process of GO modified their textural, structural and electrical properties derived from different interactions between the functional groups of GO and DAB.

The GO doping process starts with covalent bond between layers of oxidized graphite and subsequently with interaction with DAB. The use of CC, DCC, and HATU as coupling agents modified the inclusion surface reaction between the DAB and the interatomic functional groups of the GO. The coupling agents improved the degree of cross-linking and the arrangement of the graphite oxide. The presence of $-\text{N} = \text{C}-$ bond for GO-CC and GO-DCC obtained with XPS of N 1s spectrum showed a high anchoring compound between carboxyl and amine groups from GO and DAB, respectively. The formation of benzimidazoles as a final product was observed. GO-HATU presented $I_D/I_G \sim 1.04$ associated to high GO planes disorder, high thermal stability, an interplanar distance of 8.0 Å and an irreversible behaviour to oxidation-reduction reactions generated by greater electronic mobility between the material and the electrolyte, related with high $O_{\text{non-lattice}}/O_{\text{lattice}}$ ratio value.

Finally, the doping mechanism of GO and DAB produced the benzimidazoles for DCC and HATU as coupling agents allowed free functional groups $\sim \text{NH}_2$ with a tail conformation due to a partial functionalization that improving the disorder, thermal stability, and high specific capacitance values.

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