THE IMPORTANCE OF CHEMICAL SHIFT SCREENING OF THE PRECURSORS FOR INCREASING THE EXFOLIATION EFFICIENCY OF THE GRAPHITE LAYERS

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The aim of this work is highlighting the importance of precursors' choice for the efficiency of graphite layers exfoliation process. X-ray Photoelectron Spectroscopy allowed the identification carbon bonding environment, showing carbon's C_{1s} chemical shifts in the photoemission spectra, while Scanning Electron Microscopy and Energy-dispersive X-ray Spectroscopy provided 2D surface morphology and chemical composition. One-step synthesis of Graphite Intercalated Compound (GIC) was successfully used for sample exfoliation process (under ambient conditions), using H_2SO_4 as intercalant, $KMnO_4$ as oxidizing agent and H_2O_2 as reactive specie. The results showed that there is a limit of carbon's core level shifts above which chemical intercalation-exfoliation becomes difficult.

Keywords: carbon bonds, XPS core level shifts, graphite exfoliation process, graphite intercalated compound, graphene

1. Introduction

Graphene based materials are expected to rejuvenate energy storage electrochemical devices - batteries, supercapacitors - hydrogen economy, and composite materials [1, 2] due to specific favorable properties like excellent electrical conductivity, high thermal conductivity, highly tunable surface area, and chemical functionalization. If graphene-based materials are obtained as ultra-thin films with large lateral dimensions, low density defects and controlled high purity, they could be used in high-power laser experiments for particle acceleration [3, 4]. If one is to expect a technological utilization uptake of graphene, cost-efficient methods based on readily available materials and with low ecological impact have to be developed

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and scaled to large volume production. Within this context, the exfoliation methods [5] of carbon graphitic layers from bulk natural graphite are most promising for large scale multilayered graphene production. This article is a contribution to the development of bulk graphene multilayer material production methods [6] where we document an efficient and readily available selection method of graphite precursor, screening needed for efficient multilayer graphene production.

In order to clarify the role of graphite precursor quality in multilayer graphene synthesis, we chose to focus on a single well-defined intercalation-exfoliation method and evaluate, through the results obtained, the influence of the initial graphite quality and find a metric of properties that favor multilayer graphene synthesis. The chosen intercalation method uses sulfuric acid to intercalate the natural graphite powder and uses a strong oxidant to facilitate the process. Thus, in each case a set amount of graphite was intercalated with a set amount of sulfuric acid and a set amount of potassium permanganate was used at a set temperature. The whole process was carried out as identically as possible in order to eliminate possible reaction variations.

A well-known method for obtaining graphene in larger quantities involves two steps: a) the so-called modified Hummers method - an initial oxidation of graphite, leading to a graphene oxide (GO) solution that can be further subjected to an exfoliation process, followed by b) a chemical and/or heat treatment process to obtain the reduced form of graphene (rGO = reduced graphene oxide) [7 - 9]. GO is essentially graphene with additional oxygen-containing functional groups such as hydroxyls, carbonyls and carboxylic acids [10]. In addition, there are "defects" such as oxygen atoms bridging between neighboring aromatic regions, such as ethers, or along the same aromatic ring, as in an epoxide. Essentially, chemically exfoliated GO can be seen as a defect-ridden version of graphene, compared to nearly defect-free graphene sheets produced by mechanical exfoliation [11 - 16].

Exfoliation of Graphite Intercalated Compound (GIC) is considered a promising method for graphene production, as several studies have been previously reported [5], [6]. The larger graphite interlayer spacing created by the intercalated molecule in GIC provides a new synthetic route for generating a few layers graphene flakes from graphite without going through the intermediate, highly oxidized graphene state and thus preserving the quality of the graphene film [5]. By inserting atomic or molecular layers of a guest chemical species into anisotropic graphite, so-called GICs, the electronic, structural, magnetic and thermal properties of the graphene can be preserved [17].

Some preliminary considerations on a C_{1s} hybridizations and chemical shifts are briefly presented, based on which we have identified the necessary precursors using the X-ray photoelectron spectroscopy (XPS) technique, then the experiments performed to obtain the GIC exfoliation are presented, and the results

obtained and their evaluation are analyzed by different techniques such as Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS).

It is commonly assumed that graphite is composed entirely of sp^2 hybridized carbon atoms connected by covalent bonds to form a hexagonal ring, developing in-plane carbon layers. These carbon layers are out of plane connected by the weak van der Waals interaction generated by unlocalized π orbitals. Experimentally [18] it was found that natural graphite exhibits a broad set of chemical bonds as observed by XPS with C-C, C=C, C-H, C-O, C=O, π-π*. Oxygen and hydrogen are common foreign elements that can be explained as following: C-H bonds and oxygen-containing bonds are formed due to the presence in graphite of edge zones and defect zones that provide suitable anchoring sites for functionalities and sp^3 are likely edge and hole defects in the graphite.

Given the relatively large set of C_{1s} chemical shifts reported [18], [19], we decided to explore the correlations between XPS data of precursor graphite samples and the results of the graphite intercalation - exfoliation procedure.

As such, two different samples of graphite powder (named C_A and C_B) have been selected as starting materials, which were firstly characterized in terms of C_{1s} chemical shifts.

Our goal is to evaluate the development of bulk graphene multilayer material production methods, by using efficient and readily available selection method for graphite precursor, aiming for efficient multilayer graphene production. For this, we have employed a one-step synthesis of H_2SO_4-GIC, which includes the intercalation of sulfuric acid between graphite layers, followed by exfoliation of it under ambient conditions. The intercalation process was helped by $KMnO_4$ as oxidizing agent. Finally, H_2O_2 was used as reactive exfoliation specie. This method excludes any difficult chemical synthesis or high temperature treatment.

2. Experimental section - Preparation and Liquid-Phase Exfoliation of H_2SO_4- based on Graphite Intercalation Compounds

First, we prepared H_2SO_4-based intercalated graphite compounds (H_2SO_4-GICs) by mixing 25 g graphite powder with 50 ml concentrated sulfuric acid (98%) then slowly adding while mixing 2.5 g of potassium permanganate at room temperature for two hours under continuously stirred ambient conditions. The intercalation of H_2SO_4 is a rapid process, its largest part being achieved in less than 30 min. The two hours reaction time aims to ensure that kinetic effects are minimized such that final results are dictated mostly by the graphite precursor materials (Fig 1).

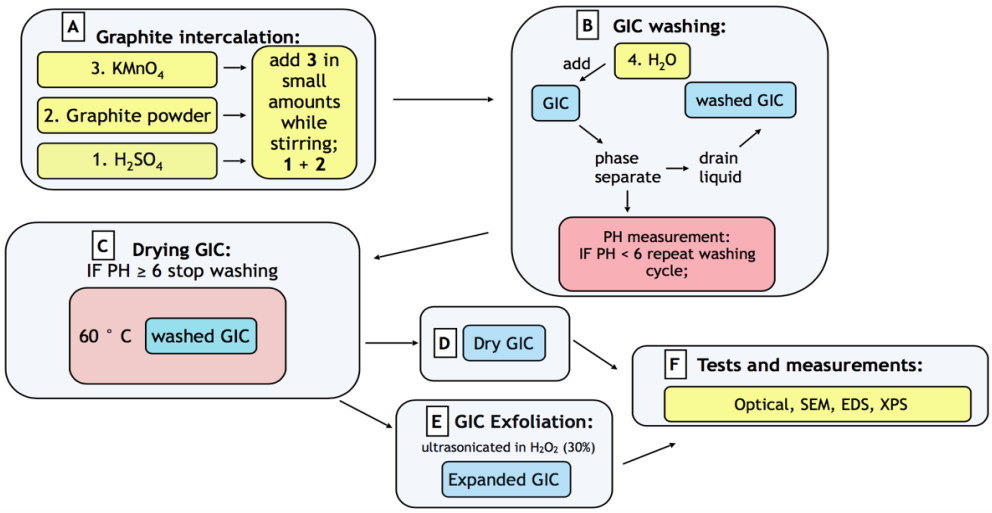


Fig 1. Workflow of the preparation and liquid-phase exfoliation of H_2SO_4- based on graphite intercalation compounds starting with A) graphite intercalation, B) GIC washing, C) - D) GIC drying, E) GIC exfoliation and F) tests and measurements

H_2SO_4-GIC dispersion was achieved using 2 different graphite sources (C_A, C_B), by sonication of the intercalate - GIC - in concentrated H_2O_2 (30%) using a low power sonic bath (P = 30 W) to meet the success of the subsequent intercalation and exfoliation process. Thus, 100 mg of each of the two batches - made with two different graphite sources (C_A, C_B) - were mixed with 10 ml of H_2O_2 and sonicated for a period of time. After a short time (20 seconds) it was observed that one of the samples (C_A) formed a prominent foam while the other remained practically unchanged (C_B). The working parameters, i.e. the amount of concentrated hydrogen peroxide (10 ml/100 mg batch) and the ultrasound times (4 hours) were kept the same, and in that way we can compare how the two samples behave in terms of exfoliation and its reproducibility needed for future processes. The foam obtained on the first sample (C_A), subjected to hydrogen peroxide exfoliation, was placed in another beaker, where 10 ml of H_2O_2 has been additionally poured in and kept it under ultrasound treatment (4 hours). The other sample (C_B) did not show any changing behavior, and therefore was subjected to agitation with ultrasound.

For C_A sample, in the initial stage, a small number of bubbles was generated at the periphery of the graphite flakes, at a slow rate. As these bubbles steadily attacked the periphery of the GICs, the grain boundaries were dislodged and led to external breakage of the graphite layers. [20] This facilitated the penetration of more H_2O_2 molecules into the interlayer spacing. As H_2O_2 reacted with the graphite layers, the process became increasingly apparent as lots of bubbles rapidly appeared at the surface of the solution. Having this visual assessment during H_2O_2 treatment, it is significant to say there is a difference between the two solutions resulted from

two different precursor carbon samples in identical reaction conditions. If the incipient sample - C_A, from which the latter foam resulted, shows a uniform continuous foam, the same cannot be stated for the other one - C_B, which shows discontinuous and rarefied foam fractions on the respective foam surface. As the sonication time increases, we have observed that the turbidity of suspension changes, which indicates a higher level of exfoliated and of the graphene in the suspension. After 240 minutes of probe sonication, the suspension appears darker, exhibiting greater extent of graphene exfoliation. In addition, we also note that, in this exfoliation process, except for the graphene layers at the surface, which are easier to expand, the exfoliation actually took place in the whole GIC flake, resulting a volume significantly increased and a homogeneous structure appearing.

3. Results - Comparison of intercalation and exfoliation results between the two H_2SO_4 - GIC experiments

XPS analysis

The level of exfoliation of the samples can be attributed to the concentration of allotropic form of carbon in their precursors [19]. To highlight such a difference in the powders, a quantitative chemical analysis is required to determine the sp^2, sp^3, C-H, C-O components in carbon-X bonds for natural graphite powders. For this, X-ray photoelectron spectroscopy (XPS) was used, which allows the separation between various components in C_{1s} photoemission spectra by peak fitting.

The XPS spectrum of C_{1s} in graphite shows a broad peak with an asymmetric tail towards higher binding energies, comprising the bond energies of sp^2-hybridized carbon, but also the bond energies of sp^3-hybridized carbon, carbon bonds with oxygen and hydrogen. The deconvolved peak at roughly 0.6 eV binding energy above highest intensity peak (sp^2 carbon) corresponds to either sp^3 hybridization, likely order defects of the the sp^2 graphite, or C-H bonds at edge sites [18], while C-O bonds indicative of covalently bond oxygen with carbon likely at the edge zones and defect zones that provide suitable anchoring sites for functionalities.

Because the C_{1s} line in graphite occurs at a lower binding energy than in diamond, we attribute the lower binding energy component to sp^2 hybridization and the higher binding energy component to sp^3 hybridization [21].

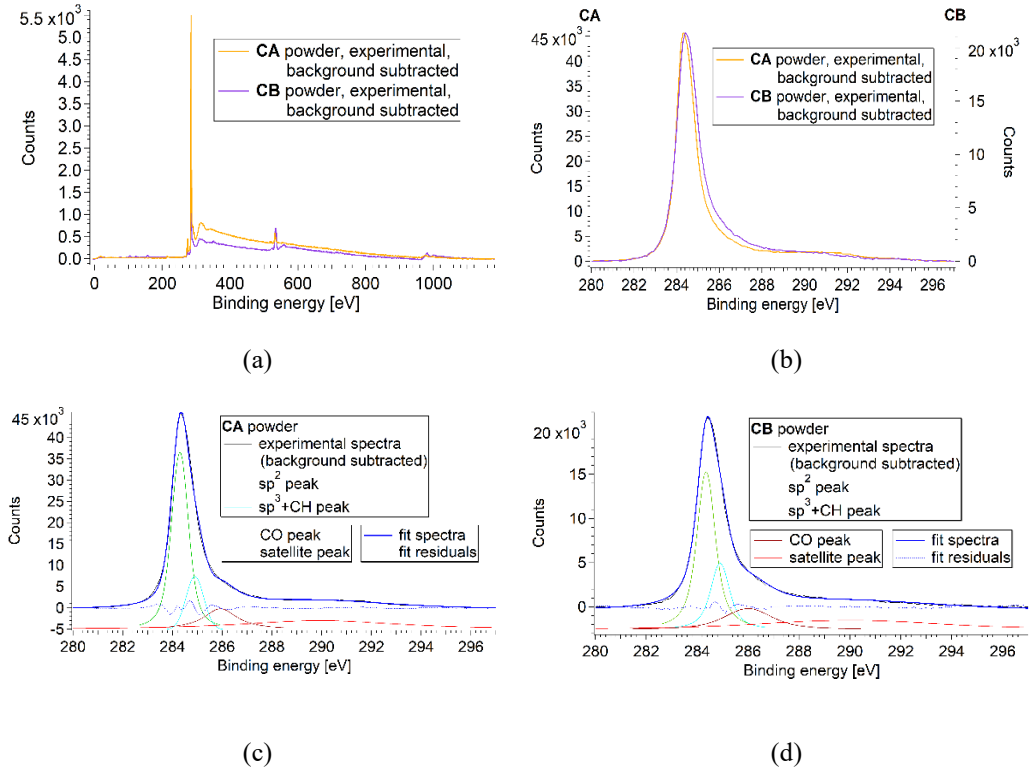


Fig 2. a)Large survey of the compositional elements in the material, namely Carbon and Oxygen, b) Acquired C_{1s} XPS spectra for C_A and C_B powders, c) Fitting graphs for C_{1s} XPS spectra of C_A powder, d) Fitting graphs for C_{1s} XPS spectra of C_B powder

XPS was performed using *Axis Ultra DLD - Kratos* equipment and data processing used *Igor Pro 7* software for peak adjustment. C_A and C_B powders were prepared by depositing a thick and uniform layer (visual inspection), sufficiently pressed on a Cu tape fixed on the aluminum stub, so the photoelectrons escaped sample only from the carbon layer and not from the tape. The spectra were recorded by a *Sigma Surface Science* photoelectron spectrometer equipped with 160 mm hemispherical energy analyzer, having a 1D detector (*ASPECT*) and using a poly-chromatic Al source with Kα (1486.6 eV) X-ray source at 13 kV, 200 W power. The equipment operation mode was constant analyzer energy (CAE) 200 eV pass energy, for maintaining a constant step of energy. The spot analysis diameter was 1.3 mm, and the pressure in the analysis chamber is maintained at ~ 3×10^{-9} mbar. A large survey (up to 1185 eV) was performed to inspect the compositional elements of the material, namely Carbon and Oxygen and used for establishing their stoichiometry with spectral acquisition at a step of ≈ 0.29 eV (Fig 2, a).

From the resulting graph based on the experimental data, we have identified the sp^2, and (sp^3+CH) bounds, C-O and π-π* peaks, determining accordingly the sp^2/(sp^3+CH) ratio in graphite powders. The acquisition process used a 17 eV range, with 0.1 eV increment, and a pass energy of 20 eV, in the C_{1s} peak band (Fig 2, b), the spectral processing being performed using *Igor Pro* software. For matching the C_{1s} spectra we have used a 4 symmetric Voigt peaks (the fourth being considered a satellite peak) after subtraction of the Shirley background. It was assumed that all O is bound to C in the O:C = 1:1 atomic stoichiometry, thus forcing the ratio of CO peak areas versus the rest of the peaks to be equal to the percentage of O/C+O obtained by the survey. The sp^2 and (sp^3+CH) areas give the sp^2/(sp^3+CH) ratio, the sp^2/(sp^2+sp^3+CH) concentration indicating the graphitization level of the raw graphite powder. After Shirley background subtraction from C_A sample's spectra, the O/(C+O) concentration was determined to be 12 %, including quantum efficiency (Table 1). Then comes out sp^2/(sp^3+CH) = 3.3 and sp^2/(sp^2+sp^3+CH) = 76.7%, determined by fitting C_{1s} spectra to the C_A sample (Fig 1, c). The CO peak area is 11.2% out of the total fitted peak area, very close to the O/(C+O) as per above, increasing the consistency of the whole fit. The same processing procedure has been used for the survey of the C_B sample and C_{1s} spectra (Fig 1, d), resulting in O/(C+O) = 17 %, sp^2/(sp^3+CH) = 2.3 and sp^2/(sp^2+sp^3+CH) = 69.7%. The CO peak area was 15.4% of the total matching peak area, also close to O/(C+O).

Table 1.

XPS data on C_{1s} hybridization ratios for the two types of as graphite powders

XPS analyzed sample	C_A powders	C_B powders
Survey O/(C+O)	12 %	17 %
sp^2 / (sp^3+CH)	3.3	2.3
sp^2 / (sp^2 + sp^3+CH)	76.7%	69.7%
C - O	11.2%	15.4%

Chemical analysis by XPS showed that there was a difference in the relative concentration of sp^3+CH hybridization, with a higher oxygen concentration of the C_B sample compared to sp^2 hybridization of the C_A sample, the latter being predominant in the C_A graphite powder than in the C_B, which is an important indication that C_B graphite would be harder to exfoliate. (Table 1)

SEM/EDS Analysis

Information about the different levels of exfoliation achieved in the samples, synthetized with different precursor materials (C_A and C_B), along with their elemental composition and surface morphology was analyzed using Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) techniques. For the SEM/EDS investigations, the samples were dispersed in ultrapure water and dropped onto the copper scotch tape. SEM images were obtained from a Scanning Electron Microscope with field emission gun (SEM MAIA3, Tescan) equipped with Energy Dispersive Spectroscopy detector (EDS X-Flash 6/30, Bruker). The measurements were performed using an accelerating voltage of 4-5 kV (optimized for light elements EDS analysis), a beam intensity of 10 nA, and 30 ° take-off angle of the EDS detector. The obtained EDS spectra were fitted using the "ESPRIT Quant" quantification software, with a measurement error estimated at about ± 1 at.%. Consequently, SEM analysis has been performed for the two separate experiments discussed above, one using C_B graphite sample as a starting material, which by means of XPS analysis showed a higher sp^3+CH hybridization than sp^2, and a second one using C_A graphite sample which presented more sp^2 hybridization type than sp^3+CH type. For an accurate comparison of the possibility and the degree of exfoliation in the samples, the two separate powders (C_A and C_B), have been treated using the same working parameters, namely the amount of concentrated hydrogen peroxide (10 ml /100 mg batch) and the ultrasound time (4 hours). The obtained results are presented in the following section accompanied by a brief discussion over the results.

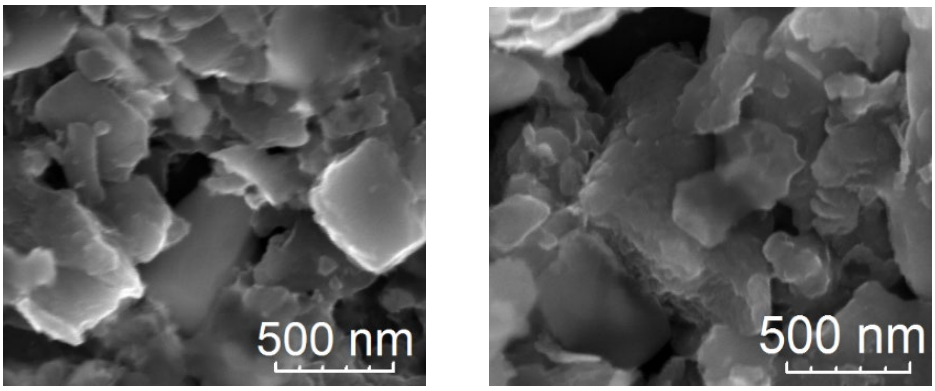
1st H_2SO_4 - GIC Experiment using C_B powder

The H_2SO_4 - GIC exfoliation process for the first type of graphite material (C_B) was started using 100 mg of chemically synthesized C_B (oxidized by means of sulfuric acid, as described above), followed by exfoliation process which included adding 10 ml of H_2O_2 (30%), and additional 10 ml of H_2O ultra pure (UP), done in continuous sonication for 4 hours.

In Fig 3. are depicted the SEM micrographs of the graphite intercalated compounds obtained using C_B graphite precursor, obtained after the chemical synthesis (Fig. 3a) by its oxidation with H_2SO_4, and after the exfoliation process (Fig. 3b) successively ultrasonicated in the presence of H_2O_2. The analyzed batches showed a very congested H_2SO_4 - GIC, with uneven morphology (Fig. 3), clear sign of little to none exfoliation taking place.

The analysis results show no difference before and after treatment, its morphology remaining compact, and no shade of graphite sheet (Fig. 3 a, b). From the EDS analysis (presented in Table 2) it can be concluded that contaminants from the initial phase (after chemical synthesis) are still present, the amount of oxygen obtained (~ 20 at %) can be correlated with that obtained from the XPS analysis

(~16%), if the contribution of the use of concentrated hydrogen peroxide is taken into account (Table 2).



a) **b)**

Fig 3. a) SEM micrograph of H_2SO_4 - GIC sample using C_B powder, after chemical synthesis, and b) after the exfoliation process

Table 2.

EDS analysis results using 2 types of precursors (C_B and C_A graphite), after chemical synthesis (oxidation with H_2SO_4), and after exfoliation process (ultrasonication in presence of H_2O_2). Sample H_2SO_4-GIC C_A after exfoliation and dilution process.

Sample	Carbon (at. %)	Nitrogen (at. %)	Oxygen (at. %)	Aluminum (at. %)	Silicon (at. %)	Sulfur (at. %)
H_2SO_4 – GIC C_B After chemical synthesis	71.04	-	19.94	1.72	2.05	5.26
H_2SO_4 – GIC C_B After exfoliation	67.53	5.39	21.11	1.55	1.23	3.19
H_2SO_4 - GIC C_A After chemical synthesis	92.51	-	6.04	-	-	1.41
H_2SO_4 - GIC C_A After exfoliation	85.55	3.21	10	-	-	1.24
H_2SO_4 - GIC C_A After exfoliation and dilution process	97.36	-	2.64	-	-	-

2nd H_2SO_4 - GIC Experiment using C_A powder

Using C_A graphite powder as a precursor, H_2SO_4 intercalation was observed highlighting the distribution of S, O, C elements, as shown in the EDS mapping area below (Fig. 4). The amount of sulfur, in the H_2SO_4 - GIC C_A sample after the chemical oxidation, was found about 1.4 at. %, lower than the intercalated graphite prepared using the C_B precursor, and remained constant after the exfoliation process (~1.24 at. %).

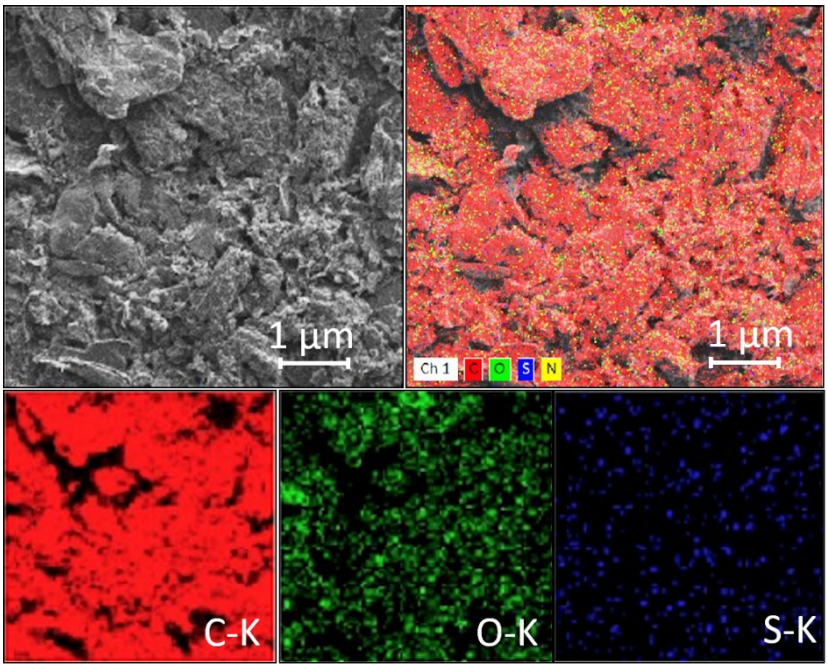
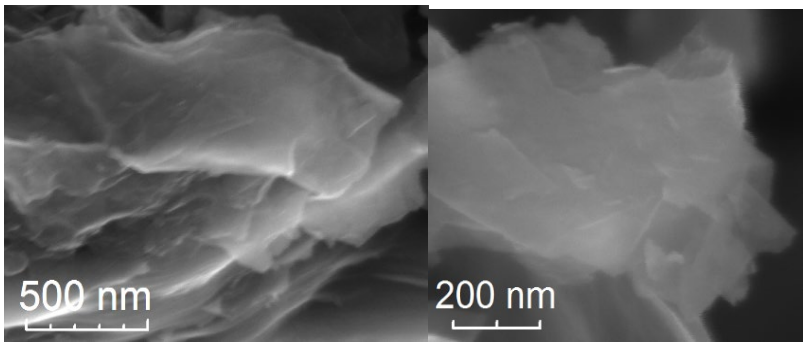


Fig 4. EDS mapping area of the H_2SO_4 - GIC C_A sample, with the distribution of elements S, O, C

In Fig 4. the distribution of elements S, O, C on the H_2SO_4 - GIC C_A sample surface is uniform. The obtained result is important for the subsequent uniform chemical exfoliation in the liquid phase. As in the experiment where C_B - type graphite was used as precursor, the process starts with H_2SO_4 - GIC obtained using 100 mg of the chemical solution synthesis described above, mixed with 10 ml H_2O_2 (30%), and followed by addition of 10 ml H_2O UP, continuously sonicated for 4 hours.



a) b)

Fig 5. a) SEM images of H_2SO_4 - GIC using C_A powder, after chemical synthesis, b) SEM images after the exfoliation process of H_2SO_4 – GIC

The morphology results of the H_2SO_4 - GIC C_A sample, where C_A graphite powder was used as a precursor, are presented in Fig. 5. The obtained data showed that partial exfoliation took place in the sample after the exfoliation process, yet some improvements are still needed for an efficient exfoliation process. However, for a single step exfoliation process it showed promising results especially from the purity point of view which was significantly improved (see Table 2). The SEM results revealed some large lateral dimensions (~ 500 nm) and many domains of exfoliated graphite, easy to notice. (Fig 5 a, b) These areas with clear signs of graphite exfoliation are, however, surrounded by large regions of conglomerates.

Consequently, a continuous ultrasonication step is necessary to improve further exfoliation. Making a compositional parallel of the H_2SO_4 - GIC C_A after exfoliation sample analyzed above, the EDS analysis showed a similar oxygen concentration of (~ 10 at %) close to the value obtained from the XPS analysis of the C_A as received powder (11,9 %), which indicates that no functional groups have been formed between the graphite sheets (Table 2).

As a general remark, the GIC sample using the C_A graphite powder as precursor material showed better results in terms of degree of exfoliation and purity than the GIC sample obtained using the C_B graphite precursor. Therefore, this sample (H_2SO_4 – GIC C_A) was selected to perform the optimization of the exfoliation process parameters, such as: sonication time, concentration of GIC solution (by controlling the amount of hydrogen peroxide and ultrapure water), number of dilutions and successive sonication steps. For this, a new exfoliation process was performed by extracting only the H_2SO_4 - GIC suspension (the foam formed at the surface of the GIC solution), to which an excess of hydrogen peroxide was added and the total ultrasonication time was increased to 8 hours.

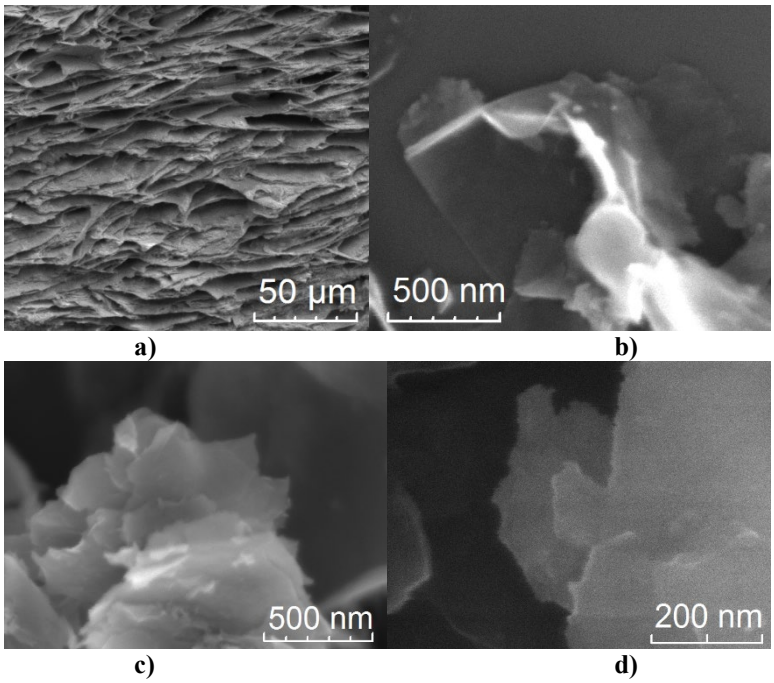


Fig 6. a) - d) SEM pictures after optimized exfoliation process of H_2SO_4 - GIC C_A sample using the foam resulted from the successful exfoliation (see Fig 5), obtaining just few layers of graphene material

The obtained results are presented in Fig 6 (a-d) and Fig 6a, representing a large magnification overview of the edge of the H_2SO_4 - GIC C_A sample, while Fig 6(b-c) show a detail of the graphene sheets at 500 nm scale bar and Fig 6d at 200 nm scale bar.

This approach, of additional exfoliation of the H_2SO_4 - GIC C_A foam, resulted in an improved exfoliation of the sample, corroborated by the SEM analysis results (Fig 6, a-d), with many more areas with clear boundaries between them, as a direct consequence of the use of additional oxygen. Successive dilutions were then carried out to facilitate further the exfoliation of the sample, in which supplementary 40 ml of H_2O UP was used, and several ultrasonication was also carried out. As observed in Fig 5b, this allowed to obtain a few-layered graphene material (Fig 6, b) with very high purity (see Table 2) and low oxygen concentration. According to the obtained results, an important remark can be also drawn regarding the quality of single/few-layered graphene sheets: the correlation between the ultrasonication time with the quantity of the hydrogen peroxide and ultrapure water used in the exfoliation process plays an important role in avoiding large defects, such as cracks, in the graphene sheets.

4. Conclusions

Our initial observation on published XPS data on graphite showed large chemical shifts and compositional variation. This was tested against experiment and found that $sp^2/(sp^3+CH)$ hybridization ratio obtained from XPS analysis correlates with the intercalation exfoliation efficiency which was investigated via SEM and EDS. The results showed that there is a limit of the contributions of carbon shifts above which chemical intercalation-exfoliation becomes difficult. Thus, the sample with sp^2 / (sp^2 + sp^3+CH) of about 77 % was a minimum quality observed for the intercalation exfoliation to readily occur. A less common method of graphite intercalation, exfoliation was implemented, in a one-step synthesis of graphite intercalated compounds using H_2SO_4 (H_2SO_4 - GIC) as intercalant, $KMnO_4$ as oxidizing agent and H_2O_2 as reactive species. In this process, all operations were carried out under ambient conditions, which provides the main advantage of a safer and simpler working condition, suitable for large scale production. The experimental results confirmed that the chemical synthesis of graphite containing more sp^2 than sp^3 or CH hybridization can be easily exfoliated by sonication in concentrated hydrogen peroxide in graphene sheets with layers of a few microns.

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REFERENCES

[1] *T. H. Han, H. Kim, S. J. Kwon, T. W. Lee, "*Graphene-based flexible electronic devices, Materials Science and Engineering", R: Reports 118, 1-43 (2017) .

[2] *D. M. Maximean, V. Cîrcu, P. Ganea, A. Bărar, O. Dănila, T. Staicu, V. A. Loiko, A.V. Konkolovich, A. A. Miskevich, "*Polymer dispersed liquid crystals films doped with carbon nanotubes: preparation methods.", Advanced Topics in Optoelectronics, Microelectronics, and Nanotechnologies IX, vol. 10977, p. 1097702. SPIE, (2018).

[3] *A. Magureanu, L. Dincă, C. Jalbă, R. F. Andrei, I. Burducea, D. G. Ghiţă, V. Nastasa, M. Gugiu, T. Asavei, O. Budrigă, D. Ticoş, V. Crăciun, B. Diaconescu, C. M. Ticoş,* "Target Characteristics Used in Laser-Plasma Acceleration of Protons Based on the TNSA Mechanism", Frontiers in Physics 10:727718, (2022).

[4] *D. Sangwan*, *O. Culfa*, *C. P. Ridgers*, *S. Aogaki*, *D. Stutman*, *B. Diaconescu*, "Simulations of carbon ion acceleration by 10 PW laser pulses on ELI-NP", Laser and Particle Beams 37 Issue 4, 346-353, (2019).

[5] *K. H. Park, B. H. Kim, S. H. Song, J. Kwon, B. S. Kong, K. Kang, S. Jeon,* "Exfoliation of Non-Oxidized Graphene Flakes for Scalable Conductive Film", Nano Letters 12, (2012).

[6] *S. Park, R. Ruoff,* "Chemical methods for the production of graphenes", Nature Nanotech 4, 217-224, (2009).

[7] *B. C. Brodie*, "On the atomic weight of graphite", Phil. Trans. R. Soc. 149, 249-259 (1859).

[8] *L. Staudenmaier*, "Verfahren zur Darstellung der Graphitsäure", Ber. Dtsch. Chem. Ges., vol. 31, pp. 1481-1487, (1898).

[9] *W. S. Hummers, R. E. Offeman*, "Preparation of Graphitic Oxide", Journal of the American Chemical Society, vol. 80, p. 1339, (1958).

[10] *J. P.-L. J. Timothy, "*Carbon Quantum Dots: Bridging the gap Between Chemical Structure and Material properties", Theses and Dissertations--Chemistry. 94, (2018).

[11] *J. I. Paredes, S. Villar-Rodil, A. Martínez-Alonso, J. M. D. Tascón*, "Graphene Oxide Dispersions in Organic Solvents", Langmuir, vol. 24, (2008).

[12] *J. T. Paci, T. Belytschko, G. C. Schatz*, "Computational Studies of the Structure, Behavior upon Heating, and Mechanical Properties of Graphite Oxide", The Journal of Physical Chemistry C, vol. 111, (2007).

[13] *J. W. Suk, R. D. Piner, J. An, R. S. Ruoff*, "Mechanical properties of monolayer graphene oxide", ACS Nano, vol. 4, (2010).

[14] *J. E. Kim, T. H. Han, S. H. Lee, J. Y. Kim, C. W. Ahn, J. M. Yun, S. O. Kim*, "Graphene Oxide Liquid Crystals", Angewandte Chemie International Edition, vol. 50, (2011).

[15] *C. Lim, H. Shi, L. Tang, Y. Wang, C. Lim, K. Loh*, "Origin of enhanced stem cell growth and differentiation on graphene and graphene oxide", ACS Nano, vol. 5, pp. 7334-41, (2011).

[16] *X. Sun, Z. Liu, K. Welsher, J. Robinson, A. Goodwin, S. Zaric y H. Dai, "*Nano-graphene oxide for cellular imaging and drug delivery", Nano Research, vol. 1, (2008).

[17] *D. Chung*, "Review Graphite", Journal of Materials Science 37 (2002).

[18] *X. Chen, X. Wang, De Fang*, "A review on C1s XPS-spectra for some kinds of carbon materials", Fullerenes, Nanotubes and Carbon Nanostructures, (2020).

[19] *J. Díaz, G. Paolicelli, S. Ferrer y F. Comin*, "Separation of the sp^3 and sp^2 components in the C_{1s} photoemission spectra of amorphous carbon film", Phys Rev B Condensed Matter., pp. 8064-8069, (1996).

[20] *A. M. Dimiev, K. Shukhina, N. Behabtu, M. Pasquali, J. M. Tour,* "Stage Transitions in Graphite Intercalation Compounds: Role of the Graphite Structure ", J. Phys. Chem. C 2019, 123, 19246−19253, (2019).

[21] *R. Haerle, E. Riedo, A. Pasquarello, A.Baldereschi*, "Sp^2/sp^3 hybridization ratio in amorphous carbon from C_{1s} core-level shifts: X-ray photoelectron spectroscopy and first-principles calculation", Physical Review B, vol 65, 045101, (2001).