

# Atomic Force Microscopy Analysis of the Surface Topography of Graphite Extracted Using the Strong Acid Drip Method

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**Abstract.** Graphene, a two-dimensional (2D) material with a hexagonal shape in its atomically thin structure, exhibits unique electrical properties and has therefore been used in various electronic devices. Hence, obtaining graphene by acid means using three strong acids, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, and HCl, proportion (1:2:2/3), understanding the correlation between the structure and the electrical properties at the nanometric scale is essential. Atomic force microscopy (AFM) techniques provide the best way to visualize these relationships through their topography, which is particularly necessary for future miniaturized devices. This article highlights the characterization of graphene's topographic properties using techniques such as AFM, scanning electron microscopy, and infrared radiation. It is beneficial to the research community working not only with graphene-based materials but also with graphene composite materials with applications in electronics.

**Keywords:** Strong acids, Graphene, Nanometric topography.

## 1 Introduction

Graphene is a material composed of a single layer of carbon atoms arranged in a hexagonal lattice, forming a two-dimensional (2D) structure [1][2]. Atoms are held together by strong covalent bonds. The weaker van der Waals forces can bind adjacent graphene layers together but allow them to slide easily [3][4]. Its hexagonal geometry allows it to have flexibility as well as electrical and mechanical qualities. By functionalization, hydroxyl, epoxide, and carbonyl groups can be obtained, joined at the base [5]. Graphene oxide (GO) has the same structure as graphene and retains excellent properties [6].

In recent years, the study of functionalized graphene layers has captured the attention of the scientific community due to their mechanical, physical, chemical, and electrical properties. Atomic force microscopy (AFM) has become a fundamental tool for graphene characterization, allowing high-resolution imaging and precise measurement of its properties at the nanometric scale [7]. A detailed understanding of their topography is crucial for their potential application in various advanced technologies, such as electronic devices, sensors, and composite materials. Recent studies have shown that graphene has a tensile strength of approximately 130 GPa and a Young's modulus of 1 TPa, values that exceed most known materials (Ramos-Hamud, 2017). One way to obtain thin graphite sheets with graphene surfaces and layers functionalized with NaNO<sub>3</sub>, KMnO<sub>4</sub>, and H<sub>2</sub>SO<sub>4</sub> at 95-98% concentration is by the Hummer method [8][9][10]. It can be done by spray coating [11] using three strong acids [12] or by non-thermal plasma in an SO<sub>2</sub> atmosphere at room temperature [13][14]. The morphology and mechanical properties of graphene have been studied [15]. The main objective is to evaluate how treatment with strong acids affects the nanoscopic surface topography of graphite. This research is needed to provide a more complete understanding of how different production methods and experimental conditions influence graphene properties, variations in preparation experimental conditions through AFM characterization [16]. To address these questions, an experimental methodology will be used that includes the characterization of graphene surface samples produced by the chemical method with strong acids applied by the drip method. This treatment can induce significant changes in the roughness, structure, and chemical properties of the graphene layers, which can influence their performance in specific applications. This study contributes to the literature by filling the existing gaps on the influence of experimental conditions and production methods on the topography of graphite flakes with graphene surfaces.

In addition, it provides practical recommendations for obtaining graphene production, which is crucial for its application in electronic devices and composite materials. The practical implications of this work include the improvement of graphene production techniques and the development of new graphene-based materials.

## 2 Methodology

### 2.1 Reagents

The materials used are 99.9% pure graphite, sulfuric acid 95-97% (EMSURE ISO), nitric acid 65% (EMSURE), hydrochloric acid, in a ratio of 1:2:2/3. and ammonium hydroxide 5%.

### 2.2 Equipment

ECO ball mill to pulverize the graphite, Analytical balance used to weigh the graphite, Branson ultrasonic sonifier and centrifuge 800D Electric Centrifuge, for characterization, scanning electron microscopy (SEM) of the VEGA TESCAN brand was used, Fourier transform infrared spectroscopy Perkin Elmer Model Spectrum two.

Atomic force microscopy (AFM): A Park Systems (Santa Clara, CA, USA) XE7 atomic force microscope was used in air contact mode using Park Systems CONTSCR tips (25 kHz, 0.2 N/m typical).

### 2.3 Strong acids

The 99% pure graphite is pulverized in the ECO BALL MILL, obtaining a 4-gram sample of pulverized graphite. It is then functionalized by dripping strong acids using the Hummer method. Sulfuric acid, nitric acid, and hydrochloric acid are added every 6 hours in proportions of 2:1:2/3 of strong acids [12].

The mixture is placed in a container for 24 hours. Once the graphite is functionalized, it is neutralized with 5% ammonium hydroxide until a neutral pH is obtained. The graphite/graphene obtained is diluted in 20 mL of de-ionized water and placed in an ultrasonic sonicator [17][18]. The mechanical exfoliation method is a simple procedure in which thin sheets of graphene are peeled off [8], at a temperature of 20 °C with a time of 20 minutes, with repetition 4 times. The sample is transferred in a 15 mL pellet to be centrifuged [19] at a speed of 1500 rpm for 15 minutes, 3 times. It is then filtered, and graphene is obtained. To characterize graphene by AFM, the sample is taken, left to dry in a vacuum, and positioned with adhesive tape on a piece of freshly exfoliated mica. For scanning electron microscopy (SEM) measurements, the graphene sample is placed on a nitrocellulose substrate to determine its shape and topography. In addition, Fourier transform infrared absorption analysis measurement is performed with the coupled attenuated total reflectance (FTIR-ATR) module.

## 3 Results

### 3.1 Scanning electron microscopy analysis

The SEM images of the samples obtained by functionalization with strong acids show GO sheets with regular morphology. Sonification and centrifugation exfoliate GO, which occurs when the graphene structures are detached from the functionalized graphite [20], as shown in Fig. 1.

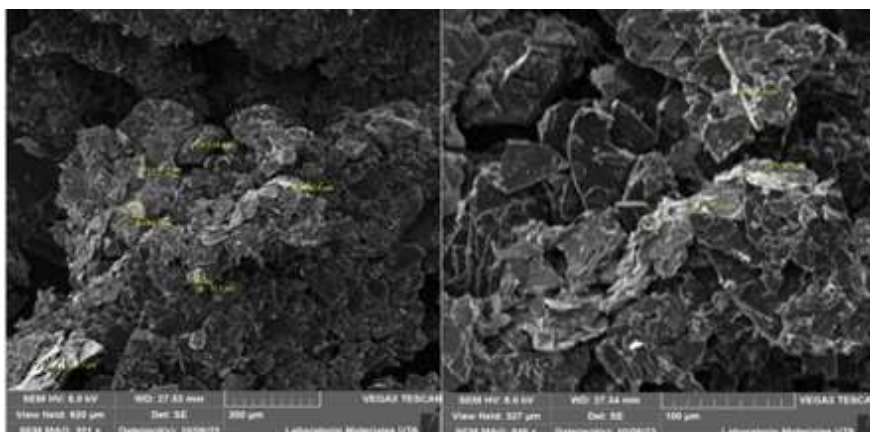


Fig. 1 Scanning electron microscopy of the graphite/graphene sample

Oxidized substances usually contain oxygen atoms at the edges of the sheets. These functional groups are usually hydroxyls, carboxyls, or carbonyls. The distance between these layers is affected by the functional groups present.

### 3.2 FTIR analysis

FTIR spectrum analysis of the synthesized sample to investigate the functional groups of the material, as shown in Fig. 2.

The graphene sample showed different types of oxygen functional peaks, assigned to stretching peaks of width 3445.3  $\text{cm}^{-1}$  and 1583  $\text{cm}^{-1}$  to OH groups. Peak 1641.9 indicates the stretching of C=O and CO belonging to the carboxylic groups [21]. Peaks 2024.96 – 2774.6 showed  $\text{sp}^3$  CH bonds, indicating that the product is made on an acid base and confirming the presence of carboxylic acid.

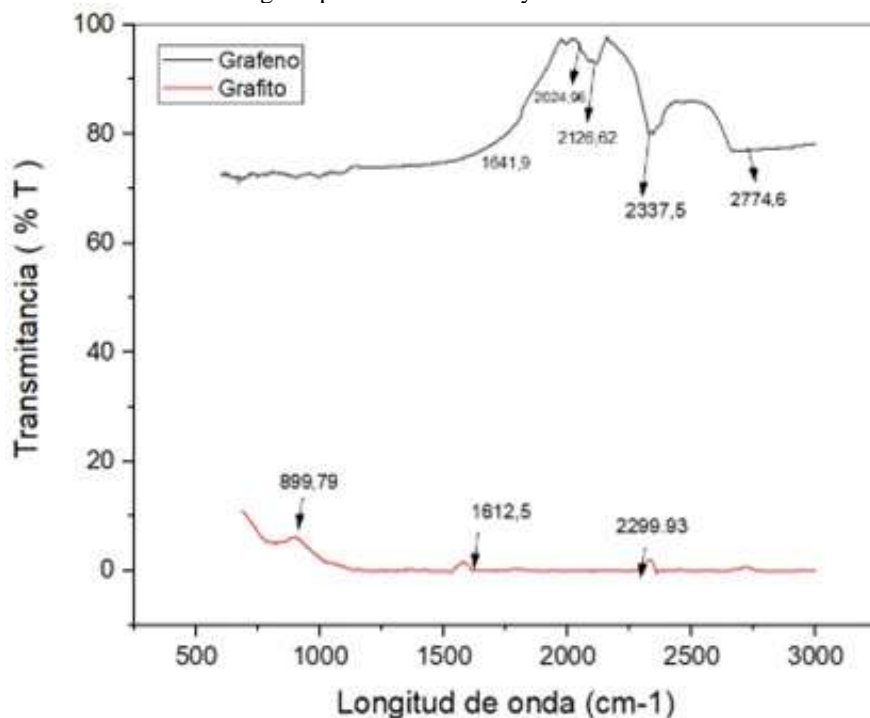


Fig. 2 FTIR of the graphite-graphene sample

### 3.3 Atomic Force Microscopy Analysis of the Graphite/Graphene Sample

In the images obtained by AFM, flakes of graphite adhered to the substrate are observed, with several layers that could be attributed to stacks of functionalized graphene sheets.

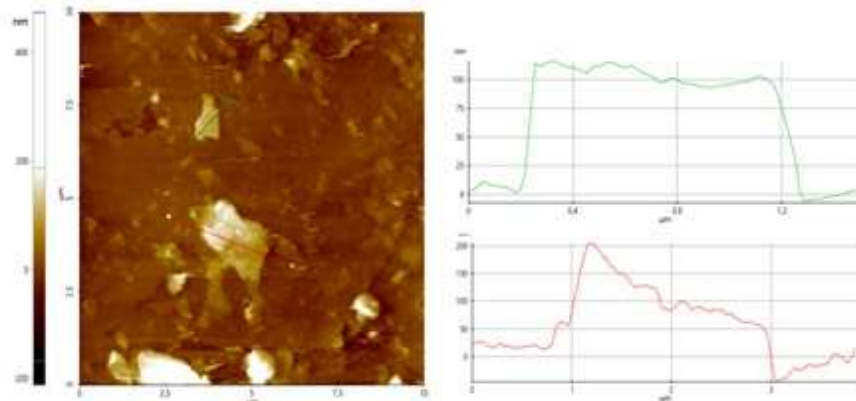


Fig.3 AFM surface topographic characterization

Fig. 3 shows the surface topographic characterization of the graphite/graphene samples by atomic force microscopy. Two topographic profiles are highlighted, obtained along the arrows indicated in the image [22]. The topographic profile shown in the AFM image shows variations in surface height horizontally of approximately  $1.4 \mu\text{m}$ , starting at  $0 \text{ nm}$  and rising sharply to around  $100 \text{ nm}$  in  $0.2 \mu\text{m}$ , remaining relatively constant with small fluctuations up to  $1.2 \mu\text{m}$ .

The lateral force contrast shows in Figure 4 different regions associated with different local friction between the tip and the sample, which may be related to different adhesion, which could involve areas of different surface chemical composition [23][24].

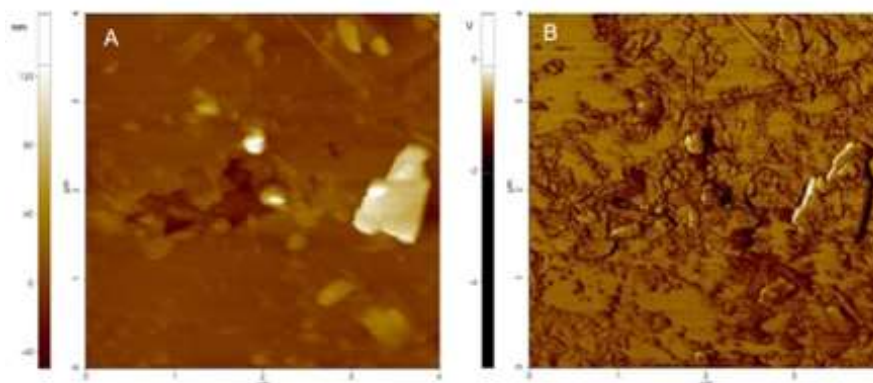


Figure 4. Surface topography (A) and lateral force (B) characterization of the graphite/graphene samples

## 4 Conclusions

Characterizing graphene's properties at the nanoscale using advanced techniques such as scanning electron microscopy (SEM) and atomic force microscopy (AFM) has allowed for a deeper understanding of its structure and properties. Graphene oxide (GO) samples obtained by functionalization with strong acids show sheets with regular morphology, FTIR peaks of  $\text{sp}^3 \text{ CH}$  bonds. The topographic profile of graphene shows variations in surface height

over a horizontal distance. The characterized graphene exhibits exceptional properties for electronic applications, sensors, energy storage, composite materials, and medicine.

## 5 Acknowledgements

The authors thank the Technical University of Ambato, the Faculty of Civil and Mechanical Engineering, the Faculty of Electronic and Industrial Systems Engineering, Food Science and Engineering, and Biotechnology. The efforts of the reviewers who provide valuable information in each submitted work are also acknowledged

## 6 Financing Statement

This research has received specific funding from the Directorate of Innovation and Educational Development of the Technical University of Ambato.

## References

- [1] M. Yadav, KY Rhee, SJ Park, and D. Hui, "Mechanical properties of Fe<sub>3</sub>O<sub>4</sub>/GO/chitosan composites," *Compos. Part B Eng.*, vol. 66, no. April, pp. 89–96, 2014, doi: 10.1016/j.compositesb.2014.04.034.
- [2] KKH De Silva, HH Huang, P. Viswanath, R. Joshi, and M. Yoshimura, "Nanoscale electrical characterization of graphene-based materials by atomic force microscopy," *J. Mater. Res.*, vol. 37, no. 20, pp. 3319–3339, 2022, doi:10.1557/s43578-022-00758-0.
- [3] A. Mulone et al., "Development of yttria-stabilized zirconia and graphene coatings obtained by suspension plasma spraying: Thermal stability and influence on mechanical properties," *Ceram. Int.*, vol. 49, no. 6, pp. 9000–9009, 2023, doi: 10.1016/j.ceramint.2022.11.055.
- [4] Y. Arao, F. Mori, and M. Kubouchi, "Efficient solvent systems for improving production of few-layer graphene in liquid phase exfoliation," *Carbon NY*, vol. 118, pp. 18–24, 2017, doi: 10.1016/j.carbon.2017.03.002.
- [5] Y. Pan, T. Wu, H. Bao, and L. Li, "Green fabrication of chitosan films reinforced with parallel aligned graphene oxide," *Carbohydr. Polym.*, vol. 83, no. 4, pp. 1908–1915, 2011, doi: 10.1016/j.carbpol.2010.10.054.
- [6] MDP Lavin-Lopez, A. Romero, J. Garrido, L. Sanchez-Silva, and JL Valverde, "Influence of different improved hummers method modifications on the characteristics of graphite oxide in order to make a more easily scalable method," *Ind. Eng. Chem. Res.*, vol. 55, no. 50, pp. 12836–12847, 2016, doi: 10.1021/acs.iecr.6b03533.
- [7] B. Vasić et al., "Atomic force microscopy-based manipulation of graphene using dynamic plowing lithography," *Nanotechnology*, vol. 24, no. 1, 2013, doi: 10.1088/0957-4484/24/1/015303.
- [8] L. Serrano-Luján et al., "Environmental impact of the production of graphene oxide and reduced graphene oxide," *SN Appl. Sci.*, vol. 1, no. 2, pp. 1–12, 2019, doi: 10.1007/s42452-019-0193-1.
- [9] NAGuliyeva, RG Abaszade, EA Khanmammadova, and EM Azizov, "Synthesis and analysis of nanostructured graphene oxide," *J. Optoelectron. Biomed. Mater.*, vol. 15, no. 1, pp. 23–30, 2023, doi: 10.15251/jobm.2023.151.23.
- [10] N. Almasov, B. Kurbanova, T. Kuanyshbekov, K. Akatan, S. Kabdrakhmanova, and K. Aimaganbetov, "Study of the structure and electrical properties of graphene oxide (GO) and graphene oxide+nanocellulose (GO+NC)," *Kompleks. Ispol'zovanie Miner. syr'â/Complex Use Miner. Resour. Shikisattardy Keshendi Paid.*, Vol. 329, no. 2, pp. 103–109, 2024, doi: 10.31643/2024/6445.21.
- [11] SH Park et al., "Spray-assisted deep-frying process for the in situ spherical assembly of graphene for energy-storage devices," *Chem. Mater.*, vol. 27, no. 2, pp. 457–465, 2015, doi: 10.1021/cm5034244.
- [12] RJ Camargo-Amado, U. Valle, F. De Ingeniería, and EDI Química, "Chemical functionalization method to obtain graphene oxide adhered to the surface of high-density pyrolytic graphite plates by acid spray coating," vol. 23, no. 2, 2021, doi: 10.25100/iyc.23i2.10838.
- [13] A. Piñeiro-García, S. M. Vega-Díaz, F. Tristán, D. Meneses-Rodríguez, G. J. Labrada-Delgado, and V. Semetey, "Photochemical Functionalization of Graphene Oxide by Thiol-Ene Click Chemistry," *Ind. Eng. Chem. Res.*, vol. 59, no. 29, pp. 13033–13041, 2020, doi: 10.1021/acs.iecr.0c01252.

- [14] M. Li et al., “Graphene: Preparation, tailoring, and modification,” *Exploration*, vol. 3, no. 1, 2023, doi: 10.1002/EXP.20210233.
- [15] A. Martín, P. Batalla, J. Hernández-Ferrer, MT Martínez, and A. Escarpa, “Graphene oxide nanoribbon-based sensors for the simultaneous bio-electrochemical enantiomeric resolution and analysis of amino acid biomarkers,” *Biosens. Bioelectron.*, vol. 68, pp. 163–167, 2015, doi: 10.1016/j.bios.2014.12.030.
- [16] H. Li et al., “Accepted Manuscript,” *Mater. Today Proc.*, vol. 22, no. 1, pp. 16–20, 2019.
- [17] S. Niyogi, E. Bekyarova, M.E. Itkis, JL McWilliams, MA Hamon, and RC Haddon, “Solution properties of graphite and graphene,” *J. Am. Chem. Soc.*, vol. 128, no. 24, pp. 7720–7721, 2006, doi: 10.1021/ja060680r.
- [18] J. Wang, X. Wang, L. Wan, Y. Yang, and S. Wang, “An effective method for bulk obtaining graphene oxide solids,” *Chinese J. Chem.*, vol. 28, no. 10, pp. 1935–1940, 2010, doi: 10.1002/cjoc.201090322.
- [19] Y. Wei and Z. Sun, “Liquid-phase exfoliation of graphite for mass production of pristine few-layer graphene,” *Curr. Opin. Colloid Interface Sci.*, vol. 20, no. 5–6, pp. 311–321, 2015, doi: 10.1016/j.cocis.2015.10.010.
- [20] X. Colom, J. Cañavate, M.J. Lis, G. Sanjuan, and I. Gil, “Structural Analysis of Graphene Oxides (GO) and Reduced Graphene Oxides (rGO),” *Afinidad*, vol. 77, no. December, pp. 167–174, 2020.
- [21] C. Galindo-Urbe, P. Calaminici, and O. Solorza-feria, “Review on graphene synthesis by liquid-phase exfoliation: Mechanisms, factors, and techniques,” vol. 36, no. 1, pp. 1–14, 2022.
- [22] R. Rasuli, A. Iraji Zad, and MM Ahadian, “Mechanical properties of graphene cantilever from atomic force microscopy and density functional theory,” *Nanotechnology*, vol. 21, no. 18, 2010, doi: 10.1088/0957-4484/21/18/185503.
- [23] Y. Yao, L. Ren, S. Gao, and S. Li, “Histogram method for reliable thickness measurements of graphene films using atomic force microscopy (AFM),” *J. Mater. Sci. Technol.*, vol. 33, no. 8, pp. 815–820, 2017, doi: 10.1016/j.jmst.2016.07.020.
- [24] W. Huang, ZF Liu, and ZY Yang, “Top or underneath? Revealing the structure of multilayer graphene domains with atomic force microscopy and theoretical analysis,” *Carbon NY*, vol. 99, pp. 131–137, 2016, doi: 10.1016/j.carbon.2015.11.072.