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# Study on the Chemical Functionalization of Graphene Materials for Electroplating Applications

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***ABSTRACT :*** *In this study, graphene was functionalized using a mixed acid treatment ($HNO_3/H_2SO_4$) to introduce carboxyl (-COOH) groups onto its surface. The structural, chemical, and thermal properties of pristine graphene (Gr) and functionalized graphene (Gr-COOH) were investigated using FTIR, Raman spectroscopy, TGA, and dispersion tests. FTIR results confirmed the successful incorporation of oxygen-containing functional groups. Raman analysis indicated an increased defect density after functionalization, as evidenced by a higher $I_D/I_G$ ratio. TGA revealed distinct weight loss stages corresponding to the decomposition of functional groups and the graphene framework. Additionally, dispersion tests showed that Gr-COOH exhibited significantly improved stability and uniformity in water compared to pristine graphene. These results demonstrate that the functionalization process effectively modifies graphene, enhancing its dispersibility and making it a promising material for applications such as electroplating.*

***KEYWORDS -*** *graphene, functionalization, characterization, carboxyl group*

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## I.INTRODUCTION

Graphene, a two-dimensional (2D) allotrope of carbon consisting of a single layer of $sp^2$-hybridized carbon atoms arranged in a hexagonal lattice, has emerged as one of the most extensively studied nanomaterials since its experimental isolation in 2004 [1,2]. The award of the Nobel Prize in Physics in 2010 to its discoverers further underscored its scientific significance and transformative potential [3]. Owing to its unique structure, graphene exhibits extraordinary physical and chemical properties, including ultra-high carrier mobility, excellent thermal conductivity, superior mechanical strength, and high specific surface area [4]. These attributes have positioned graphene as a key material for next-generation applications in nanoelectronics, optoelectronics, energy storage systems, catalysis, and sensing technologies [5,6]. At the atomic level, the remarkable properties of graphene originate from its electronic structure. Each carbon atom forms three in-plane σ bonds through $sp^2$ hybridization, generating a robust honeycomb lattice, while the remaining $p_z$ orbital contributes to a delocalized π-electron system extending over the entire graphene sheet. This conjugated π-network is responsible for graphene's exceptional electrical conductivity and optical transparency. However, the same delocalization that gives rise to these outstanding properties also renders pristine graphene chemically inert and hydrophobic, limiting its compatibility with solvents and matrices. As a result, graphene tends to aggregate via strong π–π stacking interactions, forming multilayer structures that significantly reduce its accessible surface area and degrade its performance in practical applications [7,8]. To address these challenges, surface functionalization has been widely recognized as an effective approach to tailor the physicochemical properties of graphene [9]. Functionalization not only improves dispersibility and processability but also introduces active sites that enhance interfacial interactions with surrounding media. In general, graphene functionalization strategies can be categorized into covalent and non-covalent approaches, each with distinct advantages and limitations [10]. Covalent functionalization involves the formation of strong chemical bonds between graphene and functional groups, typically at defect sites, edges, or regions activated by chemical treatments [11]. Oxidative processes using strong oxidizing agents, such as nitric acid/sulfuric acid mixtures or potassium permanganate systems, are commonly employed to introduce oxygen-containing functional groups, including carboxyl, hydroxyl, and epoxy groups. These functional groups serve as anchoring sites for further chemical modification, enabling the attachment of organic molecules, polymers, or nanoparticles. Additionally, reactions such as esterification, amidation, and cycloaddition (e.g., dienophile addition to C=C bonds) have been explored to expand the chemical versatility of graphene [11]. While covalent functionalization significantly enhances chemical reactivity and stability, it often disrupts the π-conjugated network, leading to a partial loss of electrical and mechanical properties [12]. In contrast, non-covalent functionalization preserves the intrinsic electronic structure of graphene by relying on weak

intermolecular interactions, such as van der Waals forces, π–π stacking, hydrogen bonding, and electrostatic interactions [13]. This method typically involves the adsorption of surfactants, polymers, or aromatic molecules onto the graphene surface, which prevents aggregation and improves dispersion in various solvents. Among these interactions, π–π stacking between graphene and aromatic compounds is particularly effective due to the extended conjugated system of graphene [14]. Furthermore, advanced interaction mechanisms, including cation–π, anion–π, and hydrogen–π interactions, have been investigated to design sophisticated graphene-based hybrid materials for applications in catalysis, sensing, and supramolecular assembly. Another important functionalization pathway involves the incorporation of heteroatoms or reactive species, such as hydrogen and halogens. For instance, fluorination of graphene introduces C–F bonds, which can subsequently be replaced by various functional groups through nucleophilic substitution reactions. These modifications enable further tuning of graphene's chemical and electronic properties [15]. However, excessive functionalization or harsh treatment conditions may lead to structural damage or degradation of graphene sheets, highlighting the need for controlled and optimized processes. Despite extensive research efforts, a critical challenge remains in achieving an optimal balance between functionalization efficiency and preservation of graphene's intrinsic properties [14,15]. Covalent approaches offer strong and stable functionalization but at the expense of electronic performance, whereas non-covalent methods maintain structural integrity but may suffer from limited long-term stability. Therefore, developing innovative functionalization strategies that combine the advantages of both approaches is essential for advancing the practical implementation of graphene-based materials.

In this study, we focus on the chemical functionalization of graphene surfaces, aiming to enhance their physicochemical properties and expand their potential applications. The mechanisms, methods, and effects of different functionalization approaches are systematically investigated to provide insights into the design of high-performance graphene-based materials.

## II. EXPERIMENTAL

A mixed acid solution of $HNO_3/H_2SO_4$ (volume ratio 3:1) was employed as a strong oxidizing agent to introduce carboxylic functional groups onto graphene (Gr) by oxidizing carbon atoms at defect sites. However, this mixture is highly hazardous due to the release of $NO_2$ gas during the reaction; therefore, all procedures were conducted under strict safety conditions. The extent of oxidation and defect formation increases with both the volume of the acid mixture and the reaction duration.

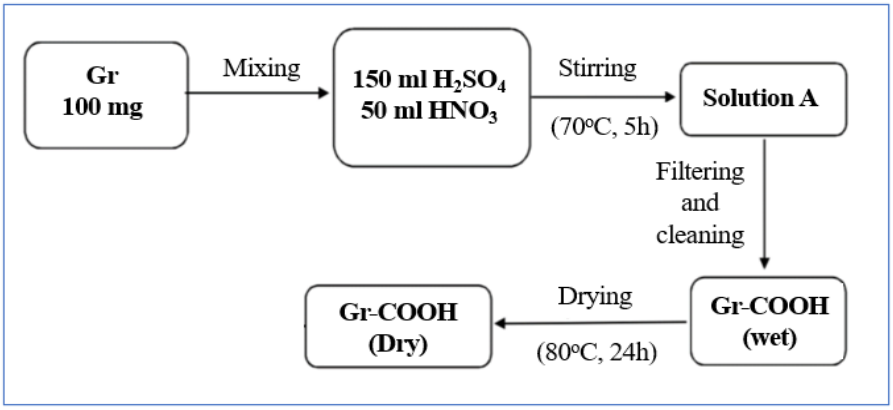


Figure 1: The functionalization process of graphene.

In a typical procedure, 100 mg of graphene was added to a round-bottom flask containing 200 mL of the acid mixture (sufficient volume to ensure effective oxidation and proper stirring). The suspension was magnetically stirred at 70°C for 4 h. Subsequently, the entire mixture was subjected to ultrasonic treatment for 5 h. After the reaction, the resulting suspension was filtered and thoroughly washed using a vacuum filtration system to remove residual acids. To ensure complete removal of acid, the pH of the filtrate was monitored using pH indicator paper. When no color change was observed, the functionalized graphene was considered free of residual acid. Depending on the initial graphene amount, product collection methods were adjusted accordingly; for smaller quantities, centrifugation can be used to obtain highly purified functionalized graphene. Finally, the obtained material was dried at 80°C for 24 h to yield carboxyl-functionalized graphene (Gr–COOH).

Pristine graphene and functionalized graphene were systematically characterized using Fourier Transform Infrared (FTIR, Shimadzu IRPrestige-21) spectroscopy, Raman spectroscopy (Horiba LabRAM HR Evolution), and Thermogravimetric Analysis (TGA, Shimadzu DTG-60H) in order to comprehensively evaluate the structural, chemical, and thermal changes induced by the functionalization process. The combination of these

analytical techniques provides complementary insights into the successful introduction of functional groups, the evolution of defect density, and the thermal stability of the modified graphene.

## III. RESULTS AND DISCUSION

Fourier Transform Infrared (FTIR) spectroscopy was employed to identify and analyze the organic functional groups present in the synthesized material. In this study, FTIR analysis plays a crucial role in confirming the successful functionalization of graphene, particularly the introduction of carboxyl (–COOH) onto its surface. Graphene sheets were treated using a mixed acid solution of $HNO_3$ and $H_2SO_4$, a commonly used oxidation method to introduce oxygen-containing functional groups. This chemical treatment is expected to generate –COOH groups predominantly at defect sites and sheet edges, thereby enhancing the chemical reactivity and dispersibility of graphene.

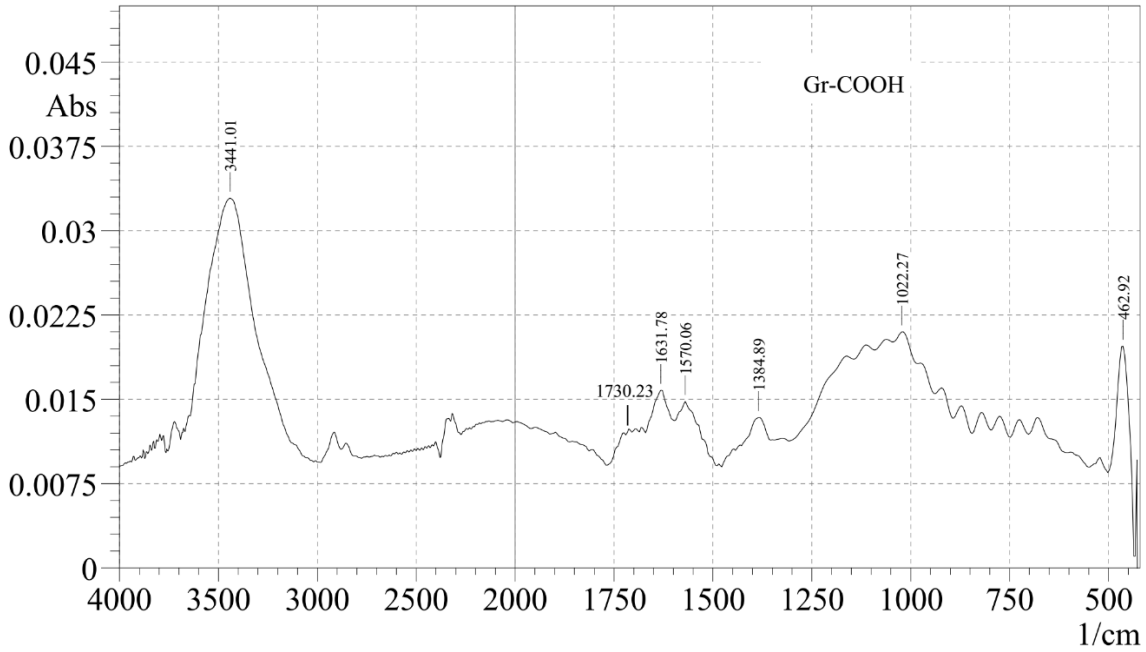


Figure 2: FTIR spectra of Gr-COOH

The FTIR spectrum of the functionalized graphene (graphene–COOH), as shown in Figure 2, provides clear evidence of these structural modifications. A broad absorption band centered at 3441 $cm^{-1}$ is observed, which is characteristic of the stretching vibrations of –OH groups. This broadening can be attributed to hydrogen bonding effects and may arise from hydroxyl groups associated with carboxylic functionalities or adsorbed moisture. The presence of this band indicates the successful incorporation of oxygen-containing groups during the acid treatment process. A prominent peak at 1730 $cm^{-1}$ is assigned to the C=O stretching vibration of carboxyl (–COOH) groups [16]. This peak is widely recognized as a key indicator of graphene oxidation and confirms the formation of carboxylic acid functionalities on the graphene surface. Additionally, the peak at 1631 $cm^{-1}$ corresponds to the C=C skeletal vibrations of the graphene lattice, reflecting the retention of the conjugated $sp^2$ carbon network despite the oxidation process. This suggests that although functional groups have been introduced, the fundamental structure of graphene remains largely preserved. Other characteristic peaks are also identified in the spectrum. The absorption band at 1022 $cm^{-1}$ is attributed to C–O stretching vibrations, further supporting the presence of oxygen-containing functional groups such as alcohols, ethers, or carboxyl groups [17]. Moreover, the peak at 1570 $cm^{-1}$ is associated with >C=C< stretching vibrations in unsaturated carbon structures, which may arise from defects or partially disrupted π-conjugation within the graphene sheets. The FTIR analysis provides strong evidence that –COOH functional groups have been successfully grafted onto the graphene surface through oxidation with the $HNO_3/H_2SO_4$ mixture. The presence of these functional groups not only confirms the effectiveness of the chemical modification process but also suggests improved interfacial interactions and compatibility in subsequent composite applications.

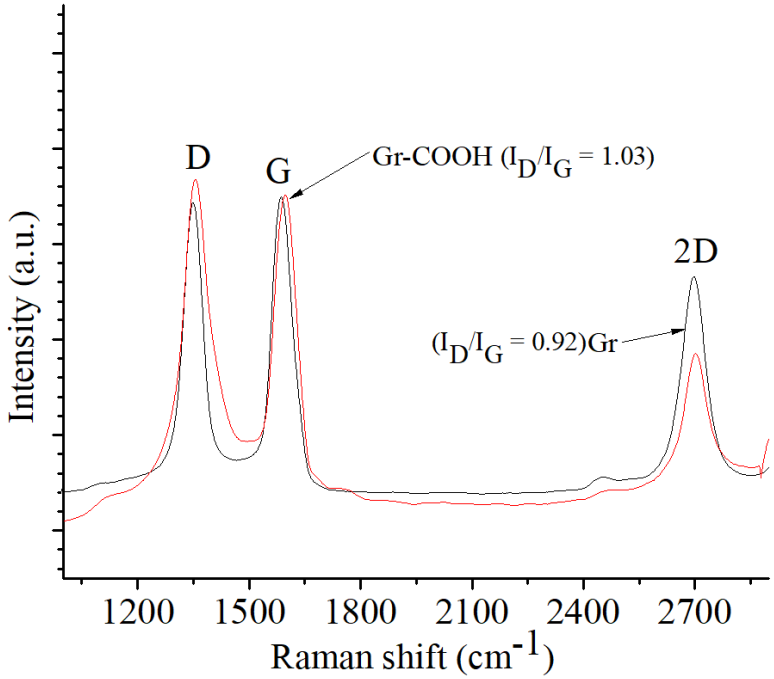


Figure 3: Raman spectra of (a) as-prepared Gr and (b) functionalized Gr.

Raman spectroscopy is widely recognized as an effective and reliable technique for investigating the structural characteristics of graphene-based materials. In this study, Raman analysis was employed to evaluate the influence of the functionalization process on the structural properties of pristine Gr and carboxyl-functionalized graphene (Gr–COOH). In particular, the degree of structural disorder and defect density was assessed through the relative intensity ratio of the two characteristic Raman bands, namely the D band and the G band ($I_D/I_G$) [18]. Figure 3 presents the Raman spectra of pristine graphene and functionalized graphene. Two prominent characteristic peaks are clearly observed: the D band located at 1353.87 $cm^{-1}$ and the G band at 1591.22 $cm^{-1}$ [19]. The G band originates from the in-plane stretching vibration of $sp^2$-bonded carbon atoms in the graphene lattice and is commonly associated with the degree of structural order and graphitic crystallinity. A strong and sharp G peak typically indicates a well-ordered $sp^2$ carbon network. In contrast, the D band is related to the presence of structural defects and disorder within the graphene framework. This peak arises from the breathing modes of $sp^3$-hybridized carbon atoms and becomes active in the presence of lattice imperfections such as vacancies, edges, or functional groups. Therefore, the intensity of the D band serves as an important indicator of defect density in graphene materials. The ratio of the intensities of these two bands ($I_D/I_G$) provides valuable insight into the level of disorder and crystallinity of the material. In this work, the $I_D/I_G$ ratio of pristine graphene is determined to be 0.92, which is lower than that of the functionalized graphene (1.03). This increase in the $I_D/I_G$ ratio after functionalization clearly indicates a higher density of defects in the Gr–COOH sample [20]. The introduction of these defects can be attributed to the oxidative treatment process, in which graphene is exposed to strong oxidizing agents ($HNO_3/H_2SO_4$), leading to the disruption of the $sp^2$ carbon network and the formation of oxygen-containing functional groups. Furthermore, a noticeable shift of the G band toward higher wavenumbers is observed in the functionalized graphene compared to pristine graphene. This shift can be attributed to lattice distortion and strain induced during the chemical modification process. Such structural distortion further confirms that the functionalization process not only introduces new functional groups but also alters the intrinsic lattice structure of graphene. In conclusion, the Raman spectroscopy results demonstrate that the functionalization process significantly increases the defect density in graphene. In other words, the introduction of –COOH groups through oxidative treatment leads to the formation of structural defects and partial modification of the graphene lattice, thereby affecting its structural integrity and properties.

Thermogravimetric analysis (TGA) provides valuable information regarding the thermal behavior and stability of functionalized graphene, particularly because the organic functional groups attached to the graphene surface are generally thermally unstable. Most oxygen-containing functional groups, such as hydroxyl (–OH) and carboxyl (–COOH), tend to decompose at temperatures significantly lower than the decomposition temperature of the graphene framework itself. Therefore, TGA is an effective technique to evaluate both the presence and thermal stability of these functional groups.

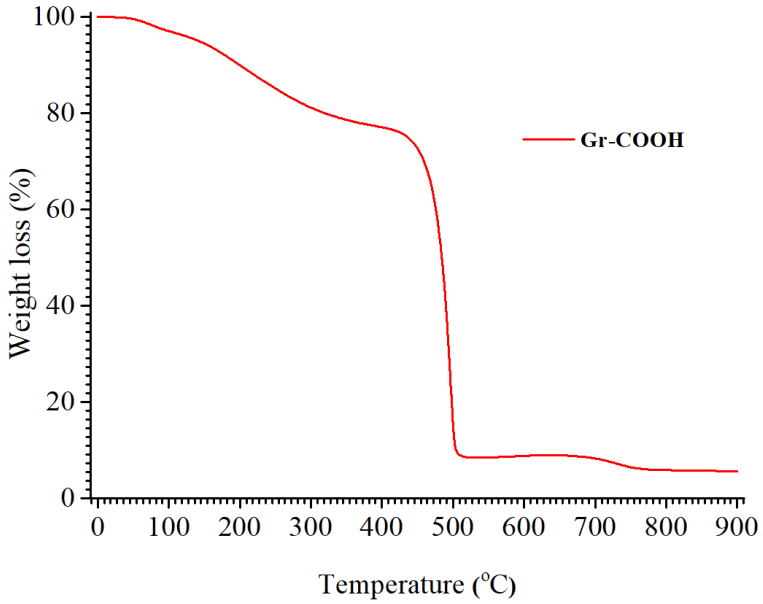


Figure 4: Raman spectra of functionalized Gr.

In this study, TGA was employed to investigate the thermal decomposition behavior of COOH-functionalized graphene, as illustrated in Figure 4. The TGA curve reveals that the material remains relatively thermally stable at temperatures below approximately 51°C, where only a slight mass loss is observed. This initial weight loss can be attributed to the removal of physically adsorbed moisture and residual volatile species on the graphene surface. As the temperature increases beyond 60°C, the mass loss becomes more pronounced and proceeds through multiple stages, indicating the presence of different thermally labile components. The decomposition process continues until it reaches completion at around 626°C. The occurrence of multiple weight-loss stages suggests that various types of functional groups with different thermal stabilities are present on the graphene surface as a result of the functionalization process. According to the TGA profile, the first major decomposition stage occurs in the temperature range from approximately 51°C to 532°C. This stage is mainly associated with the thermal decomposition of oxygen-containing functional groups, particularly carboxyl (–COOH) groups, which are known to degrade over a broad temperature range due to their relatively low thermal stability. The gradual mass loss in this region reflects the progressive removal of these functional groups from the graphene surface. The second stage, observed from 532°C to 626°C, corresponds to the combustion or thermal degradation of the graphene framework itself. In this temperature range, the carbon skeleton of graphene undergoes oxidation and structural breakdown, leading to a rapid decrease in mass. This stage marks the ultimate decomposition of the material. Overall, the TGA results clearly demonstrate that the functionalized graphene contains a significant amount of thermally unstable oxygen-containing groups, confirming the success of the surface modification process. Moreover, the multi-stage decomposition behavior provides further insight into the complexity of the functional groups introduced during oxidation. These findings highlight the strong correlation between chemical functionalization and thermal stability, which is critical for evaluating the applicability of graphene-based materials in high-temperature or thermally demanding environments.

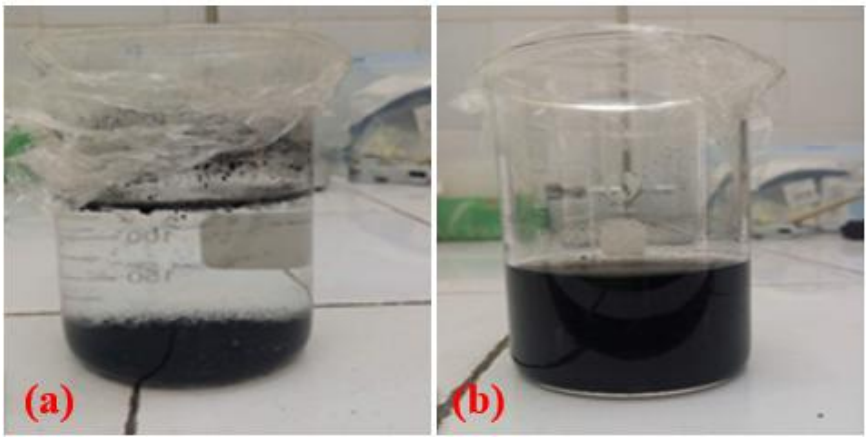


Figure 5: The dispersion of (a) as-prepared Gr and (b) functionalized Gr.

Figure 5 presents the dispersion behavior of pristine graphene (Gr) and functionalized graphene (Gr–COOH) in an aqueous medium. The dispersion stability was evaluated through visual observation after dispersing both materials under identical conditions. The results clearly demonstrate a significant improvement in the dispersibility of graphene after functionalization. Specifically, the Gr–COOH sample exhibits a more uniform and stable suspension, with no obvious sedimentation over the observation period. The solution appears homogeneous, indicating that the graphene sheets are well-dispersed throughout the aqueous medium. This enhanced dispersion behavior can be attributed to the introduction of hydrophilic functional groups, particularly carboxyl (–COOH) groups, onto the graphene surface during the oxidation process. These polar functional groups increase the affinity of graphene toward water molecules and promote better interaction with the solvent, thereby preventing agglomeration. In contrast, pristine graphene (Gr) shows poor dispersion characteristics in water. Visible sedimentation is observed, and the suspension appears non-uniform, indicating that graphene sheets tend to agglomerate and settle over time. This behavior is primarily due to the inherently hydrophobic nature of graphene and the strong van der Waals interactions between its layers, which promote restacking and aggregation in aqueous environments. The improved dispersion stability of Gr–COOH can also be explained by electrostatic repulsion and steric hindrance effects introduced by the functional groups. The ionization of –COOH groups in water may generate negatively charged surfaces, leading to electrostatic repulsion between graphene sheets and thus enhancing colloidal stability. As a result, the functionalized graphene remains well-dispersed for extended periods compared to pristine graphene. These findings provide strong evidence that carboxyl-functionalized graphene (Gr–COOH) possesses superior dispersibility in aqueous systems. This property is particularly important for applications such as electroplating, where a stable and homogeneous dispersion of reinforcing particles is essential for achieving uniform coatings and improved material performance. Therefore, the obtained results suggest that Gr–COOH is a promising candidate for use as a dispersible additive or medium in alloy electroplating processes.

## IV.CONCLUSION

In this work, graphene was successfully functionalized using a mixed acid oxidation method to introduce carboxyl (–COOH) groups onto its surface. The effectiveness of the functionalization process was comprehensively confirmed through FTIR, Raman, TGA, and dispersion analyses. FTIR results verified the presence of oxygen-containing functional groups, indicating successful chemical modification. Raman spectroscopy demonstrated an increase in defect density in the functionalized graphene, as reflected by the higher I_D/I_G ratio and the shift of the G band, confirming structural changes induced by oxidation. TGA analysis revealed distinct thermal decomposition stages, corresponding to the degradation of functional groups and the graphene framework, further supporting the successful grafting of thermally labile groups. Moreover, dispersion experiments showed that functionalized graphene exhibited significantly improved stability and uniformity in aqueous media compared to pristine graphene. This enhancement is attributed to the introduction of hydrophilic –COOH groups, which reduce agglomeration and improve interaction with water. In summary, the functionalization process not only modifies the chemical and structural properties of graphene but also significantly enhances its dispersibility. These results demonstrate that Gr–COOH is a promising material for applications requiring stable aqueous dispersions, such as electroplating and advanced composite systems.

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## REFERENCES

[1] J. Mu, F. Gao, G. Cui, S. Wang, S. Tang, Z. Li, A comprehensive review of anticorrosive graphene-composite coatings, Prog. Org. Coat. 157 (2021) 106321. https://doi.org/10.1016/J.PORGCOAT.2021.106321.

[2] W. Yu, L. Sisi, Y. Haiyan, L. Jie, Progress in the functional modification of graphene/graphene oxide: a review, RSC Adv. 10 (2020) 15328–15345. https://doi.org/10.1039/D0RA01068E.

[3] A.K. Geim, K.S. Novoselov, The rise of graphene, Nature Materials 2007 6:3 6 (2007) 183–191. https://doi.org/10.1038/nmat1849.

[4] A.R. Urade, I. Lahiri, K.S. Suresh, Graphene Properties, Synthesis and Applications: A Review, JOM 2022 75:3 75 (2022) 614–630. https://doi.org/10.1007/S11837-022-05505-8.

[5] V.B. Mbayachi, E. Ndayiragije, T. Sammani, S. Taj, E.R. Mbuta, A. ullah khan, Graphene synthesis, characterization and its applications: A review, Results Chem. 3 (2021) 100163. https://doi.org/10.1016/J.RECHEM.2021.100163.

[6] M.A. Saeed, A. Abdelkader, Y. Alshammari, C. Valles, A. Alkandary, Graphene Applications in Composites, Energy, and Water Treatment, Macromol. Mater. Eng. 310 (2025) 2400316. https://doi.org/10.1002/MAME.202400316.

[7] X. Zhang, Z. Wang, J. Guo, Strength and stability of π-π interaction between substituted benzene ring structures and graphene: Theoretical and molecular dynamics study, Sep. Purif. Technol. 355 (2025) 129678. https://doi.org/10.1016/J.SEPPUR.2024.129678.

[8] Z. Zhang, H. Huang, X. Yang, L. Zang, Tailoring Electronic Properties of Graphene by π–π Stacking with Aromatic Molecules, Journal of Physical Chemistry Letters 2 (2011) 2897–2905. https://doi.org/10.1021/JZ201273R.

[9] S. Ganguly, J. Sengupta, C.M. Hussain, Surface and interface functionalization of graphene and beyond: strategies for targeted applications, Nanoscale (2026). https://doi.org/10.1039/D6NR00009F.

[10] A.O.E. Abdelhalim, K.N. Semenov, D.A. Nerukh, I. V. Murin, D.N. Maistrenko, O.E. Molchanov, V. V. Sharoyko, Functionalisation of graphene as a tool for developing nanomaterials with predefined properties, J. Mol. Liq. 348 (2022) 118368. https://doi.org/10.1016/J.MOLLIQ.2021.118368.

[11] J. Park, M. Yan, Covalent Functionalization of Graphene with Reactive Intermediates, Acc. Chem. Res. 46 (2012) 181–189. https://doi.org/10.1021/AR300172H.
[12] C. Wetzl, A. Silvestri, M. Garrido, H.-L. Hou, A. Criado, M. Prato, The Covalent Functionalization of Surface-Supported Graphene: An Update, Angewandte Chemie 135 (2023) e202212857. https://doi.org/10.1002/ANGE.202212857.
[13] E.Y. Choi, T.H. Han, J. Hong, J.E. Kim, S.H. Lee, H.W. Kim, S.O. Kim, Noncovalent functionalization of graphene with end-functional polymers, J. Mater. Chem. 20 (2010) 1907–1912. https://doi.org/10.1039/B919074K.
[14] V. Georgakilas, J.N. Tiwari, K.C. Kemp, J.A. Perman, A.B. Bourlinos, K.S. Kim, R. Zboril, Noncovalent Functionalization of Graphene and Graphene Oxide for Energy Materials, Biosensing, Catalytic, and Biomedical Applications, Chem. Rev. 116 (2016) 5464–5519. https://doi.org/10.1021/ACS.CHEMREV.5B00620.
[15] V. Georgakilas, M. Otyepka, A.B. Bourlinos, V. Chandra, N. Kim, K.C. Kemp, P. Hobza, R. Zboril, K.S. Kim, Functionalization of Graphene: Covalent and Non-Covalent Approaches, Derivatives and Applications, Chem. Rev. 112 (2012) 6156–6214. https://doi.org/10.1021/CR3000412.
[16] J. Zhu, Z. Ren, G. Zhang, X. Guo, D. Ma, Comparative study of the H-bond and FTIR spectra between 2,2-hydroxymethyl propionic acid and 2,2-hydroxymethyl butanoic acid, Spectrochim. Acta A Mol. Biomol. Spectrosc. 63 (2006) 449–453. https://doi.org/10.1016/J.SAA.2005.05.030.
[17] T. Iwata, D. Nozaki, Y. Sato, K. Sato, Y. Nishina, K. Shiga, S. Tokutomi, H. Kandori, Identification of the CO Stretching Vibrations of FMN and Peptide Backbone by 13C-Labeling of the LOV2 Domain of Adiantum Phytochrome3, Biochemistry 45 (2006) 15384–15391. https://doi.org/10.1021/BI061837V.
[18] A.C. Ferrari, J.C. Meyer, V. Scardaci, C. Casiraghi, M. Lazzeri, F. Mauri, S. Piscanec, D. Jiang, K.S. Novoselov, S. Roth, A.K. Geim, Raman Spectrum of Graphene and Graphene Layers, Phys. Rev. Lett. 97 (2006) 187401. https://doi.org/10.1103/PhysRevLett.97.187401.
[19] A. Jorio, E.H.M. Ferreira, M.V.O. Moutinho, F. Stavale, C.A. Achete, R.B. Capaz, Measuring disorder in graphene with the G and D bands, Phys. Status Solidi B Basic Res. 247 (2010) 2980–2982. https://doi.org/10.1002/PSSB.201000247;JOURNAL:JOURNAL:15213951;ISSUE:ISSUE:DOI.
[20] S.J. Goldie, S. Bush, J.A. Cumming, K.S. Coleman, A Statistical Approach to Raman Analysis of Graphene-Related Materials: Implications for Quality Control, ACS Appl. Nano Mater. 3 (2020) 11229–11239. https://doi.org/10.1021/ACSANM.0C02361/SUPPL_FILE/AN0C02361_LIVESLIDES.MP4.