Journal of the Turkish Chemical Society Section A: Chemistry

Turkish Chemical Society

Large-scale Production of Few-Layer Reduced Graphene Oxide by the Rapid Thermal Reduction of Graphene Oxide and Its Structural Characterization

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Abstract: Graphene, a carbon allotrope, is a two-dimensional honeycomb of carbon atoms. Although graphene is a thin material, it is the strongest material known on Earth thanks to the strong carbon bonds in its structure. It is stated that the strength of these carbon bonds in graphene is about 100 times stronger than steel. In this study, graphite was first converted into graphene oxide (GO) by the Improved Hummers method, which is one of the methods suitable for large-scale production. Reduced graphene oxide (RGO) was obtained from the synthesized GOs by thermal reduction. TGA, FTIR, XRD, XPS, Raman, BET, and SEM analyses were used to characterize GO produced using the improved Hummers method and RGO reduced by thermal methods. TGA measurements show that RGO produced using the thermal approach had a lower mass loss than graphite oxidized using the improved Hummers process. This shows that the GO sample prepared using the improved Hummers approach contains a considerable number of distinct oxygen-containing groups. The novelty of the modified Hummers' method lies in its enhanced efficiency in producing graphene oxide through reduced thermal reaction times and improved scalability compared to the original approach in the literature. The C:O ratio of the GO and RGO samples was determined by XPS to be 1.88 and 11.17, respectively. The I_D/I_G ratio obtained by Raman analysis was 0.973. In addition, RGO's BET surface area was discovered to be 543.6 m^2 g^{-1}. These findings demonstrated that graphite was successfully oxidized by an improved Hummers method, and the resulting GO was thermally converted to few-layer RGO.

Keywords: Graphene, Reduced Graphene Oxide, Thermal Reduction, Graphene Oxide, Structural Characterization

Submitted: July 15, 2023. **Accepted**: January 3, 2024.

Cite this: Eksik O. Large-scale Production of Few-Layer Reduced Graphene Oxide by the Rapid Thermal Reduction of Graphene Oxide and Its Structural Characterization. JOTCSA. 2024;11(2):665-xxx.

DOI: https://doi.org/10.18596/jotcsa.1327988

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1. INTRODUCTION

The arrangement of carbon atoms in a hexagonal structure in a single plane gives graphene, an allotrope of carbon, its two-dimensional structure. Graphene, a new two-dimensional material with unique electrical and structural properties, has received a lot of interest. This structure of graphene gives it extraordinary properties. The specific surface area of graphene is extraordinarily high relative to its mass ratio (theoretically, 2650 m^2g^{-1}), a very high thermal conductivity (5300 $Wm^{-1}K^{-1}$, ten times higher than copper), and an optical transmittance of 98%. Another interesting property of graphene is that it is flexible and very durable. Due to a bond shape called sp^2 hybridization, it is as resistant to forces in certain directions as a diamond and has a high Young's modulus (1150 GPa). Due to these extraordinary properties of graphene, it enables applications in different fields of use (1-6). Today, intensive scientific research on graphene is being carried out to improve the application areas and production methods of graphene in daily life (7-8). However, there are still difficulties in producing graphene at a low cost and in large quantities. The oxidation of graphite is one of the most promising processes for producing graphene. The first example of graphene oxide synthesis was Brodie's discovery of graphite structure in 1859. One of his reactions was adding potassium chlorate ($KClO_3$) to a graphite slurry in strong nitric acid (HNO3). (HNO_3) (9). According to

Brodie's findings, the compound that is produced contains carbon, hydrogen, and oxygen in increasing proportions as the overall weight of graphite increases. With a successful oxidizer treatment, he discovered that the oxygen concentration increased to the limit value after four reactions. Brodie found that this material could be dispersed in pure or normal water but not in acidic media. acidic media. This led him to define the material as "graphite acid". Staudenmaier improved upon Brodie's oxidation of graphite in 1898 by gradually adding potassium chlorate ($KClO_3$) to fuming nitric acid (HNO_3) and concentrated sulfuric acid (H_2SO_4). (10). Later, Hofmann synthesized graphene oxide using concentrated nitric acid (HNO_3) instead of the fuming nitric acid used in Staudenmaier and Brodie's method (10). About 60 years after Staudenmaier, to achieve the same degree of oxidation, Hummers came up with a technique that involved the reaction of graphite with a combination of potassium permanganate ($KMnO_4$) and strong sulfuric acid (H_2SO_4) (10). The Brodie, Staudenmaier, and Hofmann approaches generally used $KClO_3$, concentrated HNO_3, and H_2SO_4. Nitric acid is a widely used oxidizer, and its strong interactions with aromatic carbon surfaces, including carbon nanotubes, are known. The reaction produces numerous oxygen-containing groups, including carboxyls, lactones, and ketones. Nitric acid-induced oxidation results in the emission of NO_2 and/or N_2O_4 gases (11). At the same time, $KClO_3$ is also a strong oxidizer. Potassium permanganate ($KMnO_4$) and sulfuric acid (H_2SO_4) are used in the Hummers technique. Potassium permanganate is a strong oxidizer, and this property makes the GO structure hydrophilic by containing different oxygen groups (carboxyl, hydroxyl, epoxy, etc.) on the surface of activated graphene oxide (12).

A few-layer RGO can be produced by chemical and heat reduction of GO. Many thermal and chemical approaches have been proposed for the reduction of GO. The thermal reduction methods used in graphene synthesis are thermal annealing, microwave, and photoreduction (13-14). Rapid GO heating in thermal annealing causes CO and CO_2 gases to develop between the graphene layers and rapidly expand. This process is carried out at 1050 °C, and at this temperature, the bulk graphene oxide layers separate from each other to form graphene sheets (10).

Modified Hummers' method for graphene oxide and following thermal reduction offers a relatively efficient and scalable approach for producing graphene nanoplatelets compared to other methods. The disadvantages of Modified Hummers' method of using chemicals, including the use of strong acids and harsh chemicals, pose environmental and safety risks. Another method used in graphene production is chemical reduction. The chemical reduction method mainly consists of chemical separator reduction, photocatalytic reduction, and electrochemical reduction (15-16). The modified method achieves a more controlled and reproducible synthesis of graphene oxide through alterations in reaction conditions and parameters, such as temperature, time, and precursor materials.

In this study, naturally occurring, inexpensive graphite powder was used as a starting material for the oxidation of graphite, and graphite was oxidized using an improved Hummers method. A few layers of RGO were produced by the thermal reduction of GO.

2. MATERIALS AND METHODS

2.1 Spectroscopic and Microscopic Characterization of GO and rGO

Scanning electron microscopy (SEM; JEOL JEM 1011), X-ray diffraction analysis with the Bruker D8 Discover X-Ray diffraction system, XPS analysis with the Thermo K-Alpha X-Ray Photoelectron Spectrometer, Raman analysis with the Renishaw Invia instrument, surface area analysis with the Micromeritics ASAP 2020 HD accelerated surface area and porosimetry analyzer, FTIR analysis with the Thermo Scientific iS10, and TGA analysis with the TA Instruments were used.

2.2. GO Synthesis Using an Improved Hummers Method

In the improved Hummers method, the oxidation of graphite is carried out in two stages. After the graphite pre-oxidation process, it undergoes a second oxidation process where it fully oxidizes and becomes graphite oxide (12). In the pre-oxidation step, graphite powder was treated with strong oxidizing agents such as H_2SO_4, P_2O_5, and $K_2S_2O_8$. In this step, 98% H_2SO_4 (25 mL) was heated to 90°C in an oil bath. Then, 5 g of $K_2S_2O_8$ and 5 g of P_2O_5 were added. After the reaction temperature was reduced to 80°C, 3 g of graphite powder was slowly added to the mixture. Since outgassing was observed at this stage, adding graphite powder to the hot mixture was carried out very carefully and slowly. The heating process was terminated after stirring the reaction mixture at 80°C for 5 hours. The mixture was added to deionized water, left to stand on its own for one night, and filtered using a vacuum filter. In order to remove the acidity of the solid sample obtained, it was washed with deionized water until the pH value was neutral. Finally, the synthesized pre-oxidized graphite structure was allowed to dry at room temperature for one day. The pre-oxidized graphite is oxidized to graphene oxide with the help of $KMnO_4$. Since the reactions in this process are highly exothermic, all processes were carried out in an ice bath at a temperature not exceeding 10°C. Pre-oxidized graphite powder was added to 98% H_2SO_4 (240 mL) and kept in the ice bath with stirring. Then $KMnO_4$ (30g) was added to the mixture and dissolved. During this process, care was taken not to exceed 10°C. After this step was completed, the mixture's temperature was raised to 35 °C and stirring was continued for 4 hours. In all these processes, it is critical that the temperature not exceed 50°C. After this time, 500 mL of deionized water was added to the mixture. The mixture was stirred for 1 hour, and 40 mL of 35% H_2O_2 was added dropwise to complete the oxidation process. The final mixture was kept at room temperature for one day and then subjected to filtration. The resulting product was washed with a 10% HCl solution to remove metal ions. In the last step, the mixture was washed with acetone until the pH value was neutral. The graphene oxide obtained was dried in an oven at 60°C.

2.3. RGO Synthesis by Thermal Reduction

Graphene oxide can be thermally reduced to yield monolayer and multilayer graphene. In the thermal reduction technique, the GO sample was placed in the tube furnace system at 1050°C under argon gas flow for a short time (45 seconds), and RGO was obtained by thermal shock reduction. During heat reduction, the functional groups in GO oxide containing oxygen (carboxyl, epoxy, hydroxyl, etc.) are removed from the structure. The CO and CO_2 gases formed between the layers undergo thermal exfoliation, creating high pressure and expanding. These processes are shown schematically in Figure 1.

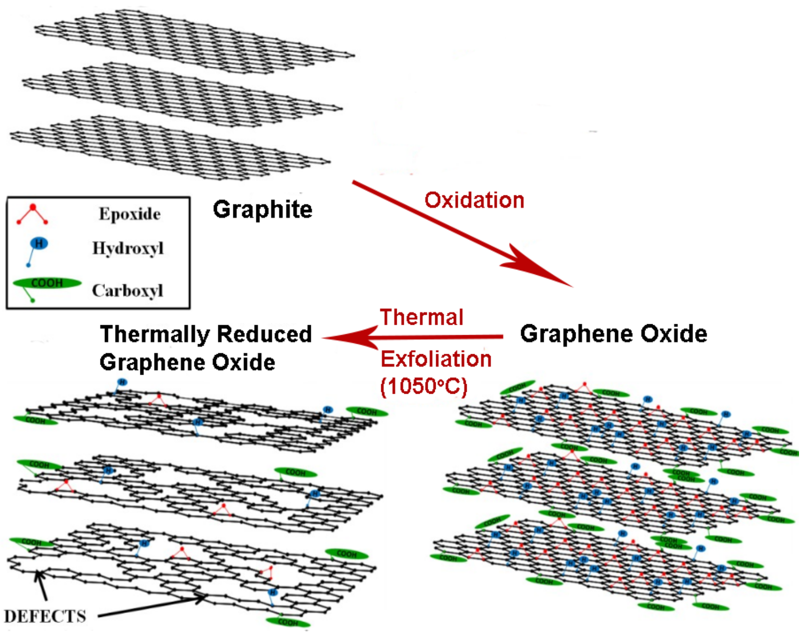


Figure 1: Thermal reduction of GO

3. RESULTS AND DISCUSSION

3.1. Graphite, GO, and RGO TGA Analysis

Figure 2 shows the thermal properties of graphite, GO, and RGO by TGA analysis. When the thermal properties of graphite were examined, no weight change was observed in graphite due to temperature change (Figure 2). On the other hand, GO obtained using the improved Hummers method showed three-stage degradation. In the first stage, between 50 and 150 °C, graphene oxide lost mass due to moisture loss (17). The second stage is between 150 °C and 400 °C. The mass loss here can be explained as removing oxygen-containing groups such as hydroxyl, epoxy, and carboxyl in the GO structure from the graphene oxide structure. In the third stage, at temperatures above 400 °C, mass loss occurred due to the degradation of unstable carbon structures in the nitrogen gas environment. The RGO obtained using the thermal reduction method lost 25% of its weight. This is due to the removal of oxygen-containing groups remaining in the structure of RGO (17-18).

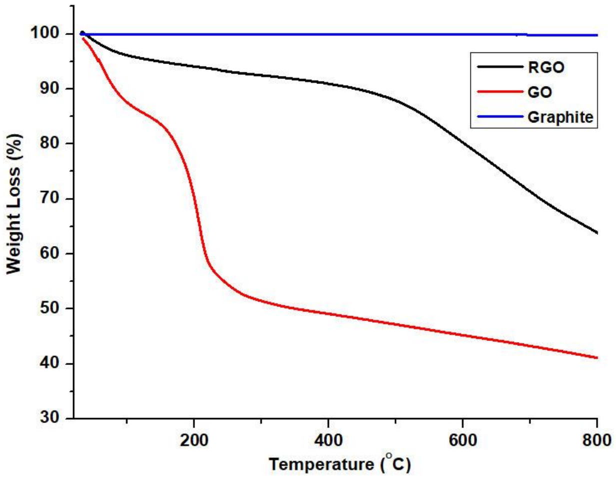


Figure 2: The TGA outcomes for graphite, GO, and RGO

3.2. Graphite and GO, Analyzed by X-Ray Diffraction

Figure 3 shows the XRD analysis of graphite and GO, respectively. Figure 3 shows a peak for graphite at 2θ = 26.5°; the peak value of graphene oxide appears as 2θ = 10.3°. In line with the values from the literature, these peaks are known to be 26.48° for graphite and 10.90° for graphene oxide, respectively (19). When the obtained data are compared with the literature data, it is seen that the oxidation process was successful. Considering the interlayer distances, 0.3 nm is for pure graphite, and 0.83 nm is for graphene oxide. The increase in the distance between graphene oxide layers due to the oxidation process indicates that the oxidation process was successful.

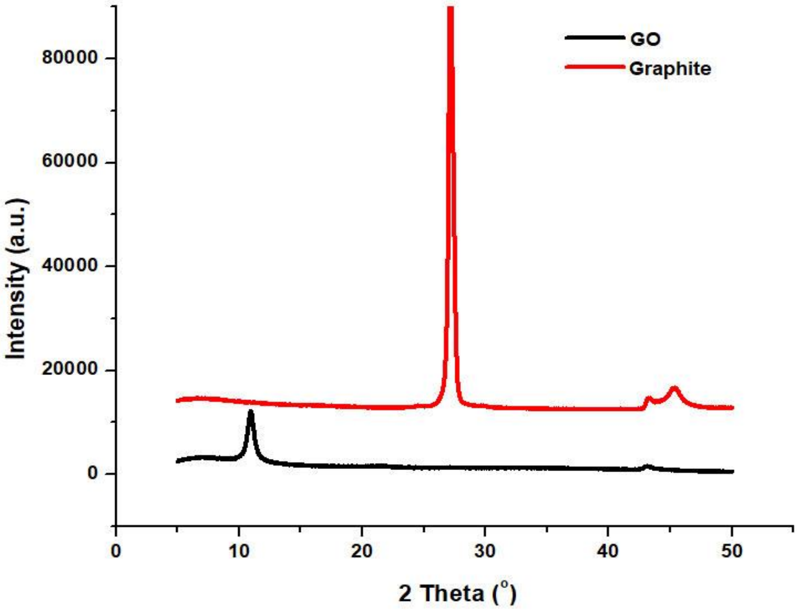


Figure 3: XRD spectrum of a graphite and GO sample

3.3. FTIR Analysis of Graphite, GO, and Reduced Graphene

FTIR spectroscopy analysis was performed to determine the functional groups such as epoxy, carboxyl, and hydroxy that are expected to be included in the structure as a result of the oxidation of graphite. As seen in Figure 4, OH stress vibration was measured at 3106 cm^{-1}, C=O stress vibration at 1714 cm^{-1}, C=C stress vibration at 1602 cm^{-1}, and C-O stress vibration at 1020 cm^{-1}. As a result of the literature research, OH stress vibration was found to be 3191 cm^{-1}, C=O stress vibration 1718 cm^{-1}, C=C stress vibration 1600–1660 cm^{-1}, and C-O stress vibration 1040 cm^{-1} (20). The graphite sample does not have any of these vibrations. These functional groups included in the structure as a result of the oxidation of graphite indicate that graphene oxide has been successfully synthesized.

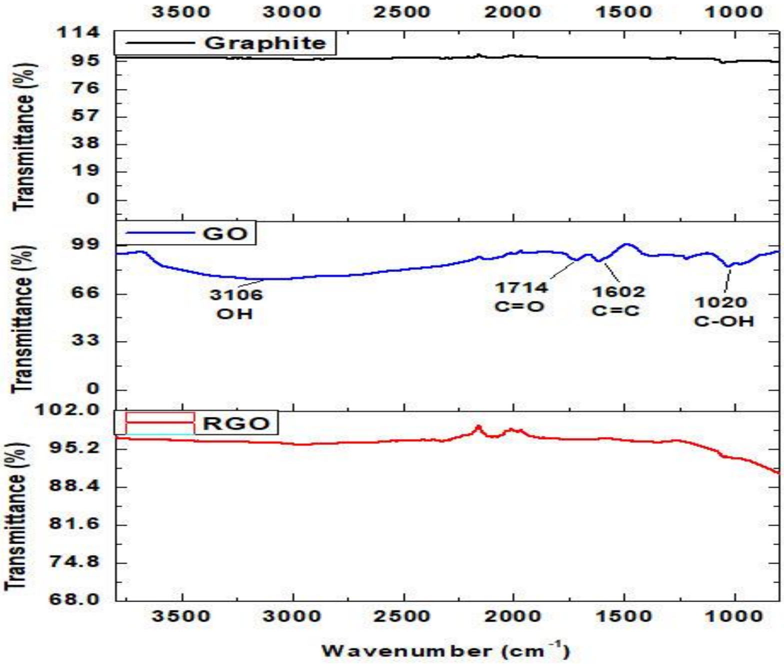
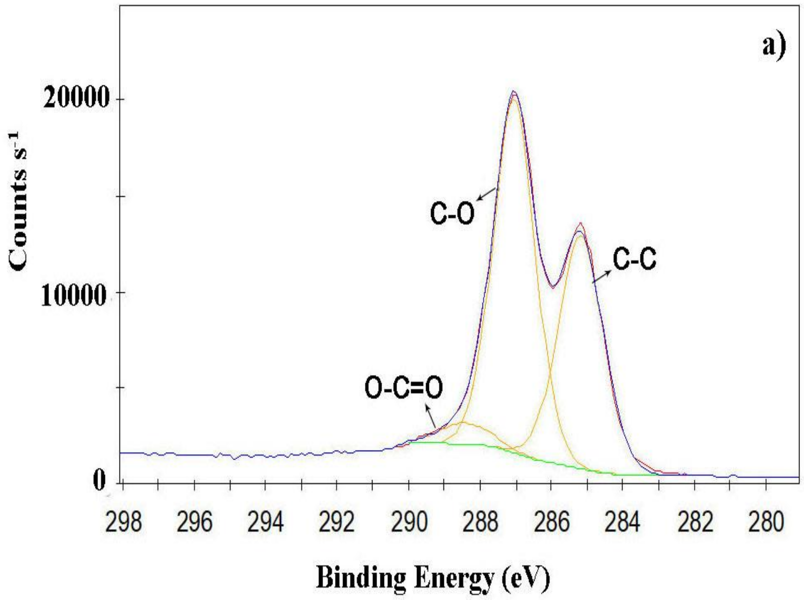


Figure 4: FTIR spectrum of graphite, GO, and RGO

The effect of thermal reduction was also investigated under the conditions studied. As can be seen in Figure 4, the characteristic peaks of graphene oxide disappear when the thermal method is used as a reductant (21).

3.4. XPS Analysis of GO and RGO

The results of the XPS analysis of GO and RGO are given in Figures 5. GO and RGO C1s XPS spectra are displayed in Figure 5. C-C peak at 284.7 eV, C-O peak at 286 eV, and O-C=O peak at 288.8 eV is all well visible in the C1s spectra of the GO sample (22). A large peak for RGO was found at 284.7 eV, corresponding to graphitic carbon, which makes up 69.1% of RGO and 23.7% of GO. The C-O atom, which makes up 22.79% of the RGO structure, is the source of the peak at 286 eV. This percentage is less than the GO percentage (37.6%). In RGO (288.5 eV), another oxygen-containing group, O-C=O, was found in extremely low amounts compared to GO. The percentage of carbon and oxygen elements in graphite oxide composition obtained as a result of XPS analysis is given in Table 1. The C:O ratio of GO was determined as 1.88. This ratio indicates that the graphene oxide process subjected the graphite layers to strong oxidation. Oxygenated functional groups are removed from the GO structure as a result of reduction by the thermal method. The C:O ratio of RGO was found to be 11.17.



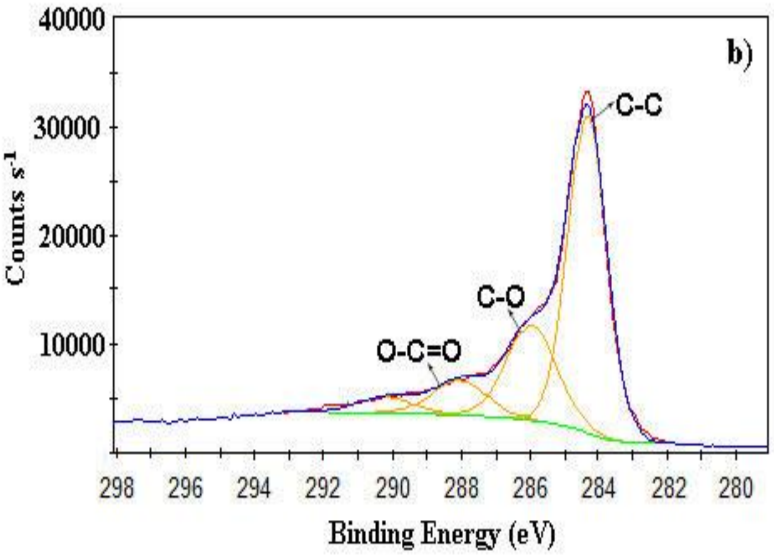


Figure 5: C1s. XPS spectra of GO (a), RGO (b)

Table 1: C:O ratios of GO and RGO samples according to XPS analysis data

Element	GO	RGO
Atomic C, %	65.3	91.8
Atomic O, %	34.7	8.3
C:O ratio	1.88	11.2

3.5. Raman Analysis of RGO Synthesized by the Thermal Reduction Method

Following the chemical oxidation of graphite, RGO was obtained by removing the oxygenated groups from GO by thermal reduction (thermal exfoliation). The crystal structure and properties of the obtained RGO were investigated by Raman spectroscopy. As expected in the Raman pattern of graphene, the D peak is observed at 1360 cm^{-1}, the G peak at 1580 cm^{-1}, and the 2D peak at 2675 cm^{-1} (Figure 6). The intensity of the D band (I_D) in the Raman pattern shows the irregularities in the structure, the intensity of the G band (I_G) shows the regular structures in the structure, and the 2D band shows the characteristic peak of graphene. The D, G, and 2D peak values of the graphene synthesized in the study are consistent with the literature (23-24).

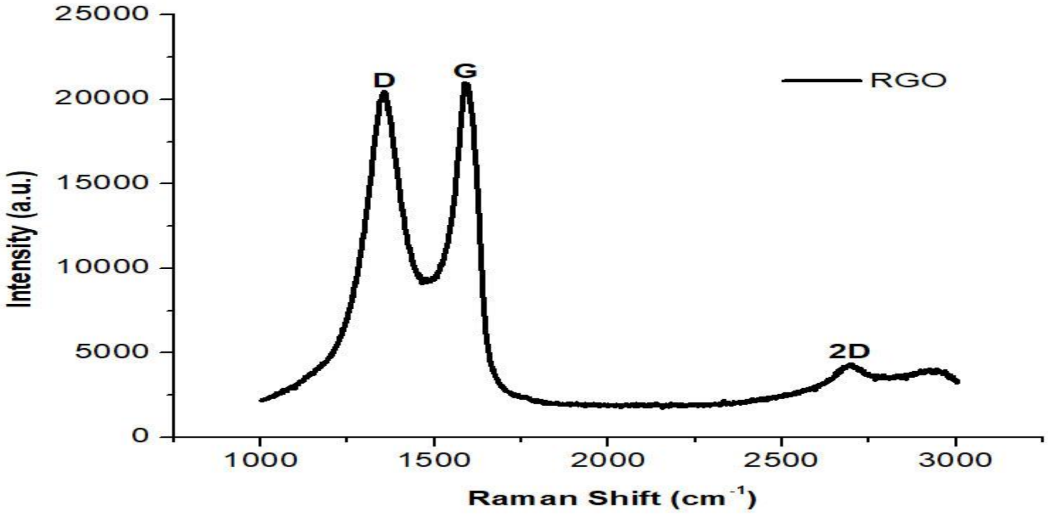


Figure 6: Raman spectra of RGO

3.6. SEM Analysis of Graphite, GO, and RGO

The surface properties of graphite, GO, and RGO samples were investigated by SEM analysis (Figure 7). From the SEM images, oxygenated groups on GO were removed as a result of the thermal reduction reaction, resulting in less layered, wrinkled RGO structures (25). SEM images of GO often depict irregular, crumpled, or wavy sheet-like structures with wrinkles and folds. GO layers are generally thicker due to the presence of oxygen-containing groups and water molecules trapped between the layers, leading to a more expanded and layered structure than pristine graphene. SEM images of rGO display smoother, more continuous, and less corrugated sheets than GO. rGO tends to have thinner layers than GO due to removing oxygen groups and water molecules, leading to a more compact and less layered structure.

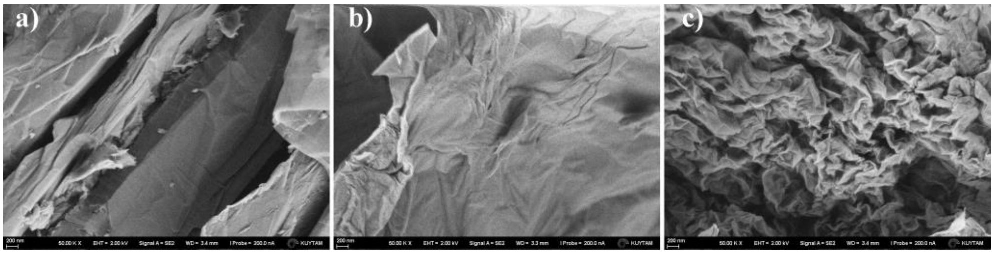


Figure 7: SEM images of graphite (a), GO (b), RGO (c)

3.7. Evaluation of BET Results

The surface area analysis of graphene samples synthesized by the thermal reduction method was performed by the Brunauer, Emmet, and Teller (BET) method. Table 2 displays the outcomes of the BET study of RGO.

Table 2: BET analysis results for RGO

Element	RGO
BET surface area (m^2/g)	543.64
Volume (cc/g)	1.005
Pore diameter (4V/S Angstrom)	90.26

As a result of BET analysis of the sample of the graphene study produced by the thermal method, the surface area of graphene was 543.64 m^2g^{-1}. The reason for this is that the oxygenated groups are separated more effectively during the production of graphene by thermal inversion of the improved Hummers-GO, forming a more porous structure and providing a high surface area. Reduced graphene oxide (rGO) produced through thermal reduction methods, particularly at high temperatures like 1050 °C, tends to exhibit a higher Brunauer-Emmett-Teller (BET) surface area compared to lower temperature reduction processes and chemical reduction processes. The high temperature facilitates the removal of oxygen-containing functional groups from graphene oxide, resulting in a more extensive restoration of the sp^2 carbon network, which contributes to a higher surface area.

4. CONCLUSION

This research focused on producing GO and RGO with a few layers from flake graphite. In addition, the characterization methods of GO and RGO were investigated. First of all, graphite was converted into GO by the improved Hummers technique, which is one of the methods suitable for extensive production. The obtained GO samples were reduced using the thermal method. GO and RGO samples were characterized by TGA, XRD, FTIR, XPS, SEM, Raman, and BET analysis. FTIR spectroscopy results indicate the existence of functional groups that include oxygen (OH, C=O, and C-OH) in the synthesized graphene oxide. XRD analysis revealed interlayer distances of 0.32 nm for graphite and 0.85 nm for graphene oxide. These results indicate that the oxidation process was successful. The results of the XPS spectrum analysis show that the atomic C:O ratios in the chemical structures of GO and RGO are approximately 1.88 and 11.17, respectively. Raman analysis of RGO samples showed that the amount of ordered crystal structure increased. Transparent and wrinkled RGO structures were detected from SEM images. As a result of BET analysis of reduced graphene oxide samples, it was determined that the surface area was approximately 543.64 m^2g^{-1}. This indicates that the synthesized RGOs have a few-layered structure. Thermal methods for producing graphene with high amounts and high surface areas can further optimize its properties, making it more cost-effective, scalable, and suitable for various industrial applications. Such as high surface area, graphene can be utilized in supercapacitors and batteries; it can be used as a catalyst support or even as a catalyst itself in various chemical reactions, including hydrogen production, environmental remediation, and organic synthesis; its use in gas sensors, biosensors, and environmental monitoring devices and graphene can be employed in water filtration and desalination processes.

5. CONFLICT OF INTEREST

There are no conflicts that need to be reported.

6. ACKNOWLEDGMENTS

This study was supported by Gebze Technical University BAP Unit Project No. 2022-A-113-04.

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