Research Article

Effect of temperature and time on hydrothermally synthesized nitrogen-doped graphene

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Abstract: Graphene attracts attention due to its high surface area and its great electrical, optical, and mechanical properties. Studies about graphene have been conducted to develop synthesis methods and to determine the effects of synthesis parameters on productivity and properties. In recent years, studies have focused on doping graphene with foreign atoms to improve its properties. Nitrogen (N) is of interest among doping materials because it increases graphene's electrocatalytic activity and electrochemical performance. In this study, the production of nitrogen-doped graphene was studied, and a 2-stage synthesis procedure was used. In the first stage, graphene oxide was obtained from graphite by using the Modified Hummers method. To obtain N-doped graphene (N-graphene) from synthesized graphene oxide, N doping and hydrothermal method were used in the second stage. To determine the effect of temperature and time on the hydrothermal production of N-graphene from graphene oxide, 3 different temperatures and 3 different times were studied. Scanning electron microscopy, Fourier transform infrared spectroscopy, X-ray diffraction analyses, and the Debye-Scherrer equation indicated that N-doped graphene was obtained at all studied parameters. The effects of temperature and time on synthesizing N-graphene were discussed within the parameters used in the hydrothermal method. Considering the minimum number of graphene layers, the parameters "18 h at 140 °C" and "6 h at 160 °C" seem more effective.

Keywords: Nitrogen-doped graphene, Graphene oxide, Modified hummers method, Hydrothermal method.

1. Introduction

Graphene is a one-atom thin, two-dimensional nanomaterial with outstanding properties formed by the arrangement of covalently bonded carbon atoms in a six-honeycomb lattice [1]. Graphene, which finds application areas such as field effect transistors, field transmitters, integrated circuit components, and conductive electrodes due to its outstanding electrical properties, also has application areas such as touch screens, photovoltaic cell applications, hydrogen storage devices, gas sensors, and batteries due to its optical properties [2,3]. Doping elements to graphene have been studied to broaden the application areas and improve the properties specific to the field of use. Among the additives, nitrogen (N) comes to the fore because of its critical role in regulating the electronic properties of carbon-based materials and its effect in improving capacitive performance [4,5]. To synthesize N-doped graphene (N-Gr), doping can be introduced into graphite (GT) or graphene oxide (GO) [6,7]. In this study, GO was obtained from GT by using the chemical method, and N doping was performed at the stage of graphene production from GO.

As mentioned in the literature, various chemical methods have been employed to synthesize GO from graphite, such as Brodie, Staudenmaier, Hummers, Modified Hummers, and Tour methods [8-10]. These methods rely on the oxidation process of GT, where functional groups are introduced into the material through oxidation, resulting in the formation of graphene oxide. Although the chemicals used in the production methods of GO are generally toxic, the Modified Hummers method offers an advantage in this regard [11]. In this study, the reason for using the Modified Hummers method in producing GO is environmental friendliness, ease of processing, and low cost.

To obtain N-Gr, studies are being carried out on the use of various methods such as chemical vapor deposition, thermal annealing, pyrolysis, arc discharge, hydrothermal method, and solvothermal method [12-14]. The thermal annealing method involves annealing reduced GO in an NH_3 atmosphere to yield N-graphene [15]. In the plasma method, N-graphene is produced by partially replacing carbon atoms with nitrogen atoms with graphene or graphene oxide under a plasma atmosphere [16]. Direct microwave irradiation between N-doped GO and aqueous ammonium hydroxide yields N-graphene in the mi-

crowave method [17]. Mixing graphene oxide and various agents allows N-graphene to be obtained hydrothermal [18]. In this study, the hydrothermal method is selected because of its ease of operation and the possibility of getting a higher N content than other alternative methods [7].

In the current study, GO was obtained from GT by the Modified Hummers method in the first stage, and it was aimed to produce N-graphene from the obtained GO by doping N with the hydrothermal method in the second stage. In this context, 3 different temperatures (140, 160, and 180 °C) and 3 different durations (6, 12, and 18 hours) were studied to determine the effect of temperature and time, which are among the parameters of the hydrothermal method, on the production of N-graphene.

2. Materials and Methods

2.1. Synthesis of Graphene Oxide

In this study, the Modified Hummers method was used to synthesize GO from GT. To initiate the process, 5 g of GT powder ($\leq$ 12 µm, AMG GK (UF), Germany) and 2.5 g of sodium nitrate ($NaNO_3$, Merck) were added consecutively into 120 ml of sulfuric acid (H_2SO_4, 95-98%, Merck) at 10 °C; then mixed in an ice bath for 15 minutes using a magnetic stirrer. Subsequently, 15 g of potassium permanganate ($KMnO_4$, Tekkim) was added to the mixture (5 g of $KMnO_4$ were added at each time, and mixed for 15 minutes between each addition) and stirred for 2 more hours in an ice bath on a magnetic stirrer. The solution was then transferred to a water bath and stirred at 35 °C for 2 hours on a magnetic stirrer. Next, the mixture was returned to the ice bath, and 200 ml of deionized water was gradually added using a burette while stirring continued. After adding 200 ml of water, which took about 1 hour, the mixture was left at room temperature for 14 hours. The mixture was then stirred in an oil bath at 98 °C for 6 hours using a magnetic stirrer. Upon completion, deionized water was added to make it 1000 ml, and the mixture was stirred on a magnetic stirrer before adding 20 ml of hydrogen peroxide (H_2O_2, 30%, Merck). The mixture was left at room temperature for 18 hours, then centrifuged at 4000 rpm for 15 minutes, washed once with hydrogen chloride (HCl, 1 mol, Merck), and washed 4 times with deionized water, followed by centrifugation (4000 rpm, 15 minutes) after each washing. Finally, the sample was dried in an oven at 60 °C for 24 hours after washing.

2.2. Synthesis of Nitrogen-Doped Graphene

Nitrogen-doped graphene was synthesized from graphene oxide using the hydrothermal method. The starting material was obtained in solution form after centrifugation, as described in the "Graphene oxide synthesis" section. The graphene oxide solution was filtered after centrifugation, and 100 ml of deionized water was added to the resulting precipitate and mixed with a magnetic stirrer. Subsequently, 30 ml of solution was subjected to ultrasonic homogenization, followed by adding 10

ml of ammonia (NH_3, 25%, Merck) and mixing for 1 hour with a magnetic stirrer. Next, 35 ml of the solution was transferred to a reactor (Berghof DAB-2), and the solution was processed at 3 different temperatures (140, 160, and 180 °C) for 6, 12, and 18 hours, respectively. The solution was then filtered, and the remaining precipitate was mixed with 100 ml of deionized water and stirred for 10 minutes using a magnetic stirrer. The mixture was centrifuged and dried in an oven at 80 °C for 24 hours.

2.3. Characterization

The obtained samples were examined using a scanning electron microscope (SEM; Zeiss, Gemini Supra 55) to determine their surface morphology and visually present their layered structure and layer thickness. Fourier transform infrared spectroscopy (FT-IR) analysis was conducted to determine the functional groups present in the samples, using a Shimadzu IR Affinity-1S instrument and studying the range of 500-4000 cm^{-1}. To determine the structure formed, X-ray diffraction (XRD) (Rigaku, SmartLab) analysis was performed with Cu Kα radiation and operating at 40kV and 30mA. The layer thickness and the number of layers were calculated using the Debye-Scherrer equation based on the XRD data obtained.

3. Results and Discussion

The primary objectives of the current study were to synthesize N-Gr using a hydrothermal process from the produced GO and to investigate the effects of temperature and duration on the resulting N-Gr powders. To achieve these, the study employed three different time intervals (6, 12, and 18 hours) and three different temperature settings (140, 160, and 180°C) during the hydrothermal process. Within the scope of the research, the analysis results of the GT powders, synthesized powders, and the parameters used during hydrothermal powders were evaluated.

The SEM image of the initial GT powders used in the current study is presented in Figure 1(a). The size of the GT powders used is generally in the range of 8-10 microns and exhibits a complex shape resembling a plate. Figure 1(b) depicts the SEM image of the GO sample synthesized from GT using the Modified Hummers method. The synthesized GO samples exhibit a stratified structure with clearly visible, relatively smooth, and partially wrinkled layers. In this context, it was determined that the sample obtained was morphologically compatible with the literature [19,20].

Figure 2(a) and Figure 2(b) show the spectra obtained from the FTIR analysis conducted to identify the functional groups present in the GT powder used and the GO sample synthesized, respectively. The FTIR spectrum of the GT powder (Figure 2a) is consistent with the literature [10]. It was determined that the absence of functional groups in the structure led to the absence of any significant peaks. The FTIR spectrum of the GO samples synthesized from GT using the modified Hum-
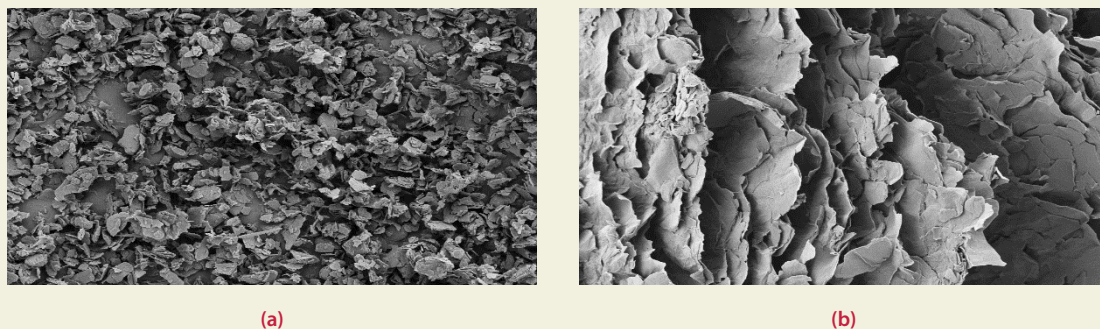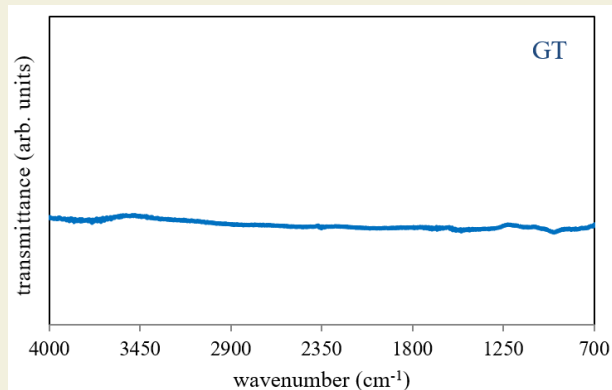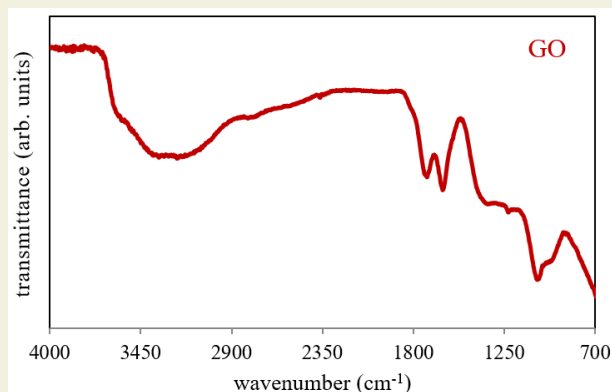
Figure 1. SEM image of the (a) GT sample; (b) GO sample

mers method (Figure 2b) was also compatible with the literature. The spectrum revealed the presence of several functional groups, such as the -OH bond at 3241 cm^{-1}, the C=O bond from the carboxylic group at 1711 cm^{-1}, the aromatic C=C bond at 1612 cm^{-1}, the COOH bond at 1323 cm^{-1}, and the C-O-C bond at 1007 cm^{-1} [10,21,22].
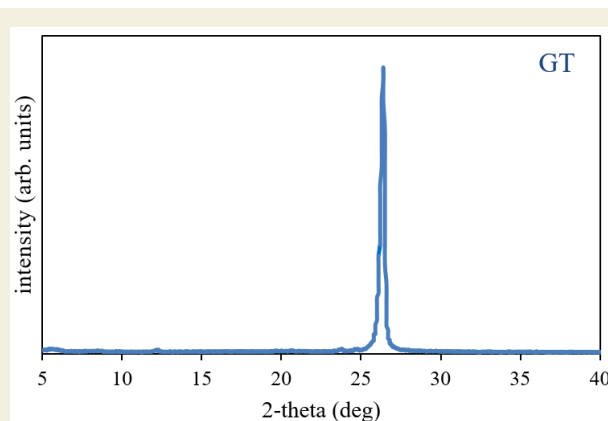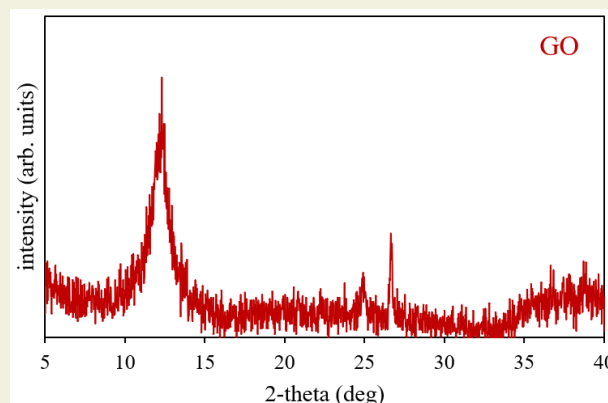

Figure 2. FTIR spectrum of the (a) GT sample; (b) GO sample

The XRD spectra of the GT powder used and the GO sample synthesized are presented in Figure 3(a) and Figure 3(b), respectively. The peak at 26.405° in the XRD spectrum of the GT powder corresponds to the characteristic peak of graphite at approximately 26° (Figure 3a). The XRD analysis of the GO sample synthesized from the

GT powders (Figure 3b) revealed that the spectrum was consistent with previous literature reports. The characteristic graphite peak at about 26° became less prominent and waned considerably after oxidation. After oxidation, the characteristic peak of GO is located at about 12° due to the functionalization of O- groups in the oxide and the addition of H_2O molecules [11,23,24]. The dominant peak seen at 12.31° in Figure 3(b) indicates the successful acquisition of GO.

Figure 3. XRD spectrum of the (a) GT sample; (b) GO sample

To synthesize nitrogen-doped graphene (N-Gr), obtained GO samples were subjected to the hydrothermal method. To investigate the impact of temperature and duration

on the hydrothermal synthesis of N-Gr, three different temperatures (140, 160, and 180°C) and durations (6, 12, and 18 hours) were examined. In Table 1, the temperatures were identified with the letters A, B, and C, and the durations with 6, 12, and 18.

Table 1. Coding of temperature and time parameters used in N-Gr production.

	6 hours (code: 06)	12 hours (code: 12)	18 hours (code: 18)
140 °C (code: A)	N-GrA-06	N-GrA-12	N-GrA-18
160 °C (code: B)	N-GrB-06	N-GrB-12	N-GrB-18
180 °C (code: C)	N-GrC-06	N-GrC-12	N-GrC-18

The FTIR spectra of the samples obtained through hydrothermal synthesis of N-Gr using different temperature and duration parameters are presented in Figure 4. In the obtained FTIR spectra, functional groups were identified to determine whether graphene was obtained or not, whether nitrogen was added or not, and also to determine the effect of temperature and time. To visually present the impact of different duration values on the functional groups obtained, the FTIR spectra of the samples obtained at the same temperature, but using different times, were presented on the same graph. To demonstrate the effect of temperature, a similar approach was taken (Figure 4).

In the FTIR analysis of the N-Gr samples obtained using the hydrothermal method, it was observed that the spectra obtained (Figure 4) were consistent with the literature; -OH and N-H stretching vibrations were observed in the wavelength range of 3000 - 3700 cm^{-1} [25-27], symmetrical and asymmetrical CH_2 vibrations were observed at 2908 and 2835 cm^{-1} wavelengths [22,28], C=N vibrations were observed at 1502 cm^{-1} wavelength [29-31], and aromatic C-N stretching vibrations were determined at 1215 cm^{-1} wavelength [32,33]. The peak at 1705 cm^{-1} wavelength indicates the deoxidation of GO, while the peaks at 1502 and 1215 cm^{-1} wavelengths indicate the presence of nitrogen [31-33].

The spectra obtained by the XRD analysis of the samples obtained by using different temperature and duration parameters during the hydrothermal synthesis of N-Gr are presented in Figure 5. To visually demonstrate the effect of different durations used during the production on the structure, XRD spectra of the samples obtained at the same temperature with different duration were presented on the same graph, and a similar situation was done for different temperatures.

The XRD spectra of the N-Gr samples obtained (Figure 5) were found to be consistent with the literature [29,34]. Previous research has pointed out that peaks around 2θ values of 25.5° in the XRD spectrum indicate the formation of graphene [35-37]. The broad and short peaks observed at 25.91° in N-GrA-6, 25.3° in N-GrA-12, and
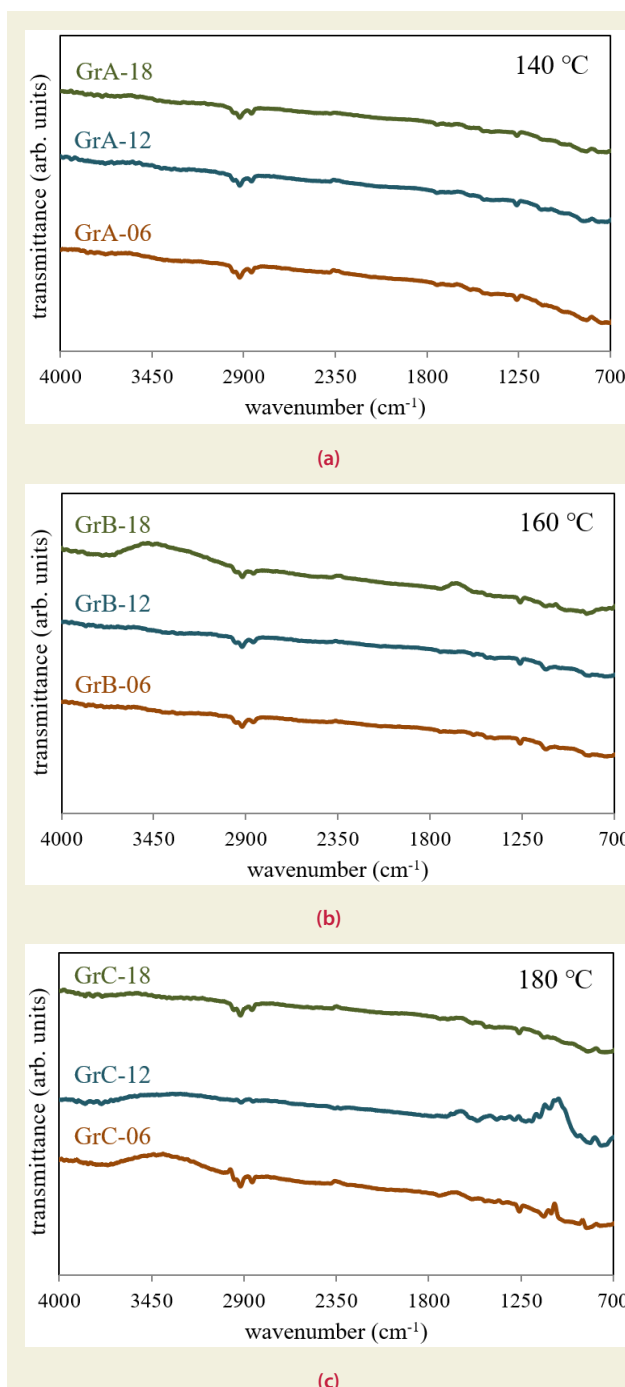
(a)

(b)

(c)

Figure 4. FTIR spectra of the samples by using different temperatures and different time values during the synthesis of N-Gr. (a) 3 different times at 140 °C, (b) 3 different times at 160 °C, (c) 3 different times at 180 °C.

25.82° in N-GrA-18 in Figure 5 support the formation of graphene in these samples. Based on their XRD results, the crystal size (layer thickness) and the number of layers of the GT, GO, and N-Gr samples were calculated using the Debye-Scherrer equation (Equation 1). The results of these calculations are presented in Table 2.

$$D = \frac{\kappa \lambda}{\beta . \cos\theta} \tag{1}$$

$$Number\ of\ layers = \frac{D}{d} \tag{2}$$
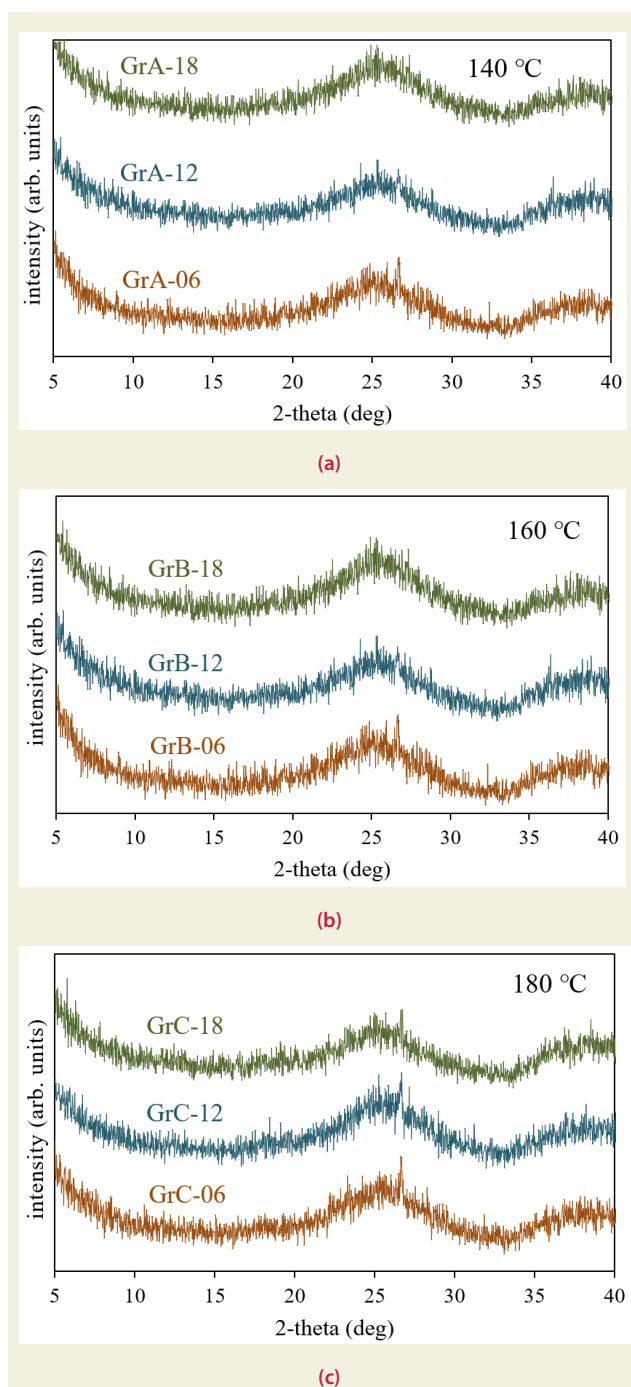
(a)

(b)

(c)

Figure 5. XRD spectra of the samples obtained by using different temperatures and different time values during the synthesis of N-Gr. (a) 3 different times at 140 °C, (b) 3 different times at 160 °C, (c) 3 different times at 180 °C.

The terms in the Debye-Scherrer relation and what they mean [8,37] are presented below.

D = Crystallite size β = full width at half maximum of the observed peak

K = Scherrer constant θ = Bragg diffraction angle

λ = Wavelength d = Inter-layer spacing

The Debye-Scherrer equation was used to analyze XRD data from GT, GO, and N-Gr samples (Table 2), and the

Table 2. Values related to the crystallite size, number of layers and distance between planes obtained using XRD results of GT, GO, and N-Gr samples.

Specimens	Crystallite size (nm)	Number of layers	Interplanar distance (nm)
GT	28.50	84.57	0.337
GO	7.02	9.77	0.718
N-GrA-06	1.55	4.50	0.344
N-GrA-12	1.70	4.84	0.351
N-GrA-18	1.52	4.40	0.345
N-GrB-06	1.53	4.40	0.347
N-GrB-12	1.63	4.68	0.348
N-GrB-18	1.57	4.55	0.345
N-GrC-06	1.55	4.45	0.348
N-GrC-12	1.60	4.62	0.346
N-GrC-18	1.58	4.48	0.352

results were consistent with literature sources [11,20,21]. Specifically, in GO obtained from GT, an increase in interplanar distance and a decrease in layer thickness were observed, which has been attributed to the addition of functional groups and water molecules during the synthesis process [11,20,21]. On the other hand, the results for N-Gr samples in Table 2 showed a decrease in layer thickness and interplanar distance compared to GO, which has been explained in the literature by the functional groups moving away from the structure [8,21].

As mentioned in [38-40], determining the number of graphene layers is crucial since the properties exhibited by monolayer graphene diminish with increasing layers per flake. As the layer count rises to 5, monolayer graphene becomes few-layer graphene; at 10, it transforms into multilayer graphene, and beyond 10 layers, it behaves more like bulk graphite. Monolayer graphene stands out with exceptional mechanical, electrical, and thermal properties, but these qualities decrease as the number of layers increases. Therefore, optimizing the number of graphene layers is vital for various applications. Notably, mechanical properties are significantly influenced by the number of graphene layers [38-40]. As seen in Table 2, the number of layers of all the obtained N-doped graphenes are below 5, lie in the range of 4.40-4.84. Although the difference in the number of layers between N-doped graphenes obtained by using 3 different temperature and 3 different duration, the minimum value 4.40 was obtained at the specimens N-GrA-18 (18 h at 140 °C) and N-GrB-06 (6h at 160 °C).

4. Conclusions

Within the scope of the study, GO was obtained from GT powder using the Modified Hummers method, and N-Gr was obtained from GO using the hydrothermal method. In the N-Gr synthesis, 3 different temperatures (140, 160, and 180°C) and 3 different durations (6, 12, and 18 hours) were employed. The results obtained from the analyses

conducted on the samples are presented below in bullet points.

- SEM analysis of GO samples synthesized from GT using the Modified Hummers method revealed that the samples exhibited a stratified structure, with clearly visible and relatively smooth, partially wrinkled layers. FTIR and XRD spectra obtained were found to be consistent with the existing literature. By employing the Debye-Scherrer relation, it was determined that functional groups had been incorporated into the structure of the GO samples, as evidenced by the increase in the distance between the planes.

- FTIR analysis of the samples obtained from the synthesis of N-Gr from GO using the hydrothermal method revealed the presence of nitrogen and deoxidation of GO, indicating the successful synthesis of N-Gr. The broad and short peaks observed in the XRD spectra of the N-Gr samples at 2θ values around 25.5° indicate the formation of graphene.

- In calculations made using the Debye-Scherrer relation, a decrease was observed in the distance between layers, layer thickness, and the number of layers of the n-Gr samples obtained from GO using the hydrothermal method. The decrease in the distance between layers is known to be caused by functional groups moving away from the structure, as indicated

in the literature. This indicates the successful synthesis of graphene.

- According to calculations using the Debye-Scherrer equation, a decrease in the interplanar distance, layer thickness, and the number of layers was observed in the N-Gr samples synthesized from GO using the hydrothermal method. As indicated in the literature, the decrease in the distance between layers is known to be caused by functional groups moving away from the structure. This indicates the successful synthesis of graphene.

- Considering the minimum number of graphene layers, the parameters "18 h at 140 °C" and "6 h at 160 °C" seem more effective in obtaining N-doped graphene.

5. Acknowledgements

6. The Declaration of Conflict of Interest

No potential conflict of interest was declared by the authors.

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