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Synthesis and Characterization of Thermally-Reduced Graphene

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Abstract: Thermally-reduced graphene was obtained from reduction of graphene oxide (GO) via heat treatment under the hydrogen in the range of 300-1100°C. In order to find optimum tempreture, the synthesized graphene has been investigated by X-ray diffraction (XRD), FTIR spectroscopy as well as Raman spectroscopy. The result indicated that the reduced graphene at 900°C (GR900) had the highest quality in comparison with the other temperatures. Additionally, GR900 exhibited a sharp (002) peak corresponding to an interlayer distance of 3.39° A, which is close to that of conventional graphene (3.4°A). However, the structure of GR900 was also investigated by transmission electron microscopy (TEM), scanning electron microscopy (SEM) and the results supported the previous findings.

Key words: Graphene, Graphene oxide · Thermal reduction · X-ray diffraction · FTIR spectroscopy and Raman spectroscopy

INTRODUCTION

Graphene crystal is an infinite two-dimensional layer consisting of sp^2 hybridized carbon atoms which belongs to one of the five 2D Bravais lattices called the hexagonal (triangular) lattice. It is noteworthy that by piling up graphene layers, in an ordered way, one can form 3D graphite. There are other pseudo-2D sp^2 hybridized carbon structures, such as bilayer- and few-layer-graphene, which exhibit particular properties that are different from both graphene and graphite [1]. Graphene has excellent in-plane mechanical, structural, thermal and electrical properties. These properties make it interesting for many engineering applications. Graphene has been made by four different methods. The first was chemical vapor deposition (CVD) [2]. The second was the micromechanical exfoliation of graphite [3]. This approach, which is also known as the Scotch tape or peel-off method, followed on from earlier work on micromechanical exfoliation from patterned graphite. The third method was epitaxial growth on electrically insulating surfaces such as SiC [4] and epitaxial growth on metal substrates [5] and the fourth method that recently is used was intercalation component between graphite layers then exfoliation of layers [6]. For a general lack of efficient methods to directly produce significant quantities of single-layer graphene sheets, the indirect route through the recovery from graphene oxides (GO) has been widely pursued [6-10]. They synthesized graphene oxide from graphite by modified Hummer's method [11]. The obtained Graphene oxide retains a layered structure, it consists of oxidized graphene sheets, it is hydrophilic and water molecules can readily intercalate into the interlayer space.

In this study, the graphene oxide is reduced via heat treatment under the hydrogen. The thermally method is used in different temperatures and the obtained graphene is characterized by Raman spectroscopy, X-ray spectroscopy, Fourier transform infrared spectroscopy (FT-IR) and subsequently is compared in each temperature and an optimum temperature is identified. The best synthesis is characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) as well.

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MATERIALS AND METHODS

For graphene oxide preparation a modified Hummers' method was utilized [11] according to following steps: Firstly a 10-L Pyrex reactor with a water cooling system utilized to mix 5 g of natural graphite (Merck), 3.75 g of $NaNO_3$ (99%, Sigma-Aldrich) and 310.5 g of H_2SO_4 (97%- Merck) together and the mixture was then stirred for 30 min. Secondly, 22.5 g of $KMnO_4$ (99%, Sigma-Aldrich) was carefully combined to the above mixture for 1 hour and the new mixture was stirred for 5 days at room temperature. Then 5 litres of aqueous solution of H_2SO_4 (5%) was slowly mixed to it during 1 hour. After stirring the solution for 2 h, 150 g of H_2O_2 (30%, Aldrich) was added to the mixture. The graphite oxide slurry was obtained at the bottom after centrifugation was washed with a 3% H_2SO_4/0.5% H_2O_2 solution and then was rewashed with deionized water until the PH revived neutral. By ultrasonication the graphite oxide was exfoliated in water and produced a homogeneous graphene oxide water based suspension. Then the graphene oxide suspension was filtered and dried for 24 hours on a vacuum oven at 70 degree centigrade. The obtained graphene oxide after above process was a brown color powder and is called as GO across the paper. To reach to a reduced graphene the GO was treated thermally while it was placed into a quartz furnace with a crucible at different temperatures 300, 500, 700, 900 and 1100°C for 30 minunes under a flow of laminar H_2 gas (99.999%). The graphene reduced at temperatures 300, 500, 700, 900 and 1100°C were called as GR300, GR500, GR700, GR900 and GR1100 receptivity.

Characterization Methods: A X-ray diffractions (Phillips PW 1840 x-ray diffractmeter with Cu-K radiation source) was utilized to study the crystal structure of the solids. The graphene distance layer can be calculated based on Bragg's law [12, 13]:

$$n\lambda = 2d_{(hkl)} \sin(\theta) \qquad (1)$$

where λ is the wavelength of the X-ray, θ is the scattering angle, n is an integer representing the order of the diffraction peak, d is the interplane distance of the lattices and (hkl) are Miller indices. The well-known Scherrer equation can obtain the mean crystallite size of powder composed of relatively perfect crystalline particle [12, 13]:

$$L_{hkl} = k\lambda/\beta_0 \cos\theta \qquad (2)$$

where L_{hkl} is the mean dimension of the crystallite perpendicular to the plane (hkl); β_0 is the integral full widths at half maximum in radians; K is a constant dependent on the crystallite shape (0.89).

To study the morphology of the products a transmission electron microscopy (CM30-Philip) and a scanning electron microscopy (S4160-Hitachi Japan) was utilized. To prepare samples for TEM analysis the products was droppd on a carbon coated copper grid and dispersed by ultrasonic in absolute ethanol and dried in room air.

Raman Spectroscopy is known as a powerful technique in characterization of carbon nanostructures. The G-band appearing at ca.1580 cm^{-1} is the most significant attributes in the Raman spectra of sp^2 hybridized carbon materials. Another band which appears at 1200-1400 cm^{-1} and called D-band indicate a certain amount of disorder or edges within the carbon structure [14, 15]. Raman spectra were performed on a Senterra model of Bruker Company (Germany) and the used Raman spectrometer was a 785 nm laser source.

Fourier Transform Infrared (FT-IR) method was employed to characterizing the material. In infrared spectroscopy, IR radiations are passed through the sample. The resulting spectrum represents the molecular absorption and transmission of the sample and create a molecular fingerprint. Fourier transform infrared (FT-IR) spectra were recorded in this study on a Bruker IFS 88 Fourier Transform Infrared spectrophotometer with KBr pellets in the 4000–400cm^{-1} region.

RESULT AND DISCUSSION

Graphene oxide cannot be used as a conductive nanomaterial without further processing when is thermally unstable and electrically insulateing. It has been demonstrated that the reduction of graphene oxide significantly can refurbish its thermal stability and electrical conductivity close to the level of graphite. To obtain graphene nano sheet the graphene oxide was reduced by a heat treatment in this work.

The figure 1 investigate the oxidation processes of GO by XRD pattern. In the XRD pattern the strong and sharp peak at $2\theta = 10.93$°C corresponds to an interlayer distance of 8.08°A (d_{002}) for the AB-stacked GO while it has 8.9 crystal size (Table 1).

The FT-IR spectrum of the GO in Figure 2 shown several peaks: a pick at 3400.04cm^{-1} originated from O–H stretching vibration indicates a broad and intense
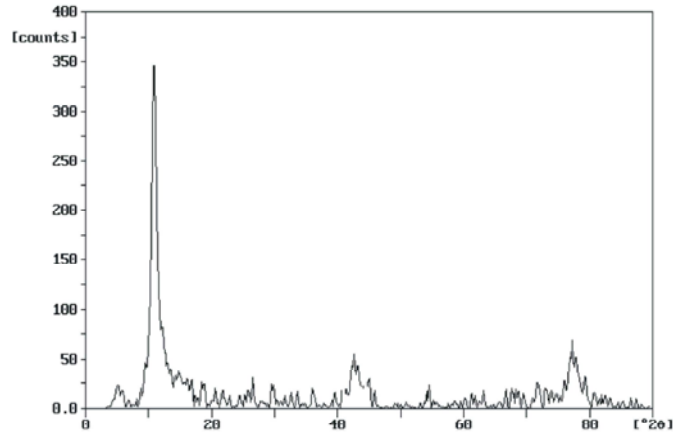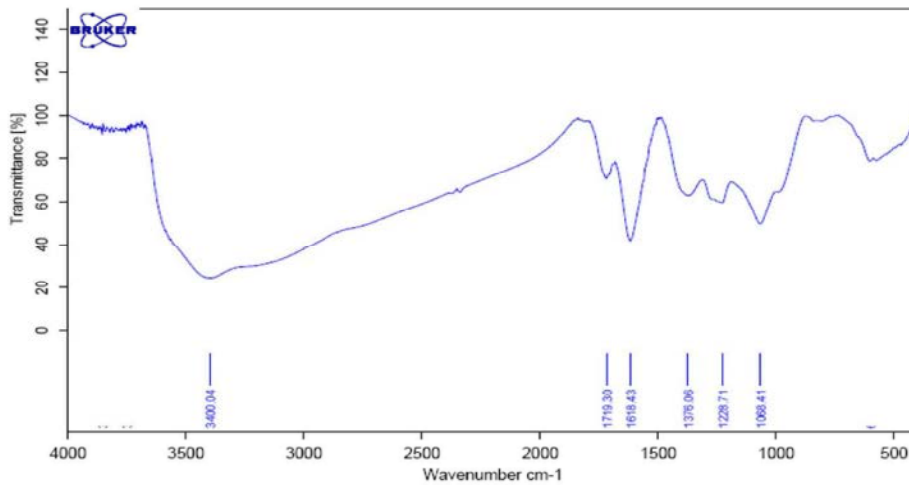
Fig. 1: The XRD pattern of GO.

Fig. 2: The FTIR spectra of GO.

Table 1: X-ray structural parameters of GO, GR300, GR500, GR700, GR900 and GR1100.

Samples	2θ	FWHM (°)	d_{002}:Layer distance (°A)	Crystal thickness (nm)
GO	10.93	0.96227	8.08	8.9
GR300	25.91	0.8583	3.43	9.7
GR500	26.09	0.91552	3.41	9.6
GR700	25.91	1.08718	3.43	8.1
GR900	26.21	1.25884	3.39	6.8
GR1100	26.34	0.5722	3.37	15.4

Fig. 3: The Raman spectra of GO.

absorption, a pick at 1719.3 cm^{-1} due to the C=O stretching of carboxylic groups placed at edges of GO sheets. Stretching vibration peaks of C–O (epoxy) and C–O (alkoxy) are observed at 1379.06, 1228.71 and 1068.41cm^{-1}, respectively. The peak at 1618.43 cm^{-1} can be attributed to in plane C=C bands and the skeletal vibration of the graphene sheets that confirming the successful oxidation of graphite [16].
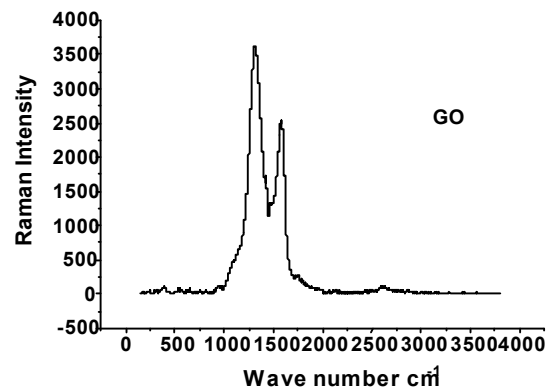
The observed G band at 1593.5 cm^{-1} and D band at 1307.3 cm^{-1} in the Raman spectrum of GO in figure 3 indicating the reduction in size of the in-plane sp^2 domains, probably due to the extensive oxidation, confirm the successful oxidation of graphite.
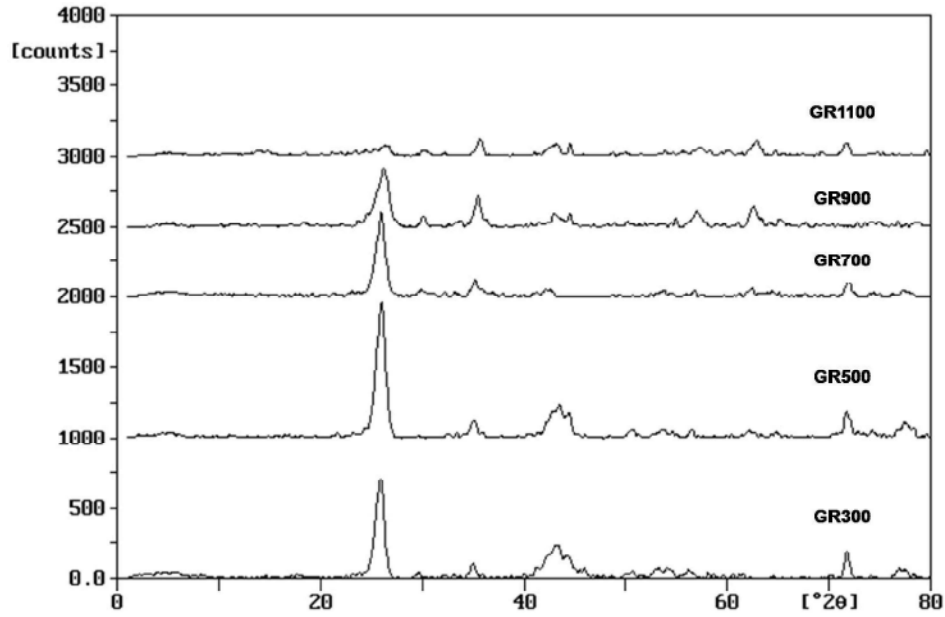
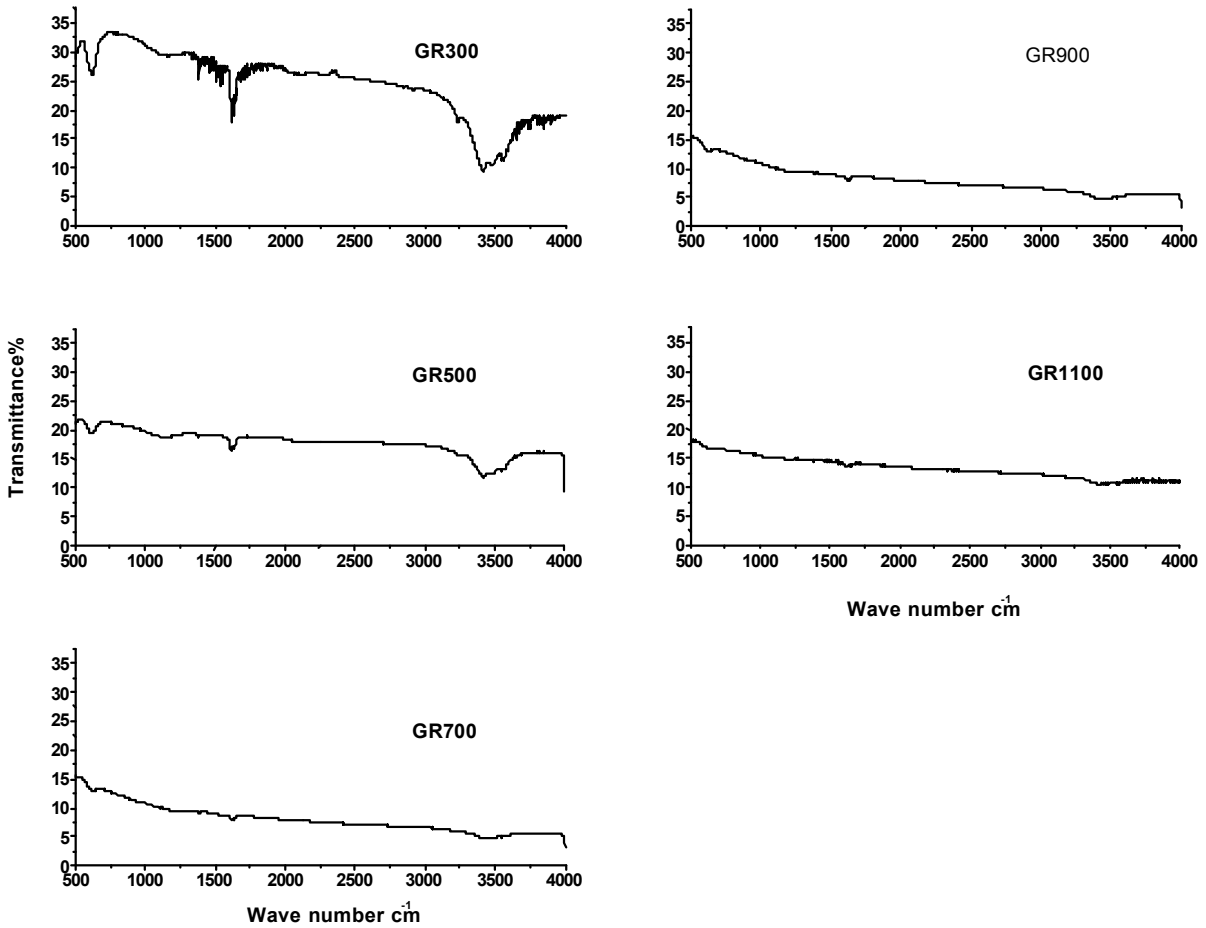Fig. 4: X-ray patterns of GR300, GR500, GR700, GR900 and GR1100.

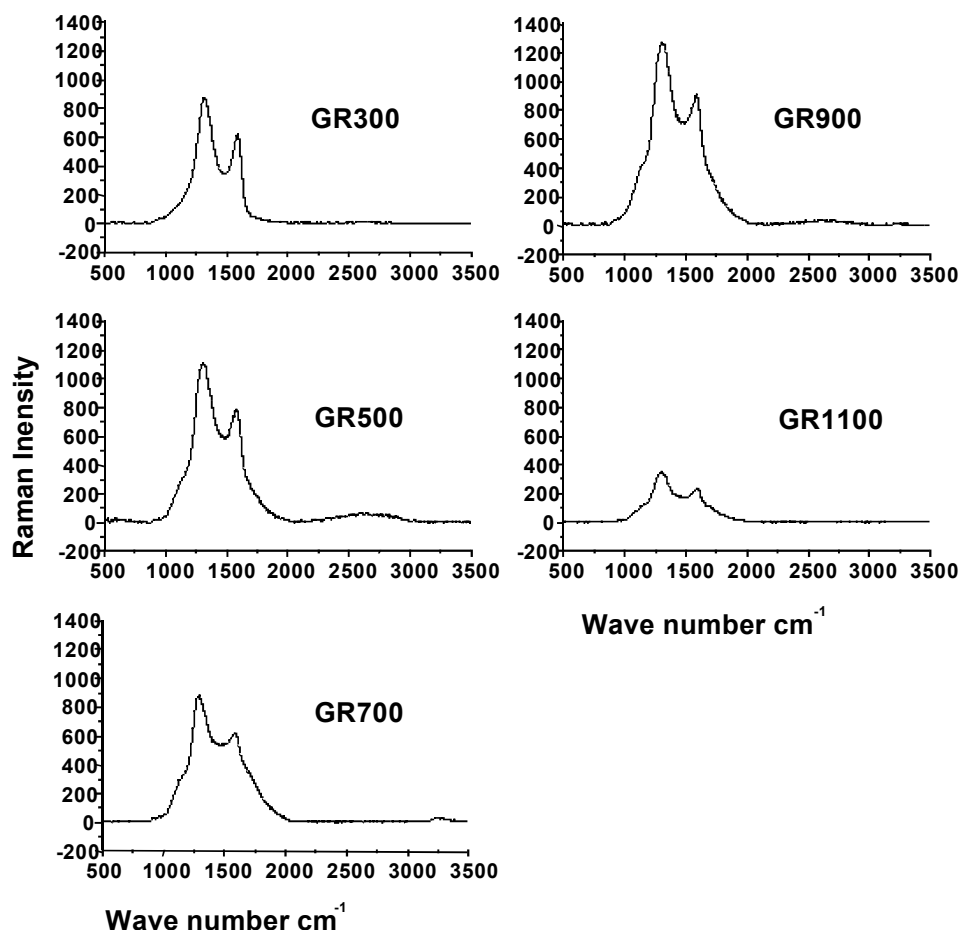Fig. 5: FT-IR spectra of GR300, GR500, GR700, GR900 and GR1100.

Fig. 6: Raman spectra of GR300, GR500, GR700, GR900 and GR1100.

The XRD patterns of graphene was obtained via reduced of GO at temperatures 300, 500, 700, 900 and 1100°C (GR300, GR500, GR700, GR900, GR1100) are recorded on figure 4. XRD patterns of GRs has a strong peak at 2θ=25-27° (Table 1). Originally, the XRD pattern of graphene has a strong peak at 2θ=25-27° [17, 18]. In addition, The exfoliation of GO sheets after rapid vaporization of the intercalated water molecules resulted a severe changes in interlayer distance of 8.08 to 3.43°A (Table 1) for the values of GO and GR300. The interlayer distance of GR300 to GR1100 as shown in Table 1 descends from 3.43 to 3.37°A. At temperatures below 200°C the water molecules are removed from GO and at temperatures between 500 and 600 most of the hydroxyl and the carboxyl groups are removed from GO and the remaining hydroxyl and epoxide groups are removed gradually at temperatures between 600 and 1000°C [16]. However, the interlayer distance of GR900 (3.39°A) is very close to interlayer distance of conventional graphene (3.4 °A) [19]. The table 1 has shown a decrease in crystal

thickness at GR300 to GR900 and then an increase at GR1100. Accordingly, the graphene that was synthesized at 900°C has the smallest crystal thickness among the studied temperatures.

The FT-IR spectra of the GRs are shown in Figure 5. The FTIR of reduced graphene by heating at different temperatures indicates that heating at 300°C results to removing the most carboxyl groups, heating at 500, 700 and 900°C removes the residual carboxyl and partial hydroxyl groups, heating at 900°C eliminates the residual hydroxyl groups and the epoxy group and heating at 1100°C lead to cracking of aromatic C=C bands.

The Figure 6 shown the Raman spectroscopy of GR300, GR500, GR700, GR900, GR1100. The Raman spectrum of the Grs includes both G and D bands as well. As shown the G band of GRs decreased to the position close to the G band of graphite [20, 21]. The G band intensity is very low at GR1100 but GR900 has a prominent G band. Additionally, order/disorder carbon ratio (I_D/I_G) of GR300 has increased (Table 2).
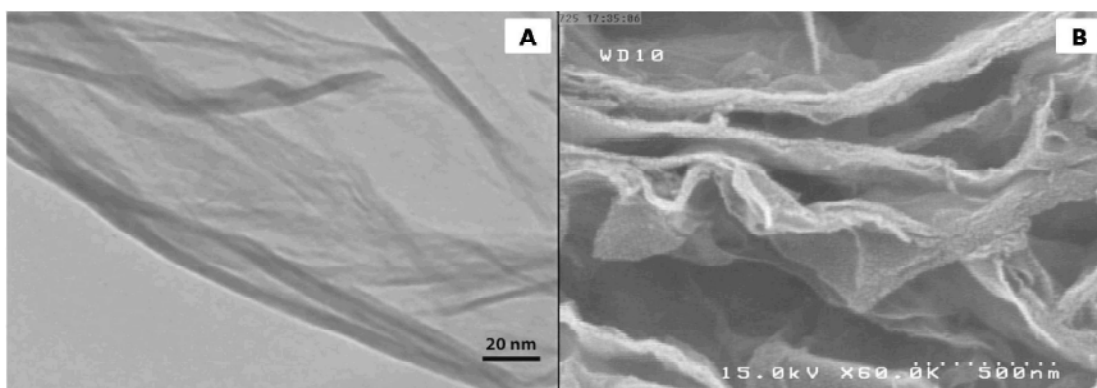
Fig. 7: A) High resolution TEM of GR900 and B) FE-SEM of GR900.

Table 2: The G band and D band position and G intensity, intensity of D band G band ratio of GO, GR300, GR500, GR700, GR900 and GR1100

Samples	D-band position (cm^{-1})	G-band position (cm^{-1})	I_G	I_D/I_G
GO	1307.3	1593.5	2523.7	1.42
GR300	1317.8	1592.8	613.4	1.42
GR500	1310.7	1578.7	777.2	1.42
GR700	1298.2	1589.2	613.4	1.43
GR900	1307.0	1584.7	905.4	1.39
GR1100	1296.4	1592.8	229.0	1.50

This implies that the average size of the sp^2 domains has decreased upon heat treatment of GO [21]. On the other side I_D/I_G intensity ratio is decreased with increase in temperature at 900 °C and then decreased with increase in temperature to 1100 °C which implies that the disordering portion of the two-dimensional carbon backbone is increased in this temperature range because of cracking C=C in plane graphite sheet that it is demonstrated via the FTIR of GT1000.

Effect of Temperature on the Growth of Graphene: The analysis of obtained results has explained that the water molecules intercalated between graphite layer and residency of oxygen functional groups on the basal has resulted a high quality graphene oxide. Then the grathene was obtained by heat treatment. With the temperature increase from 300 to 900°C the qualities of GRs have improved and the disorderliness have decreased as well. The increasing temperature to 1100°C causes to break in plane carbon band and to degrease the qualities of GR1100 and to destroy the graphene sheets. Accordingly, the optimum temperature for obtaining graphene by reduction graphene oxide under the H$_2$ was 900°C. As shown in the FE-SEM and high-resolution TEM images (Figure 7) the GR900 has some folding and wrinkling areas but the XRD and Raman analysis showed

it has high-quality structures. Furthermore, the GR900 has the flat area between the micro-folding areas shows the in-plane lattice ordering of a two-dimensional carbon network and has large size flake as shown in the TEM.

CONCLUSION

The graphene was synthesized in this study via thermal reduction processes of GO under the hydrogen in the rang 300-1100°C. The XRD analysis that have been used to investigate the products, showed the drastic changes in FWHM and d_{002} at 300°C. It can be due to escaping of intercalated water molecules from GO. However, the quality of the reduced GRs improved as the tempreture increased up to 900 °C, while the increasing tempreture upto 1100°C caused the breakage of C=C in plane bond. These results are useful for the study of the thermal reduction process that has great potential for use in cost-saving industrial mass production processes.

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