GREEN SYNTHESIS OF GRAPHENE IN MOLTEN SALT MEDIA

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Abstract

Graphene is one of the most promising materials discovered in recent years. It is usually synthesized by using "top-down" traditional methods starting from graphite such as 'modified Hummers' method, including steps requiring the use of many chemicals. Alternatively, various "bottom-up" synthesis methods were also developed including fewer steps, being environmentally friendly and economical. In this study, graphene is obtained by carbonization of various mono/poly-saccharides at two different temperatures, 600 °C and 800 °C, in molten salts (MS) of LiCl/KCl eutectic mixture. Structural properties of graphene products were determined by X-ray diffraction analysis (XRD). Also, electrical conductivities of all the synthesized materials were measured by 2-point probe analysis.

Keywords: *Graphene Synthesis, Saccharides, Bottom-up method*

1. INTRODUCTION

Graphene, which has many promising properties, is used in various types of electronic and energy-related device applications [1]. Graphene takes great attention thank its superior properties that involving high mobility, high thermal and electrical conductivity and structural stability [2]. Endeavors have been allocated to find a green pathway that reduces use of chemicals in order to synthesize graphene.

Graphene is mainly produced according to two basic approaches; top-down and bottom-up. Top-down processes depend on the mechanism breaking the stacked layers of graphite to single graphene sheets. In top-down processes, graphite is delaminated oxidatively by strong oxidant in solution, and then obtained graphene oxide is reduced in order to synthesize graphene. Also, the delamination can be achieved by ultrasonic agitation. On the other hand, in bottom-up approach, graphene is synthesized from different carbon sources [3], which proceed generally according to a mechanism with the following steps; C-radicals are produced by decomposition of a carbon precursor until the amount of solved C is saturated, followed by the organization of C atoms to yield graphene structure [4]. Direct carbonization of simple monomers such as carbohydrates at high temperatures induces to polymerization that continues by elimination of water and terminates in non-uniform carbonaceous material [7].

In this study, the bottom-up process is chosen for production of graphene; saccharides are used as a carbon source as cheap and easily obtainable materials. Furthermore, this method is environment friendly because it does not require the use of toxic chemicals such as sulfuric acid, potassium permanganate as in the Hummers method. Graphene is obtained by the carbonization of saccharides in molten deep eutectic salts of the LiCl/KCl system which has a melting point of 353 °C. Saccharides are turned into nanoporous carbons in an ionic MS medium and via fine-adjustment of the synthesis circumstances the method yields rather pure graphene. MS can dissolve the polar intermediates of saccharides dehydration. Then, MS must react along concentrated solution cycloaddition/elimination ways to the graphene sheets [7]. The MS-derived graphene frameworks are hydrophobic and show high selectivity and potential for absorption of organic molecules.

2. MATERIAL AND METHODS

Graphene was synthesized by carbonization of various monosaccharides such as glucose, fructose, xylose, arabinose and polysaccharides such as microcrystalline cellulose and starch and as well as graphite under flowing argon or nitrogen atmosphere in a stainless steel reactor surrounded by a ceramic heater. The carbon source (saccharide/polysaccharide/graphite) was mixed with the eutectic composition of LiCl/KCl (45/55 by weight) with a ratio (1:10) and the powders were homogenized by pestling into an agate mortar. The powder mixture was filled into a ceramic crucible and then loaded into the reactor. First, the system (Figure 1) was vacuumed then flushed with the reaction gas (argon/nitrogen) for 5 min. After the starting step, the system was heated to 600 °C or 800 °C with 20 °C min^{-1} ramp rate and kept at this temperature for 5 h. The system was finally cooled to room temperature by turning off the power; meanwhile, the gas flow was fed until the temperature decreased below 50 °C. The temperature of the system was controlled by Elimko E-200 Series Digital Temperature Controller.

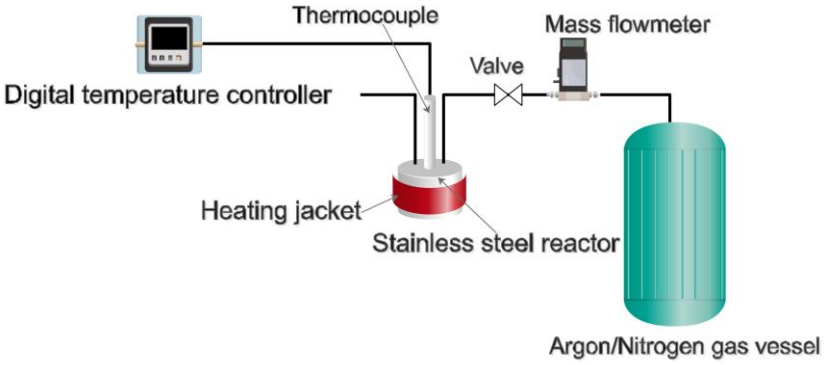


Figure 1. Experimental set – up

The acquired block of products was crushed into particles and washed with a sufficient amount of water to remove the salts. The synthesized material was dried in a drying oven at 60 °C for overnight. X-ray diffraction (XRD) patterns were obtained with a Rigaku D-Max 2200 Series equipped with Cu-Kα radiation (λ = 1.54 Å) at a scanning rate of 3° per minute. The tube voltage was 40 kV and the current was 40 mA.

Also, reduced graphene oxide (RGO) was synthesized by modified Hummers method in order to compare the electrical conductivity performances with commercial graphite (CGr), commercial graphene (CG) and carbon black (CB), the other MS-derived graphenes. For this aim, 1 g of graphite (XG Sciences) was added to 50mL concentrated sulfuric acid (95-97%, Merck) while stirring in an ice-water bath. Then, 3 g potassium permanganate (>99%, Merck) was slowly added by controlling the temperature under 55 °C. After that, the suspension was stirred at 25 °C for 25 min followed by 5 min sonication in an ultrasonic bath (Elmasonic S, 30H). After repeating the stirring-sonication treatment for 12 times, the reaction was satisfied by the addition of 200mL-distilled water. An extra 2h ultrasonic treatment was carried out. After adjusting the pH to 6 by the addition of 1M sodium hydroxide (>98%, Sigma Aldrich) solution, the suspension was further sonicated for 1h. 10 g L-ascorbic acid (99%, Carlo Erba) was dissolved in 100 mL distilled water, and then was slowly added to the exfoliated graphite oxide suspension at room temperature. The reduction was performed at 95 °C for 1h. The resultant black precipitates were simply filtered by cellulose filter paper and further were washed with a 1M hydrochloric acid solution (37%, J.T.Baker) and distilled water to neutral pH. Finally, the filtrate was dried to obtain RGO powder.

3. RESULTS AND DISCUSSION

Sixteen experiments were carried out by using eight different starting raw materials at 600 °C and 800 °C. Replicate experiments were also done to assess the repeatability of the yield results. Yields were calculated based on the amount of starting carbon source such as glucose, fructose, or arabinose, etc. as it is indicated in Equation 1.1.

$$\% \, Yield = \frac{Actual \; yield}{Theoretical \; Yield} \times 100 \qquad (1.1)$$

The amount of products calculated from the complete reaction of the starting material (carbon source) was named as theoretical yield, whereas the amount actually produced of the graphene product was the actual yield. The ratio of actual yield to theoretical yield expressed in percentage was labeled as the percentage yield. By based this calculation method, yields were obtained and graphed in Figure 2, which is seen at below.

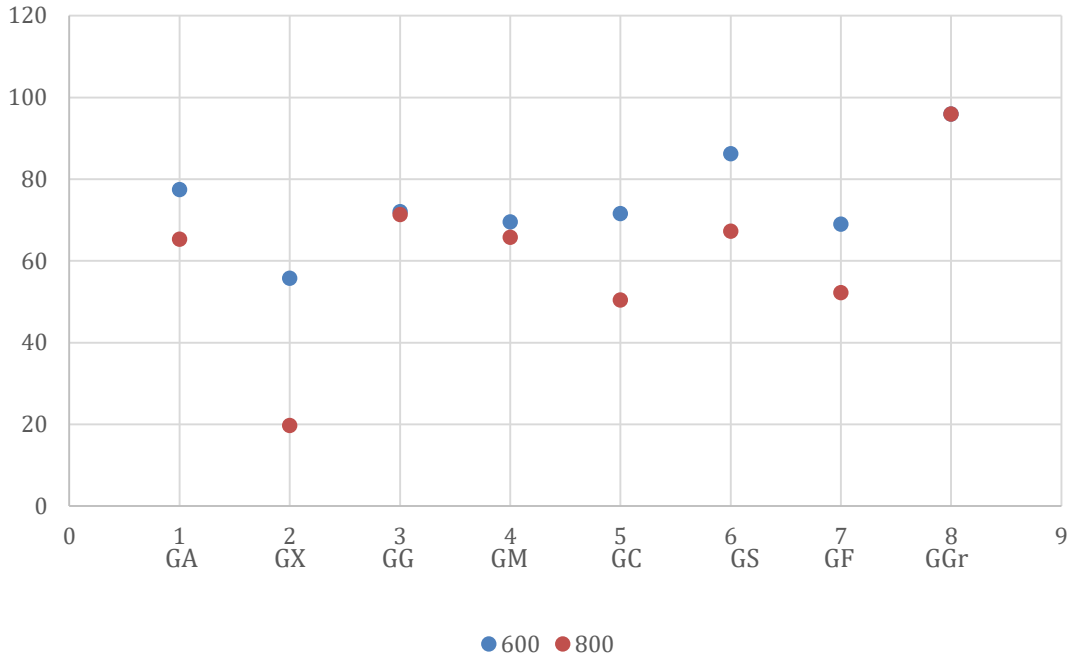


Figure 2. Yields of graphene products at 600 °C and 800 °C.

According to Figure 2, yield values obtained at 600 °C are higher than at 800 °C. Especially, the yield of graphene from xylose (GX) obtained at 600 °C is threefold higher than the one which was obtained at 800 °C. On the other hand, yields of graphene from cellulose (GC), from starch (GS), from fructose (GF) and from arabinose (GA) obtained at 600 °C are 1.2 – 1.5 times greater than those obtained at 800 °C. As it is understood from these results, temperature builds negative effect on the yield values.

The conversion of the sp^3 C-X bonds (X = C, H, or O) of saccharides into sp^2 carbon as a result of elimination of water can be detected via various spectrometers. The carbonization of saccharides includes stable change from three-dimensional sp^3 C–X bonds to the two-dimensional aromatic sp^2 C–C bonds, while the transform usually occurs amorphous carbon instead of an arranged graphene. Therefore, it is still highly challenging to synthesize graphene in large quantity simply by carbonization of sugars or simple cross-linkable monomers.

Structural analyses of graphene products were performed using XRD. Graphene thickness can be calculated by using Scherrer's equation, which is expressed by $D_{002} = K\boldsymbol{\lambda}/B\cos\boldsymbol{\theta}$, where D_{002} is the thickness of crystallite, graphene thickness, K is a constant dependent on the crystallite shape (0.89), $\boldsymbol{\lambda}$ is the X-ray wavelength, and B is the full width at half maximum (FWHM), and $\boldsymbol{\theta}$ is scattering angle. From Scherrer's equation, the number of graphene (N_{GP}) can be calculated using the following equation: $N_{GP} = D_{002}/d_{002}$ [8].

Table 1. Layer numbers of MS-derived graphene products

GG600	2
GA600	11
GX600	7.25
GF600	7.53
GM600	8.26
GC600	4.6
GS600	13
GA800	6
GX800	14
GG800	8

As seen in Table 1, Layer numbers varies between 2-14. Most of MS-derived graphene products has 8 layers in average. It can be concluded that synthesized graphene products are mostly classified as few-layer graphenes.

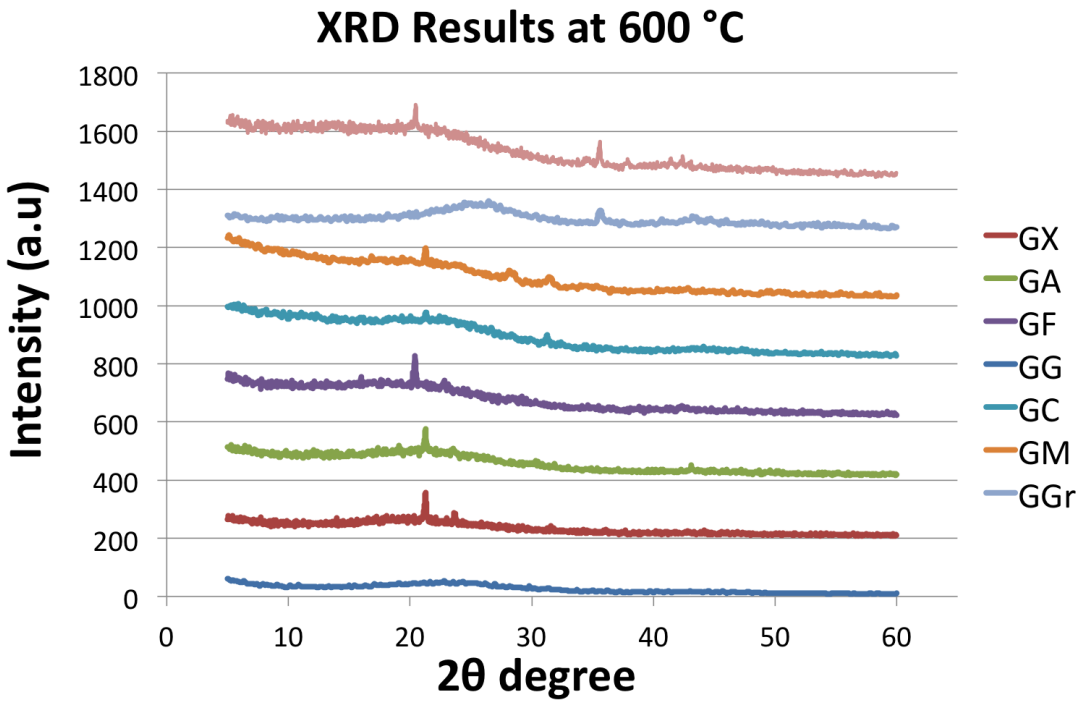


Figure 3. XRD patterns for graphene products at 600 °C

According to Figure 3; GS, GM, GC, GF, GA, GX gives a peak at 2θ = 23° around and this result is compatible with previous studies [7]. It can be seen that the as-prepared graphene shows a weak and broad diffraction peak at 2θ = 23°, corresponding to the diffraction of the (002) plane. GM, GX, and GC also show a peak at 2θ = 32°. GS and GGr show a peak at 2θ = 36.4 °. Also, GA and GS show the peak at 2θ ~ 43°, corresponding to the (100) crystal plane of graphene. GGr shows a peak at 2θ = 26.3° which is agreeable with the other studies [5]. The samples obtained at 600 °C typical of disordered glassy polymer without pronounced order, as indicated by the broadened humps in the XRD patterns.

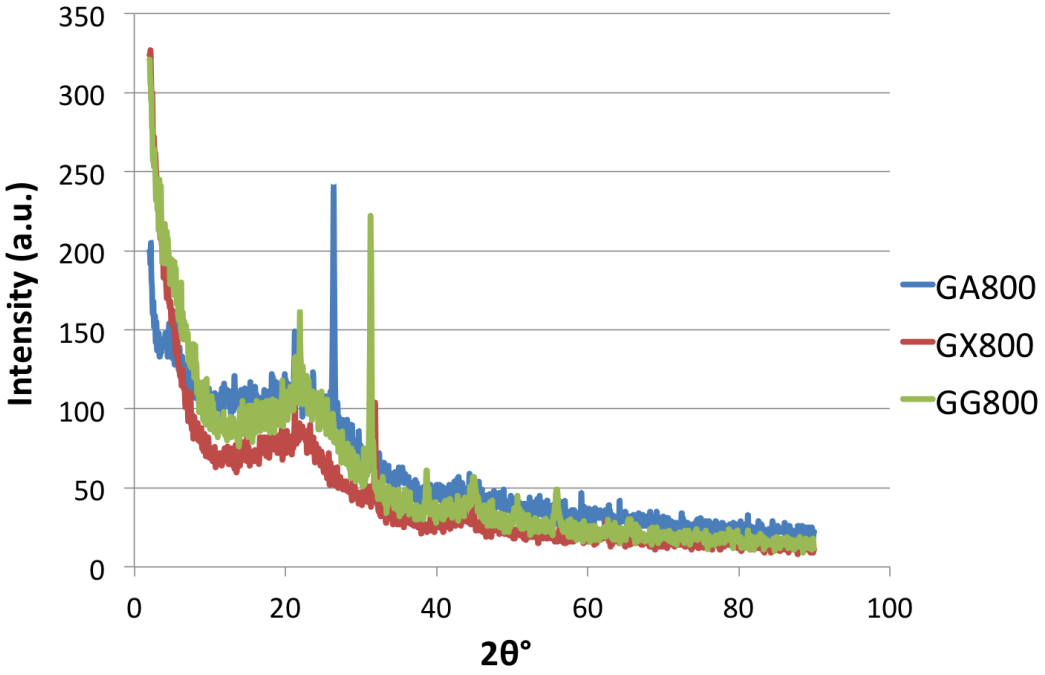


Figure 4. XRD patterns for graphene products at 800 °C.

As shown in Figure 4, XRD patterns of saccharide derived graphene products at 800 °C exhibit a slightly increased peak at 2θ=23° in all of the XRD patterns which are typical to graphene as previous papers expressed [1, 7]. Liu et. al (2013) reported that XRD pattern of graphene like structures, which are derived from glucose in molten salt media at 800 °C, show a hump at 2**θ** = 23º [7]. Some of the graphene products, that are synthesized at 800 °C, show amorphous structure in their XRD patterns.

Electrical conductivities of graphene from fructose at 800 ºC (GF800), graphene from cellulose at 800 °C (GC800), graphene from xylose at 800 °C (GX800), graphene from glucose at 800 °C (GG800), commercial graphite (CGr), commercial graphene (CG) were measured by Keithley 2400 Sourcemeter.

First, graphene powders were placed in a copper cylindrical container which has a copper cap. Then, graphene powders were compressed by a hydraulic press under 50 bar for 0.5 hours. The electrical resistivities of graphene powders were determined by 2-point probe method. A pressure is applied onto the graphene powder in copper mould during the electrical conductivity measurement by a joiner's clamp. The conductivity σ was then estimated according to σ = l/AR.

Temperatures (°C) / Graphene products' label name	600	800
	Electrical conductivities (S/m)	
GC	0,162	2,92
GS	0,112	12,30
GA	0,224	15,87
GG	0,107	8,54
GX	0,202	5,10
GM	0,198	7,62
GF	0,199	69,38
GGr	1218,9	724,6

Table 2. Electrical conductivities of MS-derived graphene products

As it is seen from Table 2, GGr (graphene produced from graphite in a molten salt media) shows highest electrical conductivities among the other MS-derived graphene products that were synthesized. After GGr, GF800 has the second highest value. The electrical conductivities that are obtained at 800 °C are higher than the ones that are obtained at 600 °C. For this reason, it can be concluded that 800 °C is the optimum synthesis temperature when comparing 600 °C.

Label name	Expansion	Electrical conductivities (S/m)
CG	Commercial graphene	115,71
CGr	Commercial graphite	317,06
CB	Carbon black (Vulcan XC-67)	341,44
rGO	Reduced graphene oxide	195,39

Table 3. Electrical conductivities of commercial graphene, commercial graphite, carbon black, and reduced graphene oxide

On the other hand, electrical conductivities of commercial graphene (CG), commercial graphite (CGr), carbon black (CB), and reduced graphene oxide which was synthesized by Hummers method (rGO) were measured by 2-point probe method and compared. According to Table 3, CB shows the highest electrical conductivity among the others. Furthermore, by comparing Tables 2 and 3, it is seen that the electrical conductivity of GGr is very much higher than the electrical conductivity of CG and rGO.

4. CONCLUSIONS

A green synthesis of graphene by carbonization of saccharides in MS media was presented in this study. It is understood that salt formed microstructure and porosity of the graphenes. Yield values obtained at 600 °C are higher than at 800 °C. Synthesized graphene products has mostly eight layers. Thus, it can be concluded that they are few-layered graphenes. XRD patterns of MS-derived graphene products exhibit a

slightly increased peak at 2θ=23° in all of the XRD patterns which are typical to graphene as previous papers expressed. Among the MS derived graphene products, GGr has the highest electrical conductivity. GG800 has the second highest electrical conductivity. Furthermore, electrical conductivities of CG, CGr, CB, and rGO have been measured and it is understood that they are rather greater than the electrical conductivities of MS derived products. But, the electrical conductivity of GGr is almost ten times higher than the electrical conductivity of CG and rGO. The saccharide-based MS-derived graphenes are quite hydrophobic and has important capacity and selectivity to absorb organic molecules. These results builds a green, malten-salt synthesis of graphene from various precursors.

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REFERENCES

[1] Garaj S., Hubbard W., Golovchenko JA. (2010), Graphene synthesis by ion implantation. Applied Physics Letters. 97(18):183103. doi:10.1063/1.3507287.

[2] Baek JJ., Kim TH. and Park DW. (2013), Synthesis of few layer graphene by non-transferred arc plasma system. J Nanosci Nanotechnol, 13 (11):7418-23.

[3] Aliofkhazraei M, Ali N, Milne, WI, Ozkan, CS, Mitura, S, Gervasoni, JL. Graphene Science Handbook: Fabrication Methods. 1st ed. Florida: CRC press; 2016.

[4] Akbar, F., Kolahdouz, M., Larimian, S. and Radamson, HH. (2015), Graphene synthesis, characterization and its applications in nanophotonics, nanoelectronics, and nanosensing. J Mater Sci: Mater Electron (26): 4347. https://doi.org/10.1007/s10854-015-2725-9

[5] Andonovic, B., Grozdanov, A., Paunović P., and Dimitrov, AT., (2015), X-ray diffraction analysis on layers in graphene samples obtained by electrolysis in molten salts: a new perspective, in IET Micro & Nano Letters, 10, (12): 683-685.

[6] Ruammaitree A., Nakahara H., Akimoto K., Soda K., Saito Y., (2013) Determination of non-uniform graphene thickness on SiC (0 0 0 1) by X-ray diffraction, Appl. Surf. Sci., (282): 297–301.

[7] Liu, X., Giordano, C. and Antonietti, M. (2014), A Facile Molten-Salt Route to Graphene Synthesis. Small, 10: 193–200. doi:10.1002/smll.201300812

[8] Adel, M., El-Maghraby, A., El-Shazly, O., El-Wahidy, E. F. and Mohamed, M. A. A. (2016), Synthesis of few-layer graphene-like nanosheets from glucose: New facile approach for graphene-like nanosheets large scale production, Journal of Materials Research, 31, (4), 455-467.