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Research Article

Investigation of The Effect of Vacuum Drying Conditions On Graphene Oxide Production

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Abstract

Graphene consists of sp2 hybridized carbon (C) atoms arranged in a honeycomb shape as single layer. Graphene oxide (GO) structures have importance over graphene, because of hydrophobic nature of graphene, non-adjustable band gap, complex production processes and its production costs. GO structures are generally synthesized using graphite or carbon sources which are similar compounds compare to graphene. GO consists of both sp2 and sp3 hybridized C atoms to which functional groups are attached at the top and bottom of the layer. The mechanical, electronical and thermal properties of GO structures can be controlled during the production phase thanks to these oxygen-containing functional groups in their structure. These functional groups consist of oxygen (O) and hydrogen (H) elements in the form of carbonyl, hydroxyl, carboxyl or epoxide and they are highly dependent on the production method. Among the various methods for producing GO structures, the Hummers method stands out with its low cost, time efficiency and ease of parameter control. In this study, GO production was carried out by improved Hummers method, which consists of steps such as mixing with strong acids and oxidizing agents, washing with water and drying. The drying process, which is the last stage of production, directly affects the physical and chemical properties of the final product. Thus, the type and the amount of functional groups in the structure may change according to the drying method applied. In this study, the effect of drying, which is one of the Hummers method production parameters, on the oxidation level of the GO structure was investigated. For this purpose, GO structures were dried at different vacuum levels and atmospheric conditions. The produced GO structures were characterized using X-Ray Diffractometry (XRD) and Fourier Transform Infrared Spectroscopy (FTIR) devices. While XRD analysis showed the difference in phase structure, oxidation degree and interlayer distance between GO layers, FTIR analysis revealed the changes of functional groups in GO structures depending on drying conditions.

Keywords: Graphene oxide, hummers method, vacuum drying

INTRODUCTION

Carbon-based materials are of great interest in both industrial applications and scientific research due to their superior mechanical, electronic, magnetic, and optical properties. Carbon nanotubes, fullerene, carbon nanofibers, amorphous carbon, graphene and graphene oxide (GO) are examples of carbon materials (Mathur, Singh, & Pande, n.d.). Within these materials graphene has emerged as one of the most promising one because of its unique combination of exceptional properties such as excellent thermal and electrical conductivity, optical transparency, high elasticity, and high strength. Graphene consists of sp2 hybridized carbon atoms arranged in a honeycomb shape. It is a single layer material and can be described a single-atom-thick graphite layer. However, the production of graphene is difficult and costly, and its properties such as its inability to be dispersed in water or other organic solvents lead to problems in various applications (Padmajan Sasikala et al., 2018). GO, which is defined as the oxidized form of the graphene layer, contains hydroxyl, epoxy and carboxyl groups in its structure (Yu, Zha, Chaoke, Li, & Xing, 2016). The production of GO facilitates to obtain functionalized GO that has lower or higher conductivity properties than pristine graphene. GO is an extremely important material due to its properties such as its easy production, low production cost, high surface area, superior mechanical properties, low molecular weight, unique optical, electronic and magnetic properties, solubility in water and being open to many chemical processes thanks to the functional groups on its surface (Zhu et al., 2010). GO materials are used in many different application areas such as gas sensors, biosensors, high performance fibers, composite membranes, energy storage devices, electrochemical applications, various transistors, photo calibrators, various filters, biomarkers and tissue scaffolds (Shamaila, Sajjad, & Iqbal, 2016). There are three main routes available for GO synthesis; these are the Brodie method, Staudenmaier method and Hummers method consist of oxidation of graphite through strong acids and oxidants (Sun, 2019). Nowadays, Hummers method and various derivatives of this method are widely used in GO production. Basically, Hummers method uses sulphuric acid mixture, potassium permanganate and water to produce GO. Hummers method differs from other production methods with its advantages such as short production time, low cost, ease of production and high yield (Shamaila et al., 2016; Zhu et al., 2010). There are various parameters that can affect the product properties in Hummers method such as reaction time, temperature, amount of chemicals and graphite, washing steps, sonication and drying procedure (Adetayo, Runsewe, Adetayo, & Runsewe, 2019; Fathy, Gomaa, Taher, El-Fass, & Kashyout, 2016; Ikram, Jan, & Ahmad, 2020). In addition to the chemicals and various production stages used in Hummers method, it has been observed that the drying process which is the last stage of production, affects the final GO structure directly (Zhu et al., 2010). In order to obtain GO in solid form by using Hummers method, the green product, which has an aqueous solution or suspension-like structure, must be dried at the last stage of production. The drying process is carried out in an atmosphere or vacuum environment, at room temperature or at higher or lower temperatures (Adetayo et al., 2019; Shen et al., 2019). Yadav and Lochab (Yadav & Lochab, 2019) successfully produced GO by using different variations of

Hummers method and carried out the drying process at 50°C in a vacuum environment at the last stage of production. Similarly, in the study made by Yoo and Park (Yoo & Park, 2019) the post-production drying process was carried out overnight at 40°C in a vacuum environment. On the other hand, Panwar et al.(Panwar, Chattree, & Pal, 2015) improved the Hummers method in their study and dried the products at 55°C for 24 hours in a vacuum environment after the washing step. Gong et al.(H. P. Gong, Hua, Yue, & Gao, 2017) carried out the vacuum drying process at 100 Pa pressure and 50°C for 48 hours to investigate the effects of different drying methods. Many studies are present in the literature on drying process in a vacuum environment. However, to the best of our knowledge there are not enough studies on investigating the level of vacuum pressure in the production of GO materials during vacuum drying. In this study, the effects of vacuum drying at different pressures in GO production by Hummers method were investigated. In this context, GO samples in the form of aqueous solutions, were dried in a vacuum oven at different pressure levels. Structural characterization of the obtained products was carried out using X-Ray Diffractometry (XRD) and Fourier Transform Infrared Spectroscopy (FTIR) devices.

MATERIALS and METHOD

Production

In this study, all the chemicals and graphite powder were purchased from Sigma-Aldrich. Briefly, GO samples were synthesized using improved Hummers method (Panwar et al., 2015) graphite powder mixed with H_2SO_4/H_3PO_4 acid mixture and stirred for 1 hour. Homogenous mixture was obtained and afterwards, $KMnO_4$ was slowly added to mixture and temperature was raised to 45 ± 5°C. The solution was kept stirred and distilled water was added to solution slowly. Solution temperature was raised to 95 ± 5°C by the addition of water. Finally, H_2O_2 and distilled water were added to solution to terminate the reaction. In the next step, precipitated mixture was washed with aqueous HCl solution and distilled water. Finally, GO solutions were dried at constant 45°C under different vacuum pressure levels which are given in Table 1.

Table 1. Vacuum drying parameters of GO samples

Sample	Vacuum Pressure (mbar)	Temperature (°C)
GO 1	50	45
GO 2	250	45
GO 3	500	45
GO 4	750	45
GO 5	Atmospheric	45

Characterization

XRD analysis (Rigaku DMax-2100 PC) was performed using Cu Kα radiation (λ=0.154 nm) with a scan rate of 1°C/min to investigate the phase structure, oxidation degree and interlayer distances of GO samples. FTIR spectra was recorded with Thermo Scientific FTIR Spectroscopy with attenuated total reflectance (ATR) module to determine

the existence of functional groups in GO structure. FTIR analysis was performed with a scanning range of 4000-525 cm^{-1} and a resolution of 1 cm^{-1}.

RESULTS and DISCUSSION

XRD analysis provides information about phase characterization of carbon materials. Thus, we analyzed both graphite powders and GO samples to reveal the formation of GO structure. Fig. 1 shows the XRD patterns of both graphite powder which was used for GO production and synthesized GO samples. As can be seen from pattern that graphite powder shows crystalline structure with a characteristic peak at 26° which corresponds to (002) plane of graphite (Hanifah et al., 2019). On the other hand, all of the GO samples showed main characteristic peak of GO which is at the 2-theta value of around 11° and corresponds to (001) plane (Marcano et al., 2010). XRD patterns of GO samples showed no other phases or impurities which shows high purity of structure. Interlayer spacing values for each sample was calculated using Bragg's law to evaluate the oxidation degree of samples (Muzyka, Kwoka, Smędowski, Díez, & Gryglewicz, 2017) and given in Table 2. It is revealed that the distance between graphitic layers increases with the oxidation process. While the interlayer distance of graphite (d_{002}) was calculated as 0.34 nm, interlayer distances for GO 1-5 samples (d_{001}) were calculated as 0.79, 0.77, 0.80, 0.79 and 0.78 nm, respectively. XRD analysis showed that, during the production of GO samples by Hummers method, interlayer distances between graphitic planes increased as the oxidation process took place. H. Hsu et al.(Hsu et al., 2015) show that interlayer spacing of GO structure increasing because of the oxygen functional group improve the high specific surface area, high mesopore volume, and certain level of electrical conductivity properties of GO. Among the samples produced under different vacuum pressure levels, GO 3 sample showed highest degree of oxidation.

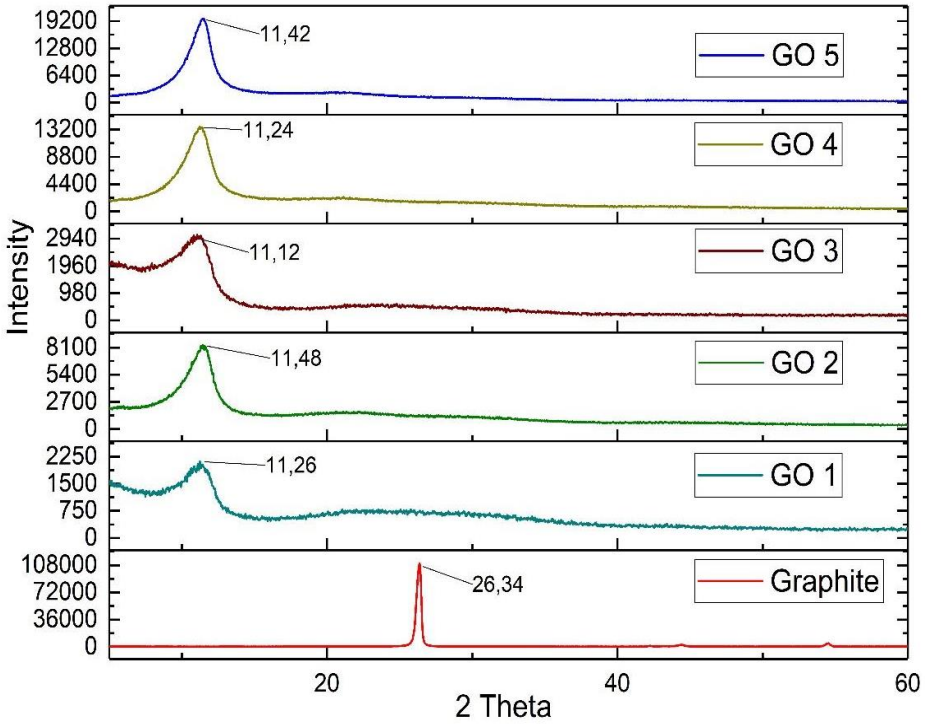

Figure 1. XRD patterns of graphite powder and GO samples

Table 2. Interplanar spacing (d) and 2-theta values of GO structures

Sample	GO 1	GO 2	GO 3	GO 4	GO 5	Graphite
2-Theta (º)	11.26	11.48	11.12	11.24	11.42	26.34
d (A)	7.9	7.7	8.0	7.9	7.8	3.4

FTIR spectra of GO samples synthesized under different vacuum pressure levels and graphite powder were given in Fig. 2. As can be seen, graphite powder does not show any considerable peaks and functional groups as a result of its characteristics (Hanifah et al., 2019) On the other hand, all of the GO samples showed characteristic peaks which proved the formation of GO structure. Strong broad peak around 3100-3400 cm^{-1} shows O-H groups stretchings or absorbed water as a consequence of oxidation process (Marcano et al., 2010). While the peak around 1720 cm^{-1} corresponds C=O stretching vibrations of carbonyls, peak around and 1620 cm^{-1} corresponds both C=C stretching and absorbed hydroxyl groups (Chen, Yao, Li, & Shi, 2013; Marcano et al., 2010). In addition, peaks around 1220, 1045 and 975 cm^{-1} corresponds to C-O vibrations, C-OH vibrations and C-O-C stretching, respectively (Nimbalkar, Tiwari, Ha, & Hong, 2020; Yoo & Park, 2019). Apart from that, absence of peaks around 2930 and 2850 cm^{-1} which appeared only in the samples dried under vacuum, revealed that during the vacuum drying procedure removal of C-H groups takes place (C. Gong, Acik, Abolfath, Chabal, & Cho, 2012). Gupta et al.(Gupta et al., 2017) investigated role of oxygen functional groups in reduced graphene oxide and found that as a result of reduction of COOH groups to CH_2 or CH_3, two sub bands appear around 2923 and 2855 cm^{-1}. Absence of same peaks in our samples shows the removal of some of the COOH groups as a result of vacuum drying. On the other hand, Fig. 2 also shows that GO 3 sample has the highest intensity for O-H groups. Thus, we can conclude that, GO 3 sample has more amount of functional groups compared to other samples, which also supports the XRD results.

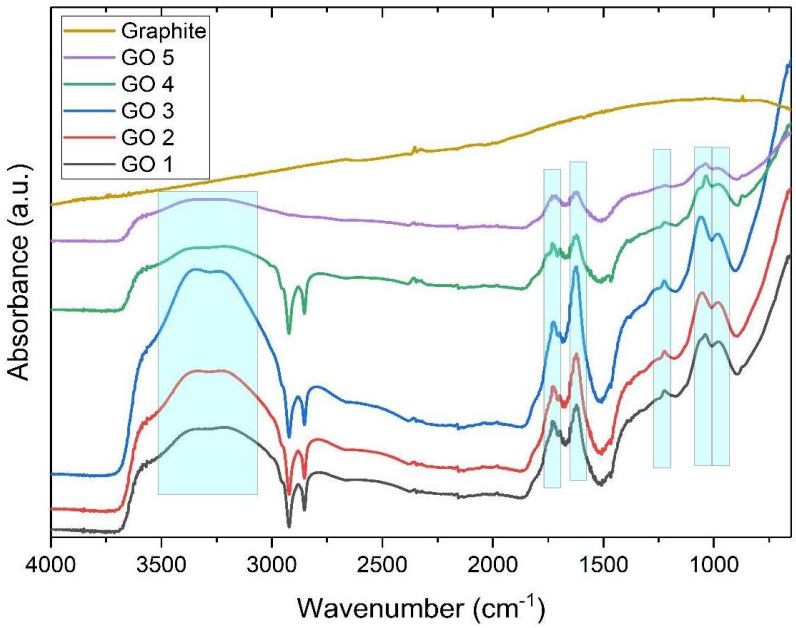

Figure 2. FTIR spectra of GO samples and graphite powder

CONCLUSIONS

In this study, GO structures successfully produced by modified Hummers method with different vacuum pressure conditions. Our study results showed that vacuum pressure in the drying procedure is an important parameter in GO production using the Hummers method. GO 3 samples which was dried under 500 mbar vacuum pressure conditions showed the highest degree of oxidation and interlayer distance. Additionally, it was found that more functional groups were present in the GO 3 sample than the other GO samples dried at different vacuum pressure levels.

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