

SYNTHESIS AND CHARACTERIZATION OF GRAPHENE OXIDE FILM

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Abstract

This research studied the synthesis of graphene oxide via a low-cost manufacturing method. The process started with the chemical oxidation of commercial graphite powder into graphene oxide (GO) by Hammer's method. It is proven that this method is promising way to synthesize graphene oxide on a large scale. GO nanocomposites thin films have been successfully deposited on ITO glass substrate. The films were deposited by spin coating method and heat treated at 80°C for 24 h. The synthesized graphene oxide was analyzed by X-ray diffraction (XRD), Energy dispersive X-ray (EDX), Fourier Transform Infrared spectroscopy (FTIR), UV-Vis spectroscopy and Field Emission Scanning Electron Microscopy (FESEM). The XRD pattern revealed a (0 0 1) diffraction peak, signifying the successful synthesis of GO. The elemental composition of GO was characterized by EDX analysis. The content of C is 67.35 % and the content of O is 29.75%. The mass ratio of C/O is 2.26. The results of FT-IR showed that C-O bond, O-H group with water molecules and C=C bond with graphene oxide. UV-Vis spectra of GO exhibited maximum absorption peak at 290 nm. SEM image confirmed that the size and synthesis of GO particles.

Keywords: Graphene oxide (GO), EDX, Hammer's method, SEM, XRD, FTIR

Introduction

Graphene is one atom layer thick carbon sheet. Graphene exhibits many interesting electronic, optical and mechanical properties due to its two-dimensional (2D) crystal structure [Avery Luedtke et al (2011)]. The charge carriers of graphene (i.e: electron) move ballistic in the 2D crystal lattice of graphene; hence it processes high conductivity despite it being an organic compound [Gianchang Li et al (2014) & F.Y. Ban et al (2012)]. Until 2004, Novoselov and Geim in the University of Manchester firstly separated the single graphene from graphite through separated simple mechanical peeling method. Graphene was increasing more and more attention in various areas of science and technology due to its remarkable physicochemical properties [Mohammed Dhenfouch et al (2014) & Jie Gao et al (2013)]. Currently, many methods had been explored to prepare graphene. Different graphene preparation method have been developed, such as chemical vapour deposition (CVD), microchemical exfoliation of graphite, epitaxial growth, chemical intercalation, and the reduction of graphene oxide. Among these methods, preparation of graphene from GO reducing has attracted considerable attention as a potential materials for use in various industrial application since it is unique cost advantage and promising for the mass-production of graphene based materials [Won-Chun OH et al (2010) & Hongyan Sun et al (2014)]. Graphene oxide is chemically similar to graphite oxide in that its surface carries many functional groups, such as C=O, O-H and -COOH. However, there are essential structural differences between graphene oxide and graphite oxide. For example, graphite oxide possesses a laminated structure, while graphene oxide does not; graphene oxide has a structure composed of one or more sheet layers peeled from GO [TataoQian et al (2013)].

Several electronic devices have been fabrication using GO as a starting material for at least one of the components. One such device is a graphene based field effect transistor [Prasanna

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Kumar et al (2014) & Vorrada Loryuen Yong et al (2013)]. Visible light transparent electrodes are important for both light emitting diodes (LEDs) and solar cell devices. Since GO can be processed in solution, using reduced graphene oxide (rGO) as transparent electrode is a convenient alternative to other transparent electrodes such as ITO for these devices [Hongiyun Sun et al (2011)]. In addition to being a transparent electrode, rGO has been used as a hole transport layer in polymer solar cells and LEDs [Nils Krame (2014)]. Nanocomposites of rGO have been used for high capacity energy storage in lithium ion batteries. In these studies, electrically insulating metal oxide nanoparticles were absorbed onto rGO to increase the performance of these materials in batteries [Zulmi Mo et al (2012) & Weifeng Zhao et al (2010)]. One use of GO in the biomedical field is as a component in drug delivery systems. Functionalized nanographene oxide has been used in several studies on targeted delivery of anti-cancer drugs [Sungjin Park et al (2009), Jianjiao Song et al (2014) and Zhigang Xiong et al (2010)]. GO and rGO have been used as components in several systems designed to detect biologically relevant molecules. GO has been used as a fluorescence quenching material in biosensors which utilize the fluorescence energy transfer effect. Folic acid functionalized GO was used as a component in a system used to detect human cervical cancer and human breast cancer cells [Michael J. McAllister et al (2007), Yunxian Piao et al (2011) & Mark Lundie (2014)].

In this study, graphene oxide (GO) was successfully synthesized by the Hummer's method. The structure of graphene oxide powders were measured by X-ray diffraction (XRD), Energy dispersive (EDX). Fourier transform infrared spectroscopy (FTIR) and the UV spectrometer will be used to measure the optical absorption properties of graphene oxide. The microscopic morphologies of GO powders were characterized by SEM.

Experimental Procedure

Sample preparation of GO powder

In this research, Graphite, Sulphuric acid (H_2SO_4), Sodium nitrate ($NaNO_3$), Phosphoric acid (H_3PO_4), Potassium permanganate ($KMnO_4$) and Hydrogen Peroxide (H_2O_2) were used as starting materials. All chemicals were analytically pure and directly used as received without further purification. Graphene oxide (GO) was prepared according to the Hummer method. In detail, 500 ml beaker was filled with 108 ml of H_2SO_4 , 5 g of graphite, 2.5 g of $NaNO_3$ and 12 ml of H_3PO_4 were added into the beaker. The suspension was stirred in an ice bath for 10 min. Next, 15 g of $KMnO_4$ was added to the suspension. The rate of addition was carefully controlled to keep the reaction temperature below $5\text{ }^\circ\text{C}$ and stirred in ice bath for 3 h. Then the mixture was put in a $40\text{ }^\circ\text{C}$ water bath for 60 min. The temperature of the mixture was adjusted to a constant $98\text{ }^\circ\text{C}$ for 60 min while water was added continuously. The color of the mixture was changed into yellow. Deionized water was further added so that the volume of the suspension was 400 ml. 15 ml of H_2O_2 was added after 5 min. The reaction product was washed by rinsing and centrifugation with 5 % HCl then deionized (DI) water for several times to reach pH 5-7. Finally, the product was dried at $60\text{ }^\circ\text{C}$ for 24 h in a vacuum oven. The obtained samples were characterized by X-ray diffraction (XRD) using (Rigaku RINT 2000) and Energy dispersive X-ray (EDX). Fourier transform infrared spectroscopy (FTIR). UV-Vis spectrometer (UV-Vis; UV-1800) was used to measure the optical absorption properties of GO. The nano structure was confirmed by scanning electron microscope (FESEM).

Cleaning of the Substrate

In the present study ITO/glass, cut into 1×1 cm square plates have been used as substrates. Prior to deposition the substrates are subjected to the following cleaning process to remove the unwanted impurities normally present on the surfaces of the glass plates exposed to the atmosphere.

1. The glass substrates are washed in soap solution by scrubbing the surfaces with a cotton swab dipped in liquid soap.
2. The glass slides are then rinsed thoroughly in deionized water to remove any trace of the soap solution left on the surface followed by acetone rinsing.
3. Then the slides are soaked in HCl acid and kept in room temperature for about two hours.
4. Finally, the substrates are rinsed thoroughly in deionized water and dried at 100°C for one hour in an oven.

Preparation of GO Paste and Spin Coating of GO Film

The GO film was prepared by spin coating method. Firstly, the GO paste was prepared by simple mechanical stirring followed by ultra-sonication. 1 g of graphene oxide was added in 100 ml of distilled water and stirred by magnetic stirrer for 1 h. After stirring, the GO solution was ultrasonicated for 1 h and stirred by magnetic stirrer at 80 °C for 6 h, then centrifuged and washed with ethanol for several times to remove the undecorated particle and unreacted chemicals. Finally, the GO paste was obtained and it was deposited onto the ITO glass substrate by spin coating technique. The structural properties of the film was measured by scanning electron microscope (SEM).

Results and Discussion

The XRD pattern of graphite and graphene oxide were shown in figure 1(a) and 1(b). According to the XRD pattern of graphite, which showed a strong and sharp diffraction peak at $2\theta=26.61^\circ$ has the interplanar distance of 0.334 nm. The graphene oxide were matched with standard library file 03-065-1528. GO shows an intense and sharp peak at $2\theta=11.07^\circ$ has the interplanar distance of 0.799 nm. The increase in interplanar distance of GO is due to the existence of oxygen functional groups. The sharp peak at 2θ value of graphene oxide for observed sample and 2θ value of graphene oxide in international journals were compared in table 1.

2θ (deg)	International Journal
10.34°	Won-Chun Oh et al 2010 Journal of the Korean Physical Society, Vol. <u>56</u> , No. 4, pp. 1097~1102 [30]
10.6°	JieGao et al , 2013 Polymer-Plastics Technology and Engineering, <u>52</u> : 553–557, [40].
10.24°	F.Y. Ban et al 2012 Int. J. Electrochem, Sci., <u>7</u> 4345 -4351 [28].

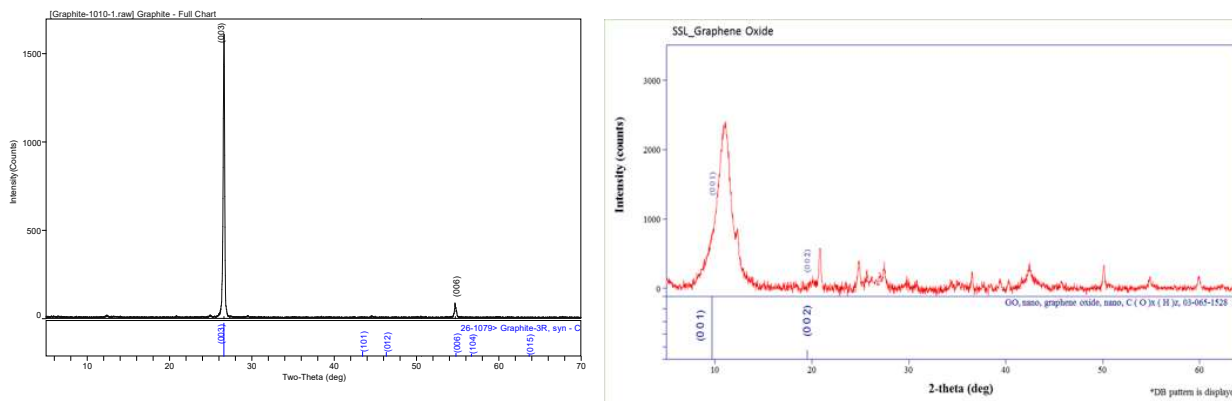
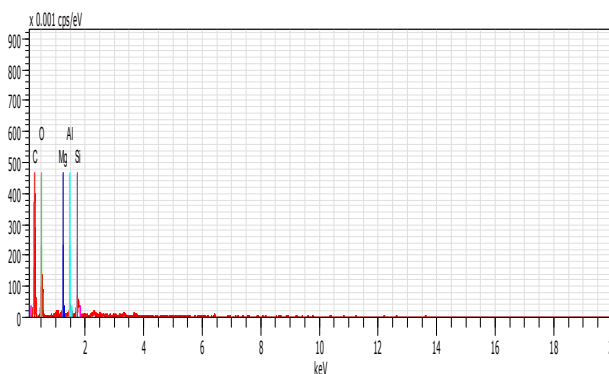


Figure 1 XRD pattern of (a) graphite and (b) graphene oxide

EDX Analysis of Graphene Oxide (GO)

The EDX figure of graphene oxide was shown in figure 2 and the results of the EDX elemental for C and O elements of GO are listed in table 2. The content of C is 67.35 % and the content of O is 29.75%. The mass ratio of C/O is 2.26. The presence of higher amount of carbon and oxygen. The oxygen and carbon peaks are then converted into a percentage, which has been used to set the current graphene oxide composition specification. Other elements were found as impurities. The percentage presence of normal concentration and atomic concentration is given accordingly. The international results of EDX for graphene oxide are listed in table 3.



	[wt. %]	[wt. %]	[at. %]	[wt. %]
C 6 K-series	67.35	67.35	74.03	13.5
O 8 K-series	29.75	29.75	24.55	8.2
Mg 12 K-series	0.53	0.53	0.29	0.1
Al 13 K-series	0.71	0.71	0.35	0.1
Si 14 K-series	1.67	1.67	0.79	0.2
Total: 100.00 100.00 100.00				

Figure 2 EDX spectrum of graphene oxide

Table 2 The results of the EDX elemental for C and O elements of GO

Table 3 The EDX elemental microanalyses for C and O elements in international journals

Element (wt. %)		C/O	International Journals
C	O		
51.32	44.27	1.15	Won-Chun Oh, et al., 2010 Journal of the Korean Physical Society, Vol. 56, No. 4, pp. 1097~1102 [30].
65.47	35.53	1.84	Yunxian Piao, et al., 2011 The Royal Society of Chemistry [39].
67.35	29.75	2.26	Observed sample

FTIR Analysis of Graphene Oxide (GO)

Infrared absorption spectrum diagram (FTIR) of graphene oxide was shown in figure 3. FTIR analysis allows qualitative discussion of the structure of graphene oxide. According to the FTIR analysis the peak at 1082.10 cm^{-1} and 1384.94 cm^{-1} which are attributed to the C-O bond, confirming the presence of oxide functional groups after the oxidation process. The peak at 1626.05 cm^{-1} can be attributed to the stretching vibration of C=C bond. The 3408.33 cm^{-1} correspond to O-H group of water molecules absorbed on graphene oxide. The presence of these oxygen containing groups reveals that the graphite has been oxidized.

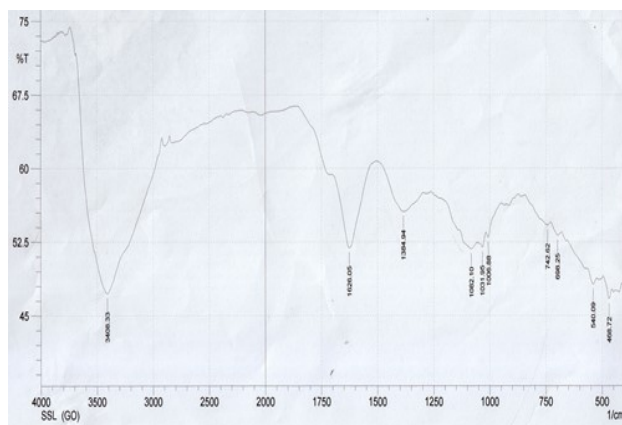


Figure 3 FTIR spectrum of graphene oxide

UV-Visible Analysis

The UV-Vis spectra of GO powder was recorded with respect to the glass substrate placed in the reference beam using beam spectrometer in the range 190 to 1100 nm. The absorption spectrum of GO deposited on glass substrate is shown in figure 4 (a). The figure shows high absorption coefficient in the UV region. [In aqueous suspension, measurements reveal strong optical absorption in the UV (Mark Lundie et al)]. The optical band energy (E_g) of the semiconductor is calculated from the Tauc relation. The resultant values of E_g for GO is found to be about 3.93 eV.

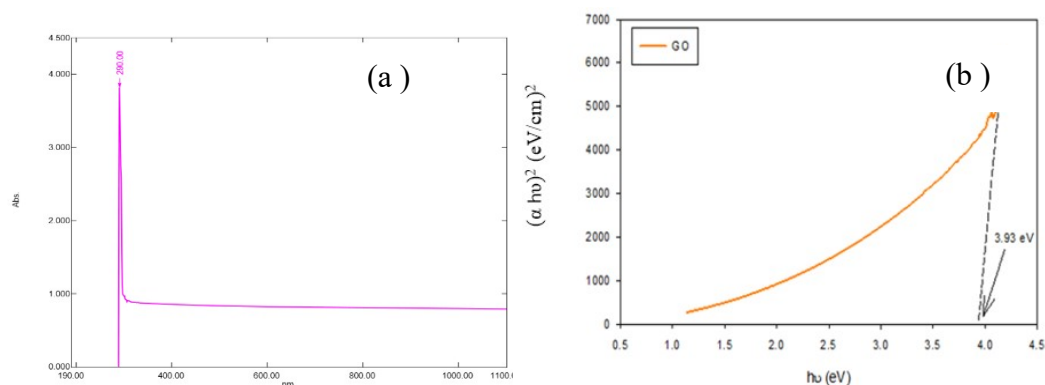


Figure 4 The UV absorption spectrum (a) and Plot of $(\alpha h\nu)^2$ vs. photon energy ($h\nu$) for graphene oxide (b)

SEM Analysis of Graphene Oxide (GO)

Figure 5 presented the SEM image of the synthesized graphene oxide, revealing a crumpled and rippled structure which was the result of deformation upon the exfoliation and restacking processes. Moreover, it indicates a flaky nature, randomly folded, few-layered and exfoliated structure. Surface of the graphene oxide was rough with some crumpling and agglomeration, which may be attributed to the residual oxygen-containing functional groups (e.g. -OH). This further shows strong oxidation of graphite by the Hummers method. From the figure 5 (b) GO film, it can be observed that graphene oxide film has a layered structure, which affords ultrathin graphene sheets. Such sheets are folded or continuous at times and it is possible to distinguish the edges of individual sheets, including kinked and wrinkled areas. Moreover, the GO sample contains several layers of aggregated and square-shaped crumpled sheets closely associated with each other to form a continuous conducting network. The edges of the GO sheets become crumpled, folded, and closely restacked, and the surface of GO exhibits a soft carpet-like morphology, possibly because of the presence of residual H₂O molecules and hydroxyl groups.

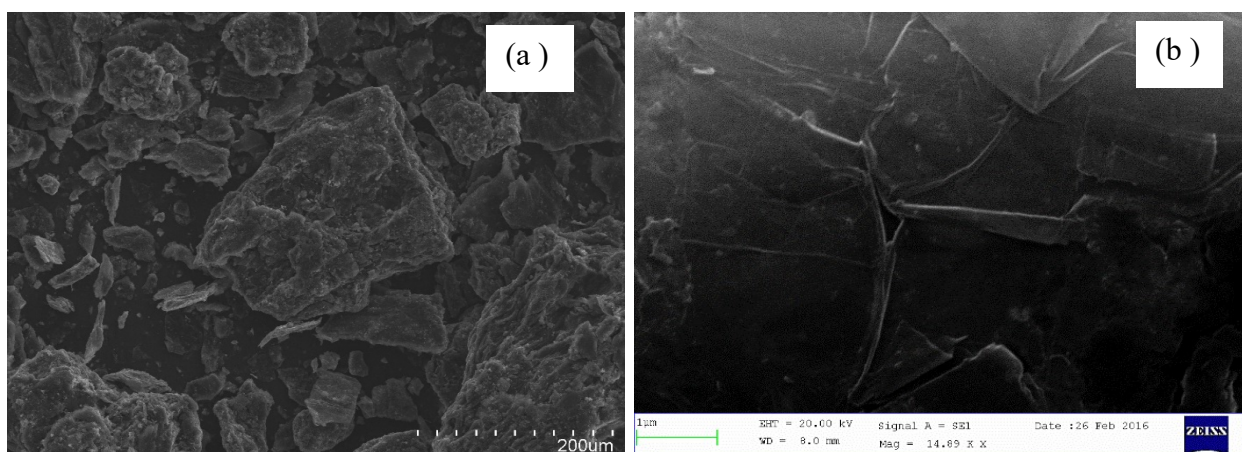


Figure 5 SEM image of Graphene Oxide powder (a) and film (b)

Conclusion

The graphene oxide (GO) has been successfully synthesized by using Hummer's method. The graphene oxide was characterized using XRD, EDX, FTIR, UV-Vis and FESEM. In XRD analysis the graphene oxide was matched with standard library file 03-065-1528. The increase in interplanar distance of GO is due to the existence of oxygen functional groups. The content of C is 67.35 % and the content of O is 29.75%. The mass ratio of C/O is 2.26. According to the FTIR analysis, the -OH groups were found and the presence of these oxygen-containing groups reveals that the graphite has been oxidized. UV-Vis spectra of GO exhibited maximum absorption peak at 290 nm. According to the SEM analysis, surface of the graphene oxide was rough with some crumpling and agglomeration, which may be attributed to the residual oxygen-containing functional groups (e.g. -OH). According to the SEM image of GO film, the sample was well deposited onto the ITO glass substrate and it was proved that the spin coating technique was suitable in the preparation of GO film. The characterization results proved that there was an interaction between starting chemicals.

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