Comparison on Graphite, Graphene Oxide and Reduced Graphene Oxide: Synthesis and Characterization

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ABSTRACT

Graphene oxide (GO) and reduced graphene oxide (RGO) are known to have superior properties for various applications. This work compares the properties of GO and RGO with graphite. GO was prepared by using Improved Hummer's method whereas the produced GO was subjected to chemical reduction with the use of hydrazine hydrate. Graphite, GO and RGO had different morphologies, quality, functionalized groups, UV-Vis absorption peaks and crystallinity. With the removal of oxygen-containing functional group during reduction for RGO, the quality of samples was decreased due to higher intensity of D band than G band was seen in Raman results. In addition, platelet-like surface can be observed on the surface of graphite as compared to GO and RGO where wrinkled and layered flakes, and crumpled thin sheets were observed on GO and RGO surface respectively. Fourier Transform Infra-Red (FTIR) analysis showed the presence of abundant oxygen-containing functional groups in GO as compared to RGO and graphite. The characteristic peaks at 26.62°, 9.03° and 24.10° for graphite, GO and RGO, respectively, can be detected from X-Ray diffraction (XRD). Furthermore, the reduction also caused red shift at 279nm from 238nm, as obtained from ultraviolet visible (UV-Vis) analysis. The results proved that GO was successfully oxidized from graphite whereas RGO was effectively reduced from GO.

INTRODUCTION

Graphite, one of many allotropes of carbon, can provide great potential in many applications such as in electronics and functional nanocomposites[1], among many others. Graphene, single layer form of graphite is a one- atom-thick planar sheet of sp^2-bonded carbon atoms which are arranged in a hexagonal lattice [2]. Both graphite and graphene have unique properties which might be limited by its dispersibility especially when mixed with polar polymer matrices [2] due to its hydrophobicity in nature.

On the other hand, GO and RGO have different properties as compared to graphite and graphene. GO is the oxide form of graphene[2], where oxygen is introduced to graphene through chemical oxidation[3]. Moreover, GO is described as heavily oxygenated, with the presence of many oxygen-containing functional groups such as epoxide,

hydroxyl, carbonyl and carboxyl groups on its basal plane[2]. Thus, with the presence of these functional groups, GO becomes hydrophilic which allows better interfacial interaction with polar polymer matrices for improvement of mechanical and electrical properties for various applications. However, the oxygen functionalization on GO reduced the electrical conductivity and therefore, GO becomes less preferable for conductive polymer-based composites[2].

Besides, RGO contains fewer amounts of oxygen functionalized groups as compared to GO which can be synthesized in chemical and thermal reduction. However, the thermal reduction requires high cost since the reduction is conducted at high temperatures, thus, the chemical reduction is preferable by most researchers [2]. There are plenty of reducing agents such as hydrazine hydrate[3], ascorbic acid[4] and others were used in the past and recently works.

In this paper, we demonstrated the synthesis of GO and RGO and investigation of their morphologies, crystal phases, optical properties, qualities and existence of oxygen-containing functional group. We also compared the SEM, FTIR and XRD results of GO and RGO with graphite to verify the successful synthesis of GO and RGO due to their different properties. The Improved Hummer's method was used to synthesize GO and it was further reduced to RGO with the use of hydrazine hydrate as reducing agent. Subsequently, both GO and RGO were subjected to several characterizations for study of abovementioned properties.

EXPERIMENTAL

Materials

Graphite powder and hydrazine hydrate were bought from Sigma Aldrich, Malaysia. Sulphuric acid (H_2SO_4), phosphoric acid (H_3PO_4, 85 %), potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2) and hydrochloric acid (HCl) were purchased from ChemoLab, Malaysia.

Procedures

Synthesis of Graphene Oxide (GO)
A mixture of H_2SO_4/H_3PO_4 at a volume ratio of 9:1 (180:20 ml) was prepared. The mixture was stirred for 15 minutes before 1.5 g of graphite powder was added. Next, 9.0 g of $KMnO_4$ was added into the mixture slowly in continuous stirring condition. The mixture was allowed to stir continuously for 72 hours. After 72 hours, 4ml of 30 % hydrogen peroxide (H_2O_2) was added to terminate the reaction. The mixture was divided into 6 separate 50 ml centrifuge tubes for cleaning. The cleaning was done by using hydrochloric acid (HCl) and deionized (DI) water alternately with the centrifugation at 5000 rpm in 15 minutes for each washing step. These steps were repeated twice. Lastly, the final product was dried in an oven at 80 °C for 24 hours.

Synthesis of Reduced Graphene Oxide (RGO)

A mixture of 1.5g of GO powder and 500 ml of DI water was prepared. The mixture was stirred for 30 minutes to form GO dispersion. Next, 0.5 ml of hydrazine hydrate was added into the dispersion. The mixture was heated to 80°C by using oil bath and was subjected to continuous stirring for 72 hours. After 72 hours, the mixture was transferred into 6 different 50 ml centrifuge tubes for cleaning. The cleaning was done by adding DI water and centrifuged at 5000 rpm for 15 minutes. These steps were repeated twice before dry in an oven at 80°C for 24 hours.

Characterization

Graphite, produced GO and RGO were analyzed by using several techniques. Raman spectroscopy (Raman, Perkin Elmer Raman spectrometer) was used to analyze the quality of the produced GO and RGO at wavelength 1000-4000 cm^{-1}. For morphological analysis, Scanning Electron Microscopy (SEM, Jeol JSM 6460LV) was used. Besides, Fourier Transform Infra-Red (FTIR, Perkin Elmer FTIR spectrometer) was used to investigate the presence of functional groups in all three samples, within the wavelength range of 4000-400 cm^{-1}. Next, X-Ray Diffraction (XRD, Bruker D2 Phaser) examined the crystallinity phase present in the samples from 8° to 70°. Lastly, optical properties for all samples were inspected within wavelength from 200-500 nm with the use of UV-Visible Spectroscopy (UV-Vis, Perkin Elmer UV-Vis spectrometer).

RESULTS AND DISCUSSION

Raman Spectroscopy

Raman spectroscopy provides the information based on the inelastic (Raman) cattering of a molecule irradiated by a monochromatic light, where laser is normally used[5]. Fig. 1 shows Raman spectra for GO and RGO.In Fig.1, two fundamental vibrations can be observed in the range of 1100 and 1700cm^{-1} for GO and RGO. The D vibration band which is formed from a breathing mode of j-point photons of A1g symmetry[6] can be seen at 1348.31 and 1353.20 cm^{-1} for GO and RGO, respectively. On the other hand, G vibration band from first-order scattering of E2g phonons by sp^2 carbon[6] appeared at 1594.19 for GO and 1586.56 cm^{-1} for RGO. Furthermore, G vibration band also contributed by the presence of the stretching C-C bond, which is common in all sp^2 carbon systems[7]. The D band and G band in the Raman spectrum (Fig. 1) symbolize the disorder bands and the tangential bands, respectively[8].

Besides, a broad and shifted to higher wavenumber of 2D band was seen at 2716.77 cm^{-1} for GO in Fig. 1. 2D band can be used to determine the layers of graphene (monolayer, double layer or multilayer) as it is highly sensitive to stacking of graphene layers[6]. Thus, the location of 2D band confirms that the produced GO was multilayer since monolayer graphene normally observed at 2679 cm^{-1} from the spectra[7]. In addition, the shifted location of 2D band also due to the presence of oxygen-containing functional groups which prevents the graphene layer to stack[6]. Moreover, RGO also has this 2D band shown at 2706.20 cm^{-1} as in Fig. 1. It is because after the reduction of GO to RGO, less amount of residue of oxygen-containing functional groups were remained and caused the RGO to stack. Furthermore, the position of 2D band in this experiment is quite near to the work demonstrated by Thakur and Karak where the reduction of GO was one by using phytochemicals extracted from leaves,

peels or other parts of plants. Phytochemicals were used as an alternative for chemicals as reducing agent [6].

ID/IG ratio for GO was determined to be 0.86. After reduction, the ID/IG for RGO was increased[3, 9] due to the restoration of sp^2 carbon and decreased in the average sizes of sp^2 domains upon reduction[10, 11]. Higher intensity in D band also suggested that more isolated graphene domain were presented in RGO as compared to GO and also due to removal of oxygen moieties from GO after reduction [9, 12].
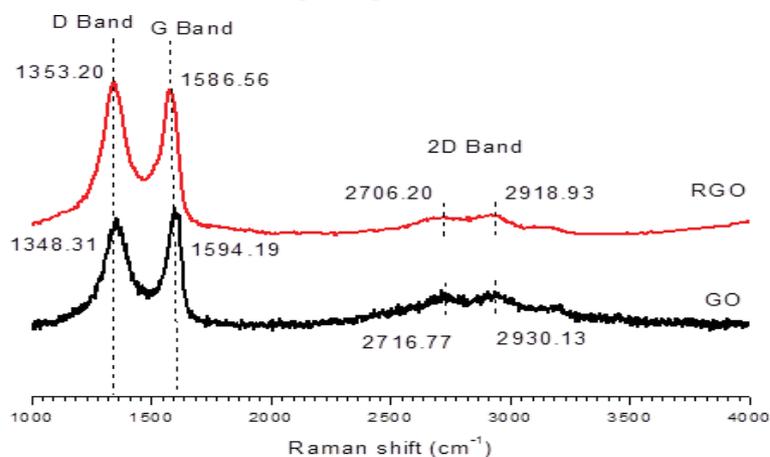

FIGURE 1. Raman spectra for GO and RGO.

Scanning Electron Microscopy (SEM)

SEM was used to check on the morphologies of graphite, GO and RGO samples. The micrographs obtained from SEM gave a highly magnified image on the surface of a material[13]. Figure 2 shows the micrographs for graphite, GO and RGO samples at magnification of 10000x.

Figure 2 (a) shows the micrograph of graphite. The micrograph indicates the graphite had platelet-like crystalline form of carbon[14]. However, the SEM micrograph of GO in Fig. 2 (b) shows that the wrinkled and layered flakes were seen on the surface. Therefore, the presence of flakes implies that the graphene layers were fully oxidized to GO[15]. In addition, Fig. 2 (c) exhibits the micrograph of RGO where chemical reduction by using hydrazine hydrate was conducted, the RGO surface contained crumpled thin sheets which accumulated to form disordered structure material[15, 16].

The morphologies of RGO (Fig. 2c) are quite similar with the work reported by Loryuenyong et.al although they used modified Hummer's method[14] as compared to our method, improved Hummer's method.
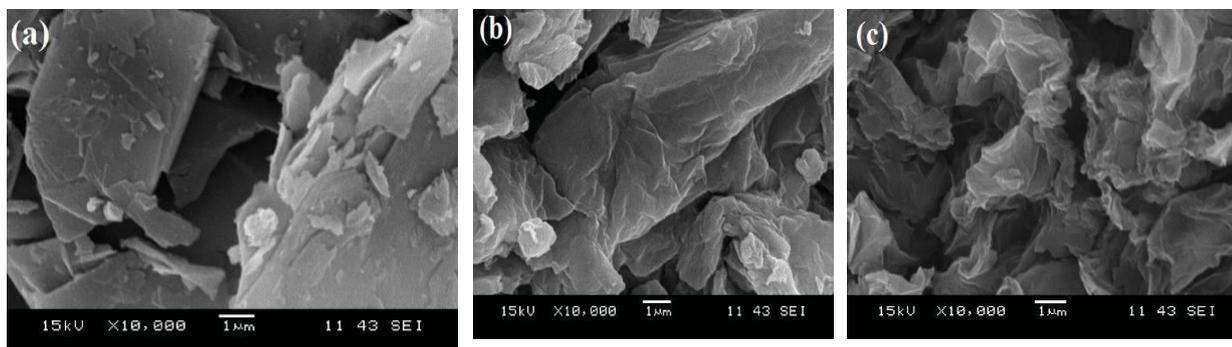
**FIGURE 2**. SEM micrographs of a) graphite b) GO and c) RGO.

Fourier Transform Infra-Red (FTIR)

Figure 3 shows FTIR spectra for graphite, GO and RGO. FTIR was used in order to investigate the presence of functional groups in the samples from the obtained vibrational (transmittance/absorption) spectra. This analysis is based on the vibrational excitation of molecular bonds by absorption of infrared light energy [17], within the wavelength from 4000 to 400 cm^{-1}.

GO, the oxide form of graphite, is expected to contain more oxygen-containing functional groups after oxidation process. However, with reduction, RGO is expected to have minimal amount of oxygen-containing functional groups.

From Fig. 3, no significant peak was found for graphite[18]. On the other hand, for GO, the intense and broad peak that appeared at wavelength of 3420cm^{-1} confirmed the presence of O-H bond (hydroxyl group). Besides, – C=O stretching (–COOH group) was presented at 1739 cm^{-1} whereas C-O-C stretching (epoxy group) can be seen at wavelength of 1226 and 1015 cm^{-1}. With the presence of all these carboxylic, hydroxyl, epoxide and carbonyl groups, oxygen molecules (O) were confirmed to be greatly occupied at the edge and basal plane of GO[3] which can be concluded that GO was synthesized successfully [19].

For RGO, the peak at 3420 cm^{-1} became less broad as compared with GO proving that the hydroxyl group was removed significantly. It is also noticeable that other peaks at 1739, 1226 and 1015 cm^{-1} became less intense than those peaks at the same location in FTIR spectra of GO, which were also due to the removal oxygen by using hydrazine hydrate[3] during the reduction. Therefore, the oxygen-containing functional groups were successfully removed partially and the low amounts of residue of functional groups are still remain at the edge and basal plane of RGO.
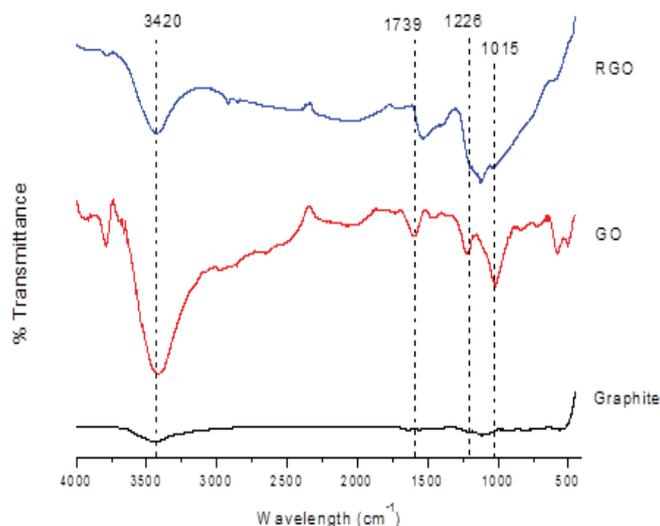
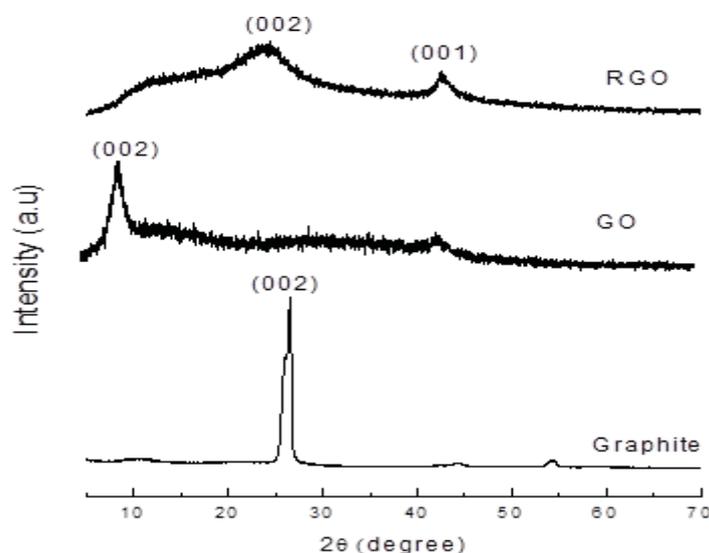**FIGURE 3.** FTIR spectra for graphite, GO and RGO.

X-Ray Diffraction (XRD)

XRD was used to investigate the crystal phase and to determine the interlayer spacing for graphite, GO and RGO[9]. Figure 4 shows the XRD spectra for graphite, GO and RGO.

For graphite, one sharp peak can be observed at $2\theta = 26.62°$. This peak confirmed the presence of well-arranged layer structure with 0.3346 nm d-spacing (FWHM = 0.3456), along the (002) orientation with ICDD File 9012230 (Reference pattern 01-275-2078)[3].

For GO, the 2θ peak can be seen to be shifted to 9.03°, which indicated that the graphite was fully oxidized into GO[9]. Furthermore, the interlayer distance of GO was increased with d-spacing of 0.9794 nm (FWHM = 0.6298). This increment was resulted from the intercalation of oxide functional group at the carbon basal plane such as epoxy, hydroxyl, carbonyl, and carboxyl groups during chemical oxidation reaction[20-22]. Therefore, the distance between consecutive carbon layers increased.

After oxygen-containing functional groups were eliminated significantly during the chemical reduction, a broader peak can be seen for RGO at 2θ = 24.10°. This indicates that the π-conjugated structure of graphene has been restored considerably at the produced RGO [6, 9]. The presence of broad peak (002) for RGO implied that the crystal phase (002) was arranged randomly as compared to the high crystallization structure of graphite where a sharp and intense (002) peak can be observed (Fig. 4). The poor arrangement could be caused by the formation of single or only a few layers of RGO after reduced from GO [3, 6]. In addition, the d-spacing of RGO was reduced from 0.97942 nm to 0.36895 nm which proved that oxygen-containing functional groups were removed efficiently [5], [6, 23, 24]. It also revealed that the thin RGO nanosheet were stacked to each other to form thick piles structure due to the exist of strong Van der Waals' forces between each layer [25]. Another less intense peak can be seen at 2θ =42.60° with (001) orientation which attributed by the turbostratic band of disordered carbon materials[3].
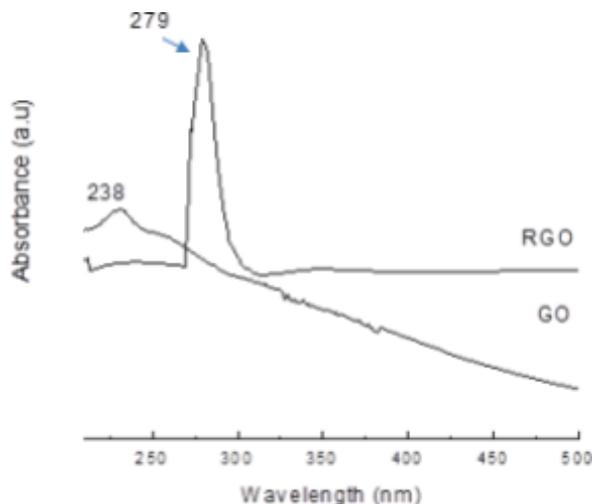

FIGURE 4. XRD spectra of graphite, GO and RGO.

UV Visible Spectroscopy

UV-Vis spectroscopy was done in order to monitor the degree of oxidation of GO and RGO[3]. The spectroscopy would produce individual spectra for both GO and RGO as shown in Fig.5.

In Fig. 5, the absorption peak of GO dispersion was seen at 238 nm. This is quite similar with the work reported by Li et.al (2008) where the absorption peak was observed at 231nm and it was shifted to higher wavelength (>231nm) with increasing of reaction times[26]. This strong absorption peak found at around 230 nm was ascribed to the $\pi–\pi^*$ transitions of graphitic C-C bonds[3, 6, 24]. After reduction, there was a redshift towards higher wavelength for RGO

from 238 to 279nm (Figure 5). The absorption peak was found at 279 nm. The shift was similar with the work reported by Li et.al (2008) due to the $\pi–\pi^*$ transition of graphitic C-C ring[3].

FIGURE 5. UV-Vis spectra of GO and RGO.The value of the optical band gap was estimated through a Tauc plot of $(\alpha h\upsilon)^2$ vs. $h\upsilon$ with linear extrapolations (Fig. 6). For GO, its optical band gap range was 1.6-2.5 eV while for RGO, its optical band gap range was 1.1-1.4 eV. The similar pattern of GO having higher optical band gap than RGO can be observed in the work reported by Velasco-Soto and co-workers (2015) where 2.70 eV and 1.55 eV were estimated as optical band gap for GO and RGO, respectively. They used glucose, fructose and ascorbic acid as reducing agents instead of hydrazine hydrate[4].

FIGURE 6. $(\alpha h\upsilon)^2$ vs. $h\upsilon$ graph for GO and RGO, in determining the optical band
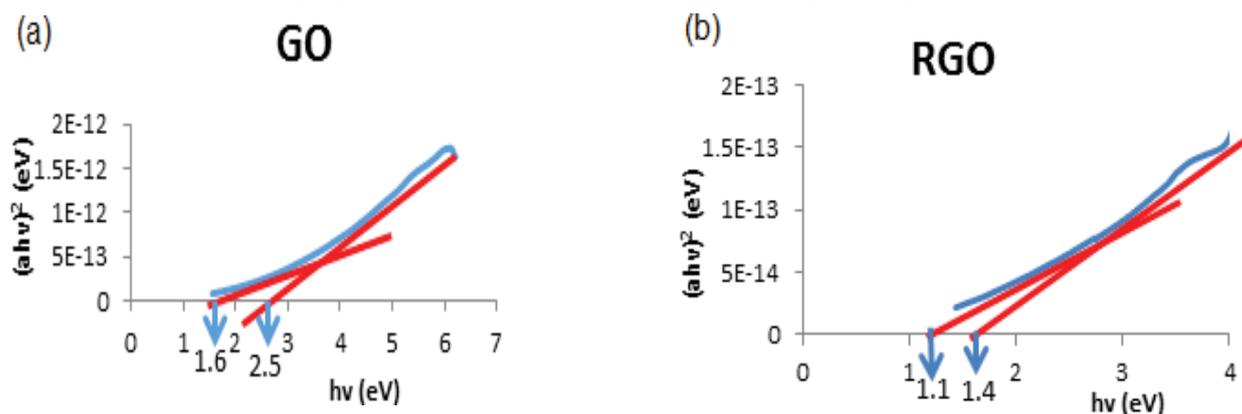
gap.

CONCLUSIONS

In conclusion, both GO and RGO were successfully prepared. GO was prepared by using improved Hummer's method and with the use of hydrazine hydrate, GO was reduced to RGO. The comparison results of XRD, SEM and FTIR results between GO and RGO with graphite indicated that GO and RGO were synthesized successfully. In SEM images, graphite, GO and RGO showed distinctive morphologies. Besides, FTIR results showed that the amounts of oxygen-containing functional groups were removed significantly in RGO as compared to GO. Furthermore, graphite, GO and RGO displayed their unique characteristics XRD patterns at 26.62°, 9.03° and 24.10° respectively. These unique properties possessed by graphite, GO and RGO could open up possibilities to satisfy the needs in various applications.

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