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EFFECT OF REDUCTION TIME ON OPTICAL PROPERTIES OF REDUCED GRAPHENE OXIDE

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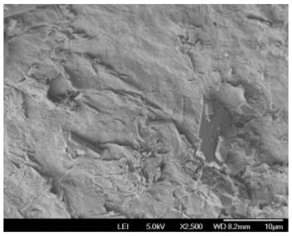
Graphical abstract



Abstract

Graphene and its' derivatives received tremendous attention. The characteristics and properties of graphene made the material suitable to be used in many applications such as polymer composites, transistors and sensors. Graphene oxide (GO) and reduced graphene oxide (rGO) are few examples of graphene derivatives. GO can be synthesized in many ways. In this study, GO was produced via modified Hummer's method. Meanwhile, sodium borohydride ($NaBH_4$) is chosen as a reductant to further reduce the GO via chemical reduction. The material was characterized using FT-IR, UV-Vis and FESEM to observe the characteristics which occurred during the reduction process. From the FT-IR spectrum it is clearly shown that the carbonyl (C=O) and epoxy groups were eliminated on rGO. On the other hand, the band gap value of rGO reduced gradually as the reduction time increase. Besides that, the morphology of GO and rGO was also compared under the magnification of 2500x.

Keywords: Band gap, modified Hummer's method, reduced graphene oxide, chemical reduction, graphene

1.0 INTRODUCTION

Recently, the research of graphene and graphene-based polymer received tremendous attention due to the increasing discovery in the field of nanoscience [1]. Graphene oxide (GO) has a higher capacitance than graphene because of the pseudocapacitive behavior due to oxygen-containing functional group [2]. Modified Hummers method is the most common method used to produce GO that takes into account in terms of safety and productivity [3]. Basically, this method does not release any hazardous ClO_2 gas [4] and the reaction time takes only about 2 h to finish [3].

GO is a graphene sheet with carboxylic groups at its edges while phenol, hydroxyl and epoxide groups on its basal plane [5]. Meanwhile, many of the functional groups on will be eliminated on the surface of reduced graphene oxide (rGO) and it can be obtained through thermal annealing or chemical treatment [5]. It is found that chemical reduction of GO is commonly used due to several advantages such as the product can be produced in bulk and graphene with processability and functionality can be obtained [6]. In addition, this method is very suitable to be carried out under mild conditions [7] and cheaper [8]. Hence, chemical reduction method is chosen to synthesis rGO in this study.

The most common reductant that can be used to reduce GO is hydrazine, sodium borohydride ($NaBH_4$) and hydrobromic acid (HBr) [9]. Reduction via hydrazine and its derivatives like hydrazine hydrate and dimethylhydrazine is usually obtained by adding the liquid reagents into GO aqueous dispersion. The hydrophobicity improves but the graphene-based nanosheets agglomerates. The rGO shows that the highest electrical conductivity is 99.6 S cm^{-1} while the C:O ratio is 12.5 [8]. However, the use of hydrazine as a reductant could give rise to several problems. Hydrazine is one of the powerful reducing agent that is corrosive and highly flammable. Therefore, hydrazine can cause danger to health and also an environmental hazard because of the production of hydrazine-reduced GO. Besides that, the fragment of hydrazine could be destructive to few applications like organic solar cells because it could decrease solar cell donor compounds such as poly(3-hexythiophene) and lead to complexity of photovoltaic cell manufacturing [10]. The use of hydrazine also will cause the rGO to have high sheet resistance that is not suitable for some applications [11]. Hydrazine introduce heteroatomic impurities. Meanwhile, the residual C-N groups will cause rGO to be functioned as n-type dopants [12].

Due to environmental and health issues, $NaBH_4$ is the common reductant used to produce rGO as it is efficient, non-toxic, non-corrosive and also cheap. This reagent able to reduce aldehyde and ketone to alcohol [13]. However, $NaBH_4$ is unable to reduce carboxylic acids, esters, amides and nitriles [14]. Interestingly, study reported that $NaBH_4$ is much efficient than hydrazine to reduce GO [11]. Even $NaBH_4$ will be hydrolyzed by water slowly but the reaction is kinetically slow and still the GO can be reduced [8]. The C:O ratio is found to be around 5.3 when GO is reduced using $NaBH_4$ [11]. Meanwhile, the sheet resistance is found to be at 59 k□/m^2 as compare to 780 k□/m^2 when GO is reduced with hydrazine. rGO has an unique structure with remarkable physical properties such as conductivity, mechanical strength and flexibility [15].

It is known that, the reduction of GO will partially reestablished the structure and properties of graphene. One of the main reason GO need to be reduced is to restore the electrical conductivity (10 – 1000 S cm^{-1}) [16] and thermal stability near to graphite [7]. On the other hand, rGO has less of all the functionalities which result in restoration of graphitic domains with an extensive conjugated sp^2 carbon network. Thus, rGO is hydrophobic and insoluble in most solvents [17] because most of their oxygen-containing groups are removed in the reduction step [9]. However, the nature of rGO will depend on the reduction process and it has not been study thoroughly. So, the characteristics and properties of rGO is not well known. Therefore, this study will elucidate the characteristics of rGO based on the reduction time. The effect of reduction time on the band gap of rGO also will be discovered as it is essential for certain applications like photocatalysis that can be used to degrade toxic pollutants [18].

2.0 METHODOLOGY

GO was obtained using modified Hummer's method. 4 g of graphite powder was added into 100 ml of concentrated sulfuric acid (H_2SO_4) and followed by the slowly addition of 4g of sodium nitrate ($NaNO_3$). Next, 12 g of potassium permanganate ($KMnO_4$) was added slowly under stirring and the temperature of the mixture was kept below 10 ^{O}C in ice bath. The dark-blue mixture was stirred at 35 ^{O}C for 30 min before 100 ml of deionized water was added to the mixture and it turned to yellowish brown. The mixture was stirred again for 30 min at 95 ^{O}C. Next, 600 ml of distilled water, 20 ml of 30 % hydrogen peroxide (H_2O_2) aqueous solution and 100 ml of 10 wt% hydrochloric acid (HCl) were added after brilliant yellow color with bubbles appeared in the solution. Then, the mixture was centrifugated and washed with deionized water to expel metal ion and acid until neutral pH was obtained. GO film that produced was dried in an oven for 12 h at 60 ^{O}C [19].

To obtain rGO, 0.8 g of GO was sonicated in 50 ml of water for 30 minutes. $NaBH_4$ solution was prepared and the pH value was adjusted with NaOH to pH 12 to prevent any occurring hydrolysis. After half an hour, $NaBH_4$ solution was added drop-wise into GO solution and the solution was heated at 80°C for 8 hours with continuous stirring. Then, the mixture was filtered out via vacuum filtration and washed with EtOH and distilled water for several times. The product was dried in an oven at 70 ^{O}C for 24 hours to obtain reduced graphene oxide. The procedure was repeated with different reduction time (8, 16, 24 and 32 hour) [20]

For characterization, attenuated total reflectance fourier transform infrared spectroscopy (ATR-FTIR) (Perkin Elmer, FT-IR Spectrometer Frontier) was used to study the existing functional groups of the product. The IR spectra was collected after 32 scans in the 4000 – 500 cm $^{-1}$ region in ATR mode at a resolution of 4 cm $^{-1}$. To obtain the band gap value, ultraviolet-visible-near infrared spectrophotometer (UV-Vis-NIR) (UV-3101PC) from 200 – 1000 cm^{-1} was used. Then, to determine the band gap of GO and rGO Tauc's equation was used $ahv = A (hv - E_g)^{n}$. ahv^2 vs hv graph was plotted first and extrapolation of the linear region gave the value of optical band gap (E_g) since $E_g = hv$ when $ahv^2 = 0$. The morphology of the material was also studied under field emission scanning electron microscope (FESEM) (JEOL, JSM-6701F). The sample was observed under the magnification of 2500x and 10,000x respectively to identify the differences that occurred during the reduction process.

3.0 RESULTS AND DISCUSSION

The FT-IR spectra (Figure 1 (a)) shows that there are peaks around 3195 and 1718 cm^{-1} which indicates that hydroxyl (-OH) and carbonyl (C=O) groups exist on the surface of GO respectively. Meanwhile, intense peak at 1620 cm^{-1} shows bending mode of water molecules. Peak at 1224 cm^{-1} indicates that epoxy group exist on GO [21]. Interestingly, when GO is reduced with 0.5 M $NaBH_4$ some of the peaks are vanished from the spectrum (Figure 1 (b)-(e)). It is believed that, some of the oxygenated functional groups have been successfully removed from the surface of GO through the reduction process [22]. When GO is reduced, it is clearly shown that there are no peaks can be found at 1718 cm^{-1} which indicates the C=O groups have been removed from the surface of the material. Peak at

2919 cm^{-1} is found when GO is reduced for 8 h (Figure 1 (e)) indicates that there is C-H asymmetric stretching vibration mode [23]. Based on the spectrum, it can be said that as the reduction time increase, the –OH peak become broader. This result may be explained by the fact that $NaBH_4$ able to reduce aldehyde and ketone to alcohol [14]. Overall, peak in the range of 1300 – 1450 cm^{-1} indicates tertiary alcohol bending [21].

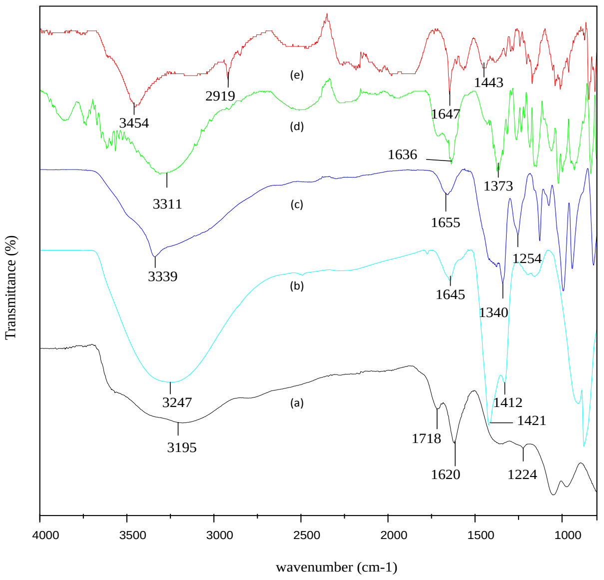


Figure 1 FT-IR spectrum of (a) GO (b) rGO 32h (c) rGO 24 h (d) rGO 16 h (e) 8 h

Band gap can be defined as energy difference between valence band (highest occupied molecular orbital, HOMO) and conduction band (lowest occupied molecular orbital, LUMO) [24]. Energy gap (E_g) shows a significant meaning of semiconductor which determines their applications. To characterize semiconductor thin films, UV-VIS absorption spectroscopy is the mostly used [25]. By using Tauc equation, the optical band gap of GO and rGO has been calculated from the reflectance spectrum [26]:

$$ahv = A (hv - E_g)^n$$

where

a = absorption coefficient
A = absorbance
E_g = average band gap of the material
v = photon frequency
h = Planck's constant
n = 2 (direct semi-conductor)

Table 1 Bandgap energy value of GO based on reduction time

Reduction time (h)	Bandgap energy (eV)
8	4.90
16	4.50
24	4.25
32	4.05

The Tauc optical gap associated with the thin films can be determined by extrapoliation of the linear trend observed in the spectral dependence of $(ahv)^2$ over a limited range of photon energies, hv [27]. From Table 1, it shows reducing trend of band gap with increasing reduction time. When GO is reduced for 8 h, the band gap increased to 4.90 eV and decreased to 4.50, 4.25 and 4.05 eV when the reducing time increased to 16, 24 and 32 h at 80 ^{O}C. The decreasing value of band gap in rGO is due to the removal of some functional groups on the surface of the material [21] and also consequent conversion of sp^3 carbon to sp^2 [28]. The obtained band gap value shows that rGO able to be photocatalyst in water treatment. This is because, a group of researchers stated that at 5.0 eV zirconium dioxide is a photocatalyst for water splitting [29].

The morphology of GO and rGO was studied using FESEM under the magnification of 2500x (Figure 2). Figure 2 (a) shows that there was a few of small wrinkles that form on the surface of GO [30]; [5]. The wrinkles are believed to give the conducting characteristics to the GO. Furthermore, the formation of the wrinkles and crumples like structure might be due to the existence of H_2O molecules and hydroxyl or carboxyl groups [31]. Supposely, the morphology of rGO obtained in this study shows wrinkles and crumples just like GO. Unfortunately, no crumples and wrinkles were detected when GO was reduced for 8 h (Figure 2 (b)). Meanwhile, as the reduction time increased, the rod shape became thinner and smaller. Interestingly, the rod shape vanished when rGO was reduced at 24 and 32 h (Figure 2 (d) - (e)) and the wrinkles were obviously seen. Therefore, it is proven that the reduction process can increase the conducting properties of the GO due to the wrinkles and crumples that exist on the surface of the material.

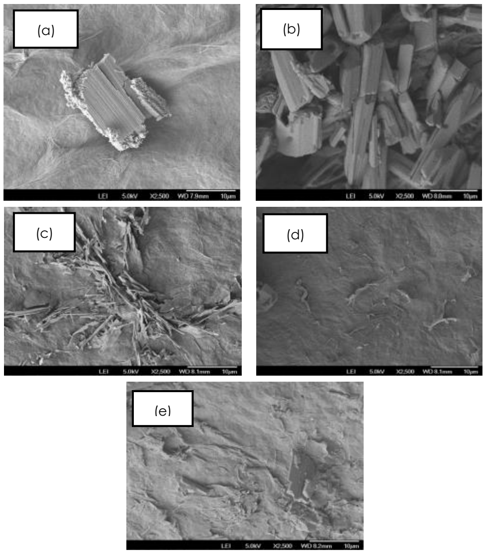


Figure 2 Morphology of (a) GO (b) rGO 8h (c) rGO 16 h (d) rGO 24 h (e) rGO 32 h under 2500x magnification

4.0 CONCLUSION

It is found that the reduction process able to reduce carbonyl groups on the surface of rGO. The morphology of GO and rGO shows some differences between the materials. Meanwhile, the band gap value concludes that the reduction of rGO can also be applied in certain applications as the range of band gap value (<5.00 eV) suitable for photocatalyst. It can be said that rGO shows more wrinkles on the surface compare to GO which indicates that it has better conducting properties.

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