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Abstract

We report a modification of the liquid-phase exfoliation (LPE) method in order to produce reduced graphene oxide (rGO) material by varying the heating temperature. The rGO was obtained by dissolving graphite powder into a surfactant solution and then heated by varying the heating temperature. There is an intercalation process on the graphene layers as the heating temperature was increased. The rGO material were tested using UV-vis, FTIR, Raman spectroscopies, and conductivity measurement based on Ohm principles.

1. Introduction

Graphene is a two-dimensional single-atom thick membrane of carbon arranged in a honeycomb crystal. Graphene has received much attention in the recent years due to its excellent optical, mechanical, and electrical properties [1]. Based on these properties, many utilization of graphene have been reported, such as display, supercapacitor, nano-sensor, and so on [2, 3]. However, there remain many challenges for the development of graphene-based materials because of their poor solubility and mass production of pristine graphene.

There are many methods developed to produce graphene, such as chemical vapor deposition (CVD) [4], mechanical exfoliation [5], and chemical reduction of graphene oxide (GO) [6]. Among them, chemical reduction of GO is most efficient way to produce graphene on large scale using graphite as the raw material. GO can be synthesized by oxidization of graphite by Hummers chemical exfoliation method [7]. GO can be viewed as graphene decorated by oxygen containing groups on the basal planes and at edges [8]. GO can be reduced to graphene-like sheets called reduced GO (rGO) by eliminating oxygen containing groups with recovered conjugated structure. Many solution-based processes are used for exfoliation of graphite to GO followed by hydrazine, amphiphilic polymers, and pyrene derivatives [7]. The solvents that may be used in the dispersion process are N-methyl-2-pyrrolidone (NMP), surfactant, and N-dimethylformamide (DMF) [9]. However, chemical oxidation disrupts the electronic structure of graphite and introduce many carbonyl ($-C=O$), hydroxyl ($-OH$) and epoxy functional groups in the sheets. This reduction may leave defects that affect the electronic properties of graphene [10].

Thermal reduction is another method to obtain rGO. It consists of inserting the GO in an inert and high-temperature atmosphere. The two prime objectives that are to be achieved during the reduction of GO are removal of functional groups and treatment of the structural defects. The two effects that should be considered during the removal of functional groups are whether the complete elimination of functionalities is possible and whether defects caused by the removal of functional groups can be repaired to a conjugated structure to have a definite pathway for carrier transport within the rGO sheets [11]. The removal of functional groups by applying heat creates defects in the carbon lattice plane [12]. Thermal annealing of GO at 200 °C and 550 mtorr of pressure in argon atmosphere for 6 h can eliminate the hydroxyl groups and partially eliminate both carboxyl and epoxy groups. Moreover, increasing the annealing time improves the C/O ratio [11]. Gao *et al* (2010) carries out a detail theoretical analysis of thermal reduction of GO. They reported that the binding energy of the hydroxyl group attached at the inner part is less stable as compared to a similar group attached at the edge [13].

This method uses high temperature to modify graphite into GO. A top-down method known as the liquid phase exfoliation (LPE) can produce stable dispersion monolayer or few-layer defect free graphene. The LPE using ultrasonication produces effective exfoliation method and has the potential to produce monolayer or few-layer graphene at relatively high concentration. Typically, the power of sonication is used to induce physical or chemical changes in some systems through the generation of cavitation bubbles [14].

This research introduces a modification method where the synthesis of rGO is conducted without having to synthesize the GO material. This method utilizes surfactant as the solvent combined with heating method. Graphite is dissolved in surfactant solution. The mixture is heated at some temperature variations of less than 100 °C. The material produced is then tested to prove that the material obtained is rGO using UV-vis, FTIR, and Raman spectroscopy, and also conductivity measurement based on Ohm principles.

2. Materials and method

Materials used were graphite powder, distilled water, and linear alkylbenzene sulfonate (LAS). The first stage was to make a graphite solution by mixing 1 gr of graphite powder into 28 ml of distilled water. Then 1 ml of LAS was dissolved into 10 ml of distilled water. Both solutions were mixed and stirred for 1 h using a magnetic stirrer. The solution was heated with temperature variations of 60, 70, 80, and 90 °C for 2 h and was directly ultrasonicated for 2 h at a frequency of 30 kHz. To separate the deposits with the liquid part, the solution is filtered using a filter paper. The deposits were dried using an oven at 80 °C for 4 h.

The samples were analyzed using UV-vis, FTIR, and Raman spectroscopy instruments. The UV-vis spectrophotometer used was the Shimadzu UV-2400 series (wavelength used is 200–800 nm with step of 0.5 nm). The samples for UV-vis tests were prepared by dissolving 0.1 mg of rGO into 0.3 ml distilled water. The solution was ultrasonicated for 2 h at a frequency of 30 kHz. The FTIR spectroscopy used was Shimadzu 8201PC series with the wave number used was in the range of 4000 cm^{-1} to 400 cm^{-1} . The Raman spectroscopy was conducted using a custom made instrument from Thunder Optic. The laser source used was 532 nm. The samples were prepared by placing 0.1 mg of rGO on a glass with a square spread of approximately $0.2 \times 0.2 \text{ mm}^2$. The conductivity measurement is done by using simple Ohm's equation. The sample were prepared by dissolving 1 mg of rGO into 3 ml distilled water and ultrasonicated about 1 h. The solution of rGO then taken as much as 1 ml and dropcast on a glass and then dried in vacuum container about one day. The dimension of the sample is $30 \times 15 \text{ mm}^2$ with a rectangular geometry. The samples were then measured using four-point probe given voltages from 1 mV to 20 mV which changed constantly and the fluctuating current was measured. The distance between the probes is set to be 2 mm. A graph of the relationship between the voltage and the current was produced, from which the conductivity value is obtained following the analysis by Smits (1958) in [15].

3. Results and discussion

In this study, the graphite powder is synthesized into rGO without going through the GO process. Hence, it is quite low cost and environmentally friendly. This method uses intercalation and heating methods. Intercalation is a method of changing the distance between the atomic bonds in a crystal layer [14], while heating is a method that serves to break the bonds between atoms in the crystal. Graphite is composed of graphene layers having van der Waals bonds between adjacent layers and covalent bonds between carbon atoms. The spacing between two adjacent graphite layers is around 0.35 nm [16, 17]. The graphite is mixed with surfactant, which has a molecular size of around 1.0 nm to 1.5 nm based on an assumption that the surfactant has a linear chain (tail) of 10 atoms where each atom has a size of around 1 angstrom³. Hence, the spacing between graphite layers is smaller than the molecular size of the surfactants. Indeed, this difference in length may be used to widen the distance between adjacent layers of graphene via intercalation as shown in figure 1.

The surfactants fill the spaces in between layers of graphene. Because surfactants consist of head and tail, then the tail of surfactant binds to the graphene sheet, while the head binds to the solvent (distilled water) (figure 1(a)). In the end, the sheets of graphene will be covered by surfactants (see figure 1(b)), which causes the weakening of the van der Waals bonds. The dissolved graphite in the surfactant solution has weak van der Waals bonds such that when heated the bonds should break. The weakening of this bond is caused by the increase distance between the graphene sheets, i.e.: the wider the distance, the weaker the bonds. The exterior of the atom causes the van der Waals bonding to break down more easily than covalent bonds. The breakage of the bonds causes the graphene sheets to be formed, but still in the dissolved phase in surfactant. To get the rGO material, centrifugation or filtration may be conducted. The deposits obtained are dried using an oven so that rGO in the form of powder is obtained.

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³ Private communication with Suparno PhD, a physics lecturer of the Physics Education Department, Universitas Negeri Yogyakarta

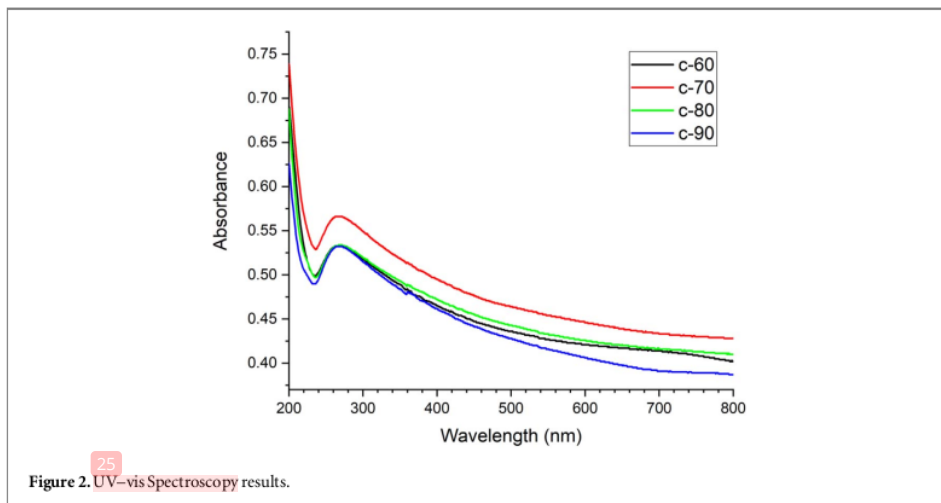
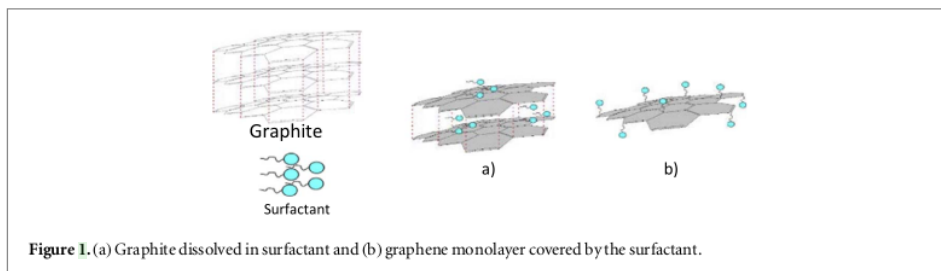


Figure 2 shows the optical absorption spectra of rGO resulted from UV-vis spectroscopy. There is an absorption band around 270 nm due to π - π^* transition of the conjugate system of graphene for rGO [8]. The variation of heating temperature, namely from 60 °C to 90 °C does not produce any peak shifts. This indicates that the electron configuration does not change despite heating. For heating variations of 60 °C, 80 °C, and 90 °C there is also no significant absorbance change. The UV-vis results may also indicate that the rGO material obtained has been separated from the surfactant molecules. Moreover, the absent of surfactant absorption peak at 225 nm [18] in the UV-vis results in figure 2 may also indicate that most surfactants are removed from the surface of the rGO material through filtering and heating.

Further, in order to determine the structure bonding of rGO, we use the FTIR spectroscopy. Figure 3 shows the FTIR spectra of rGO with variation of temperature. In all variant of rGO spectra, we can observed that a band at around 3400 cm^{-1} is due to the (-OH) stretching vibrations of surface absorbed water molecules. The bands around 1600 cm^{-1} and 1033 cm^{-1} correspond to C=C and C-O stretching vibrations, respectively [12]. Moreover, we can see that increasing the temperature tends to decrease the intensity of the functional group bands, which confirms the decrease of the their presence. This suggests that the formation of rGO is expected as the -OH function groups disappear to get a rGO that is almost close to graphene-like material. The disappearance of the -OH functional groups is caused by several factors, such as constant heating. Furthermore, the -OH functional groups are bonded to the tail of the surfactant, so it can be said that the functional group is dissolved into the surfactant. However, the C=C functional groups are also reduced. This can certainly indicate that the formed rGO does not have much C=C bond and may only have a small surface area.

The quality of exfoliated rGO is characterized with Raman spectroscopy. The instrument used is a self-assembled Raman spectroscopy where the components are purchased from Thunder Optic. The laser source used is 532 nm. The results of the characterization using the Raman spectroscopy are shown in figure 4. The development of interference in the sp^2 carbon hybridization system results in a Raman spectrum, thereby making Raman spectroscopy one of the most sensitive techniques for characterizing interference with sp^2 carbon materials. There are two peaks, the G and D peaks. The D peak is derived from the vibration layer, which is associated with the presence of structural defects, such as irregular structure of graphene, around 1350 cm^{-1} , and 2D around 2690 cm^{-1} . The G peak is caused by the mode of E_2G at Γ Point. The G peak occurs from stretching the C-C bond

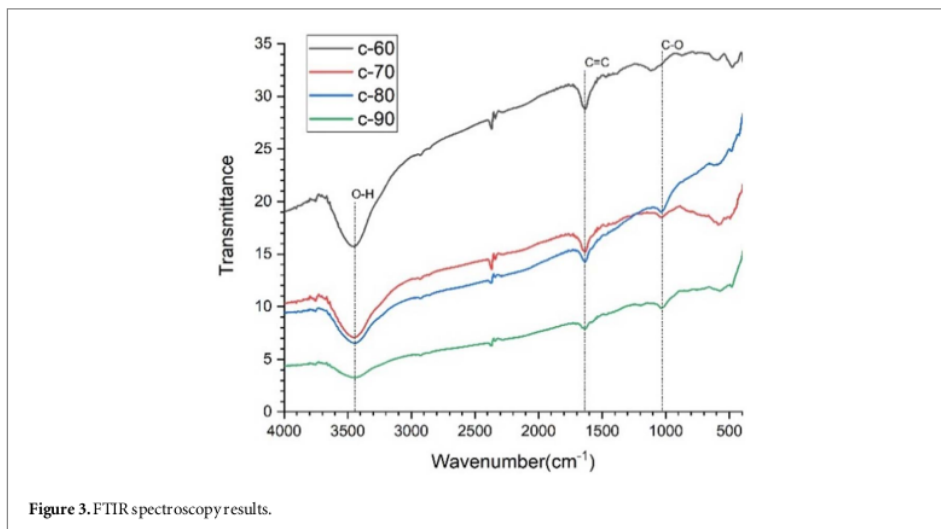


Figure 3. FTIR spectroscopy results.

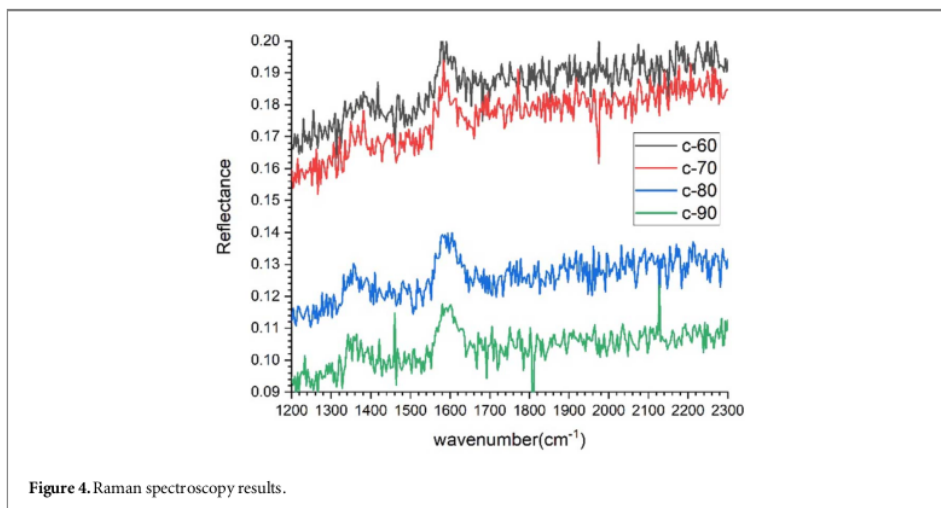


Figure 4. Raman spectroscopy results.

in the material and occurs on all carbon sp^2 systems, around 1580 cm^{-1} . The 2D peaks indicating the thickness of the rGO layer cannot be shown due to the limitation of sensor sensitivity. We can see from figure 4 that this is an original signal from custom made Raman spectroscopy. The signal looks like a noise, but if we viewed it carefully, the signal has peaks around 1370 cm^{-1} and 1600 cm^{-1} . From the signal pattern, we use a few smoothing to find the peaks, such that we obtain the D and G peaks. This may be observed in figure 5.

It may be observed that every peak from the variation of temperature does not shift, but the reflectance decreases with increasing temperature. The intensity ratio of the D-band (I_D) and G-band (I_G) indicates the quality of the produced graphitic structure [10]. The variation in temperature does not change the D and G values significantly. However, it appears that the higher the temperature, the more the reflectance is decreased. The I_D/I_G ratio is an indicator of the degree of irregularities in graphene. The I_D/I_G values from 60°C to 90°C are 0.931; 0.927; 0.916; and 0.903, respectively. The greater the value of I_D/I_G , the lower the quality of graphene. Hence the best quality of graphene is obtained for heating temperature of 90°C .

Finally, in order to support the existence of the rGO material in the samples produced, simple conductivity measurements are done based on Ohm principles. The graph of the current (mA) versus the voltage (mV) obtained from the four-point probe measurement may be observed in figure 6. This produces a conductivity value of $5 \times 10^{-3}\text{ S mm}^{-1}$ or $5 \times 10^{-2}\text{ S cm}^{-1}$, which is an appropriate result for rGO material.

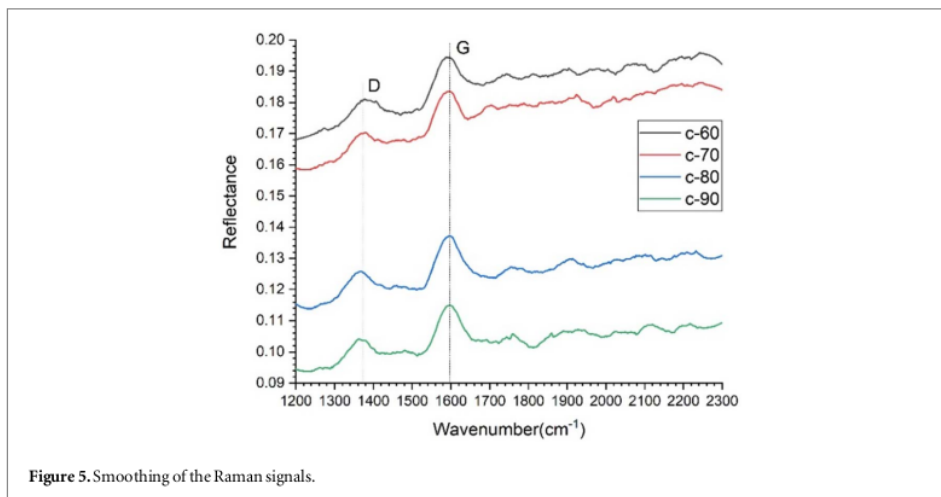


Figure 5. Smoothing of the Raman signals.

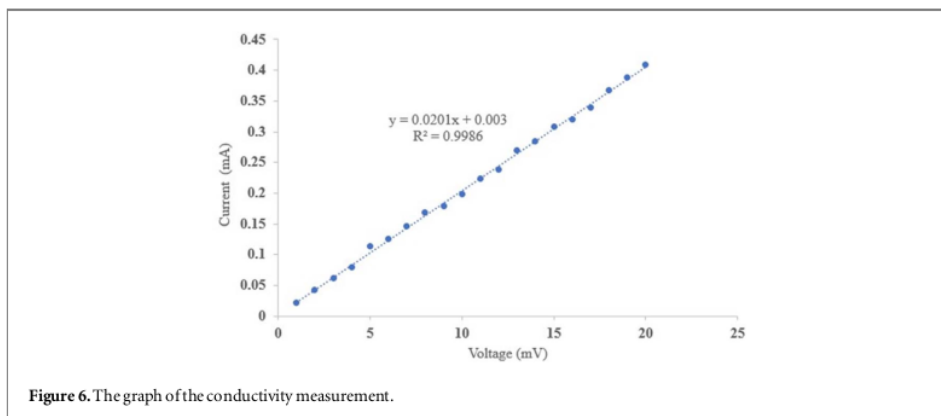


Figure 6. The graph of the conductivity measurement.


4. Conclusions

rGO material based on a modified LPE method has been produced, which is a combination between the LPE and heating process. It is obtained that the higher the heating temperature, the better quality of rGO obtained based on the characterization results of Raman spectroscopy. The FTIR results support the aforementioned finding where the -OH groups tend to disappear as the heating temperature is increased. However, the heating temperature does not change the absorbance peak of the UV-vis results. Further studies include characterizing the samples using TEM, AFM, and XPS, which has not been conducted here. In order to improve the quality of the Raman test results, the samples may be further tested in liquid state or coated onto a thin layer to obtain higher D and G band values, as well as obtaining the 2D peak. Furthermore, the proportion of the rGO material obtained via this method should also be studied to determine the quality and possibility of large-scale rGO production.

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