Simple synthesis of rGO (reduced graphene oxide) by thermal reduction of GO (graphene oxide)

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Abstract. The rGO has been synthesized successfully by combination of modified Hummers method and thermal reduction. First, the GO was synthesized by modified Hummers method (chemical exfoliation) of graphite flake. This reaction obtained graphite oxide (GrO) as intermediate material. The materials were characterized by FTIR, XRD, TG/DTA and SEM. The FTIR data shows the functional group of graphite, GrO, GO and rGO, while XRD data shows crystal parameter of them. The TG/DTA was used to study the rGO formation at various of temperature (200, 300 and 400 °C). The rGO had carbonyl, carboxyl, hydroxyl and alkene functional groups and 2 theta peak at around 25° corresponds to [002] plane. The rGO layer by thermal reduction of GO had wrinkle sheets structure from SEM image appearance. In this result, the simple thermal reduction strategy of rGO is possible to control functional group and layer number depends on its application.

1. Introduction
Graphene, two-dimensional (2D) sheet material from graphite is arranged of sp²-hybridized carbon atoms that has unique characteristic [1,2]. This material has attracting characteristic, high thermal conductivity, good elasticity, high specific surface area and good mechanic stability [3]. Firstly, graphene was discovered in 2004 by mechanical exfoliation of graphite with adhesive tape [4]. Today, graphene becomes a popular material and be applied in many applications. Graphene can be applied in nanotechnology, electronic devices, agriculture, foods technology and etc [5,6].

The synthesis of graphene attracts researcher to obtain graphene at higher amount and easier strategy than mechanical exfoliation. The Hummers and its modified method are the most popular method to synthesis graphene. This method was introduced by Hummers and Offeman in 1958, before Novoselov et al (2004), named by graphene oxide (GO). Hummers and its modified method refer to chemical exfoliation process on graphite flake [7]. This method usually occurs in strong acid and oxidizing agent solution mixture. Therefore, it is difficult to determine the mechanism of formation and oxygen functional group of GO clearly [8]. Controlling the oxygen functional group content can be approached by reduction strategy of GO. The reduction of GO results rGO which has
more similar structure with pure graphene. The GO can be reduced via thermal, chemical, solvothermal, electrochemical, photo and multistep reduction [5,9]. The thermal reduction has advantages on high reduction degree, environmentally friendly and lower cost. This reduction method had been done in previous study, but mechanism of the influence of thermal to GO structure is not reported yet [6].

In this work, GO was synthesized by chemical exfoliation (modified Hummers method) of graphite powder. This reaction resulted GrO as intermediate of GO which is obtained by ultrasonication of GrO. GO was reduced by simple thermal reduction then obtained rGO. All of materials were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), thermal analysis (TG/DTA) and scanning electron microscopy (SEM) to know the formation of rGO.

2. Experimental

2.1. Materials

Graphite powder as graphene precursor, sulphuric acid (H₂SO₄) and hydrogen peroxide (H₂O₂) were obtained from Merck. Potassium permanganate (KMnO₄) was obtained from SIGMA-ALDRICH and aquadest was supplied by Laboratory of MIPA Terpadu UNS.

2.2. Procedure

Chemical exfoliation method was used to synthesize GO from graphite powder that refers to Hummer’s modified method [6,7,9]. A mixture of 2 g graphite powder and 80 mL H₂SO₄ was stirred continuously until dark homogenous mixture was obtained. The oxidizing agent (KMnO₄) 8 g was added slowly to the mixture with constant stirring. The temperature of mixture was maintained with ice flakes to avoid excessive raising temperature oxidation reaction. This mixture changed from dark to dark green homogenous suspension then maintained for 24 hours at room temperature. The H₂O₂ 0.4 mL was added to dark brown suspension so the oxidation process was terminated (brown suspension). The brown suspension was added by aquadest to reach pH of 7. Then, the brown suspension was concentrated by eliminated the water content. The brown condensed was dried under vacuum freeze drying for 3 days until brown powder was obtained.

The dried brown powder was known as graphite oxide (GrO). A mixture of GrO 200 mg and 200 mL of aquadest was ultrasonicated for 3 hours to exfoliate graphene sheets in GrO powder. Subsequently, the mixture was condensed and dried under vacuum freeze drying for 3 days so dark brown powder (GO) was formed. The reduced graphene oxide (rGO) was obtained by thermal reduction of GO powder. GO powder was reduced by annealing at 200, 300 and 400 °C. The dark brown powder was changed to dark powder after thermal treatment as rGO powder.

2.3. Characterization

The FTIR was used to investigate functional group was recorded by Shimadzu with IRPrestige-21 type, The XRD was performed by Rigaku Miniflex 600 Benchtop with CuKα radiation (λ = 0.15406 nm), The TG/DTA was carried out by STA Linseis at 30 - 600 °C temperature (10 °C/min), The morphology imaging was observed by SEM from Vega 3 Tescan with 15.0 kV resolution under high vacuum condition.

3. Result and Discussion

The rGO was synthesized successfully by thermal reduction of GO. While, The GO was obtained from chemical exfoliation of graphite powder, it was known as Hummers and its modified method. The graphite powder was oxidized by KMnO₄ in extremely sulphuric
acid condition. The oxidation process caused a color change from dark to dark green suspension and it was maintained for 24 hours. The oxidation reaction was stopped by adding of H$_2$O$_2$, so the dark green suspension become a dark brown suspension as GrO suspension. The GrO powder was ultrasonicated with aquadest for 3 hours to exfoliate graphene sheets in GrO then the dark brown suspension was dried to obtain GO powder. The alteration of functional group of graphite, GO and rGO can be seen in Figure 1.

The FTIR spectra of GrO and GO show the peak at 1050, 1310, 1630, 1740 and 3320 cm$^{-1}$. Respectively, these peaks correspond a functional group of C-O, C-OH, C=C, C=O and OH. The existence of alkene, carbonyl and hydroxyl functional group ensure that GO was synthesized successfully [6,9]. The clear alteration of FTIR pattern can be seen from graphite to GrO and GO. There is no difference between GrO and GO FTIR spectra because GO just exfoliated sheets from GrO so both of them have same FTIR pattern.

Then, rGO was obtained via simple reduction treatment of GO powder. The GO powder was annealed at various temperatures (200, 300 and 400 °C) in oven. The annealing process of GO caused a dark brown powder changed to dark powder as rGO material. The alteration is caused the decreased of oxygenated functional group on GO sheets. The decreased of carbonyl and hydroxyl functional group can be seen in Figure 2. The carbonyl and hydroxyl have higher absorbance (in Figure 1) than Figure 2, so reduction process of GO have occurred. The rGO-200 and rGO-300 have same FTIR pattern that show peaks at 1220, 1630 and 1740 cm$^{-1}$, respectively correspond a functional group of C-OH, C=C, and C=O. But, the difference phenomenon is showed by rGO-400. The rGO-400 has significant peak at 610, 1120, and 3410 cm$^{-1}$ correspond as C-H, C-O and O-H functional group. The existence of C-H shows that the functional group of GO is reduced by adding of H atom. The carbon atom bonding also was broken and formed O-H functional group then the structure rearrangement occurred. This reason is correlated by thermal analysis data in Figure 3.
Figure 2. Effect of annealing temperature on functional group of rGO.

The figure 3 is TG/DTA graph of GO that shows structure decomposition of GO against temperature increasing. Figure 3 shows the decomposition steps of GO that corresponds with functional group on GO sheets. First step (I), GO was decomposed (21%) at 30 °C until 200 °C, shows as the elimination of water molecule and unstable oxygen functional group. Second step (II), the decomposition was occurred at 200 °C until 430 °C (30%). This decomposition is caused by elimination of more stable oxygen functional group. Then, third step (III), the weight loss is 32% that was occurred by decomposition of unstable carbon (CO and CO$_2$) started at 430 °C [9]. Afterwards, DTA curve (blue line) shows the structure transformation of GO sheets become rGO sheets. There are exothermic peak at 230, 430 and 450 °C as transition phase of GO sheets that is correlated with FTIR data (Figure 2) [10]. The FTIR data of rGO-200 and rGO-300 are significantly different with rGO-400 because from DTA data was occurred a high decomposition (% weight loss) of GO sheets at temperature more than 400 °C. This decomposition also leads structure rearrangement of rGO sheets. Furthermore, the structure of rGO sheets is shown in Figure 5.

Figure 4 shows diffractogram of crystal structure transformation of graphite, GrO and GO. The diffraction of graphite shows an intense peak at 2 theta of 26.08° as [002] plane. This peak is disappeared at diffraction pattern of GrO as intermediate compound of GO. The highest peak shifts from 26.08° to 10.0° which corresponds to [001] plane. The interlaminar space (d-space) value also changes from 0.35 nm to 0.89 nm, respectively for graphite and GrO (Table 1). This is can be proof that oxygen functional group from oxidation process is entrapped in interspace of graphite layers [6,9]. The GrO diffraction pattern also shows a peak at 42.28° corresponds to [100] plane. The GrO diffraction shows a broad peak around 20° - 40° indicating that GrO is an intermediate state between graphite and GO.
The crystal height \( L_c \) of GrO is lower than graphite (13.26 to 48.61 nm) also indicates that carbon bonding in graphite layers is partially broken. So, The GrO contains a mixture compound of graphite with interspace inserted oxygen functional group and partially interrupted. Whereas, the GO has similar the highest peak with GrO diffractogram. The [001] and [100] plane of GO appear at 2 theta of 10.54° and 42.61°, then interlaminar space value and crystal height of GO are close with GrO (respectively, 0.84 nm and 11.47 nm). But, there is no broad peak (at 20° - 40°) in GO diffractogram, which means that GO sheets totally formed without intermediate compound remaining. The GO sheets are arranged by 14 of graphene layers (Table 1), this value is drastically decreased from the number of graphene layers of graphite (131 layers). The decreasing of the number graphene layers indicates that chemical exfoliation of graphite is successfully applied.

**Figure 3.** Thermal graph (TG/DTA) of graphene oxide (GO).

**Figure 4.** Diffractogram of graphite, GrO and GO.
Table 1. Crystallographic characteristic parameter of graphite, GrO, GO and rGO.

| Material | 2 theta (deg.) | (d_{002}) [002] or [001] | (L_c) [100] | (L_a) | (N_c) |
|----------|----------------|--------------------------|-------------|-------|-------|
| Graphite | 26.08          | 0.34                     | 44.82       | -     | 131   |
| GrO      | 10.00          | 42.28                    | 0.88        | 13.11 | 10.72 | 15    |
| GO       | 10.54          | 42.61                    | 0.84        | 11.32 | 14.72 | 14    |
| rGO-200  | 24.93          | 43.57                    | 0.36        | 1.78  | 4.93  | 5     |
| rGO-300  | 24.72          | 43.74                    | 0.36        | 1.85  | 5.12  | 5     |
| rGO-400  | 26.18          | 42.58                    | 0.34        | 1.06  | 4.68  | 3     |

d_{002} : Interlaminar space, L_c : Crystal stack height, L_a : In-plane crystallite size, 
N_c : Number of graphene layers

The diffraction pattern of rGO is shown in Figure 5. The highest peak of diffraction shifts from 10.54° (GO) to around 25° (rGO) corresponds to reappearance of [002] plane [6]. The rGO-200 and rGO-300 have similar diffraction pattern that corroborates with the FTIR data of both. So, rGO-200 and rGO-300 are indicated in the similar crystal structure and supported by crystallography data in Table 1. However, this appearance is not shown by rGO-400 that has broadening peak at around 2theta of 20 - 40°. The broad peak shows lower crystallinity that indicates the defect of rGO structure. The defect of structure is caused by functional group elimination, so rearrangement of compound occurs at 400 °C, but not perfectly. The number of graphene layers of rGO-400 is also fewer than rGO-200 and rGO-300 (Table 1) which shows decomposition of functional group not only impacts on weight loss but also breaks the graphene interlayers bonding, and the crystal height of rGO-400 is decreased.

Figure 5. Effect of annealing temperature on crystallite characteristic of rGO.
The morphology of graphite, GO and rGO is known in Figure 6. Graphite has three dimensional (3D) structure which is seen in Figure 6(a). Graphite is arranged by many graphene layers, that can be known in Table 1 (131 layers). So, from SEM image, graphite shows crystal stack. While, GO and rGO are 2D material and can be seen in Figure 6(b and c). The arrangement of GO causes highly reduction of graphene layers. Moreover, the morphology of material is not like crystal stack but sheets look that indicates GO is successfully synthesized with modified Hummers method. The different appearance is shown by rGO image, which is seen wrinkled sheets. The thermal reduction of GO occurs rapidly, so it impacts on structure rearrangement of graphene layers. But, the formation of rGO by simple thermal reduction is successfully arranged from SEM images.

![Figure 6. SEM images of (a) graphite, (b) graphene oxide (GO) and (c) reduced graphene oxide (rGO).](image)

4. Conclusion
The reduced graphene oxide has been successfully synthesized by chemical exfoliation (modified Hummers method) of graphite powder and simple thermal reduction. The chemical exfoliation of graphite obtains graphene oxide with graphite oxide intermediate. The rGO formation can be known from FTIR and XRD characterization, then corroborated with TG/DTA and SEM image data. The different temperature of thermal reduction results a different functional group and crystal structure. So, the controlling functional group and crystal structure of rGO is possible by temperature control.

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