



New Route to Synthesize of Graphene Nano Sheets

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<http://dx.doi.org/10.13005/ojc/340120>

(Received: November 20, 2017; Accepted: December 01, 2017)

ABSTRACT

Synthesis of graphene nano sheets were carried out by using new route and ammonia as well as to produce gram scale graphene. Graphene nano sheets was characterized by using Fourier transform infrared spectroscopy (FTIR), X-ray powder diffraction (XRD), and Scanning Electron Microscopy-Energy Dispersive X-Ray (SEM-EDX). The results of XRD showed that the reemergence of diffraction lines C(002) at $2\theta = 26.5^\circ$, and the distance between the planes is 3.35 Å, which shows the typical structure of graphite and multiple layer of graphene. The results of SEM-EDX showed that the particle size and the graphene nano sheets has a smaller pore size and uniform and randomly arranged aggregates with a thin layer which is closely related to one another. Graphene nano sheets has small size or shape is small and thin also aggregate related with each other.

Keywords: Graphite, Graphene Oxide, Graphene Nano Sheets, FTIR, XRD, SEM-EDX.

INTRODUCTION

Graphene is a two-dimensional carbon with one layer. Graphene possesses superior properties including unique electronic properties due to its high electron mobility ($20 \times 10^3 \text{ cm}^2 \text{ v}^{-1} \text{ s}^{-1}$),¹ mechanical resistance.² Super-thermal properties ($\sim 5000 \text{ Wm}^{-1}\text{K}^{-1}$),³ large surface area ($2630 \text{ m}^2 \text{ g}^{-1}$),⁴ so it can be used in fuel cells and capacitors.

Graphene production may be carried out by various methods: (i) mechanical methods, via adhesion tape or chemical exfoliation methods¹ embedded in graphite to collect carbon powder samples, and gradually released to produce graphene sheets. However, this method has a weakness in the aspect of its irreproducibility (it cannot be produced further), (ii) epitaxial growth method in silicon carbide that is heating silicon carbide at high temperature ($> 1.100^\circ\text{C}$). This



process produces a graphene epitaxial with dimensions depending on the size of the SiC substrate and the resulting small sample which does not allow it to be used in electronic application fabrication techniques, (iii) epitaxial growth methods on the metal substrate. This method has the disadvantages of not producing a sheet of graphene with a uniform thickness, and the bond between the bottom graphene sheet and the substrate can affect the properties of the carbon layer. The cost required for this graphene synthesis is also relatively expensive, both adhesion tape method and epitaxial growth method.

Currently, the production of graphene is mostly done by chemical method by oxidizing graphite to graphene oxide and then reducing with hydrazine to produce graphene. This method is very simple and can produce large scale production of graphene.⁵ The disadvantage of this method is the graphene is not single layer and also hydrazine is very toxic (carcinogenic agent).

The reduction of graphene oxide to be graphene is very important in order to produce graphene. Reduction of graphene oxide by non-hydrazine is needed be developed. This is caused, hydrazine is carcinogenic. In this study, we used ammonia as a reducing agent to reduce graphene oxide to be graphene nano sheets. That is possible due to ammonia is an environmentally friendly reducer in a small concentration range. In this research, the ammonia is expected to interact with the carbonyl, hydroxyl, and epoxide groups of graphene oxide. Therefore, we reported the simple and inexpensive method to produce graphene by oxidation of graphite to be a graphene oxide and then it was reduced to generate graphene.

MATERIALS AND METHODS

Synthesis of Graphene Nano Sheets

0.2 g of graphite powder was inserted into 250 mL erlenmeyer, then it was added 0.2 g NaNO_3 and 15 mL H_2SO_4 96%, respectively and stirred for 2 hours. After that, it was gradually added 1 g of KMnO_4 and stirred for 24 h to generate graphite solution. Subsequently, the solution was added 20 mL of H_2SO_4 5% and 1 mL of 30% H_2O_2 , respectively and stirred for one hour. Then, the solution was centrifuged at a speed of 3000 Rotation per Minute (RPM) for 20 min. to separate the filtrate and

supernatant. The filtrate was added 10 mL ammonia 10 M and stirred for 48 h and separate filtrate and precipitate. Finally, precipitate was dried at 80 °C for 24 h and characterized by using XRD and SEM-EDX, respectively.

RESULTS AND DISCUSSION

Analysis of XRD

The XRD pattern of graphite, graphene oxide and graphene nano sheets can be shown in Fig. 1. The graphite (Fig. 1) shows a sharp and tight peak ($2\theta = 26.5^\circ$ and 23.88°) which corresponds to the diffraction line C (002) with the intercellular spacing in the crystal (d) respectively is 3.36 and 3.72 Å. The data shows the typical crystal structure of graphite. The graphene oxide (Fig. 1) shows a wide diffraction peak that is at $2\theta = 11.6^\circ$ with the spacing between plane (d) is 7.5 Å. Increasing the distance between fields in the graphene oxide is due to the presence of oxygen-functional groups and water molecules into the carbon layer structure. These are typical vertical oxides of graphene/

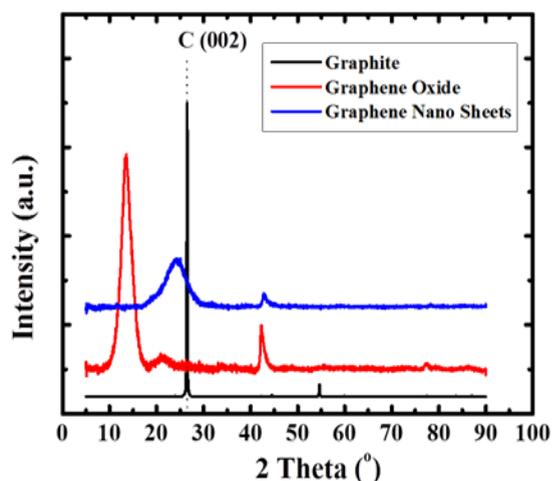


Fig. 1. XRD patterns of Graphite, Graphene Oxide and Graphene Nano Sheets.

graphite oxide.⁵ The small peaks are still observed at $2\theta = 20.1^\circ$; 23.9° and 26.4° which indicates that graphene oxide is not fully interconnected with oxygen atoms.^{6,7} The Fig. 1 shows that the chemical reduction of graphene oxide to graphene nano sheets using NH_3 , returns the structure of the crystal graphene nano sheets to be a more regularly. However, NH_3 has not been able to create a single layered graphene nano sheets structure.

The resulting graphene nano sheets has a structure between the crystalline and amorphous structures. This is evidenced by the reappearance of the diffraction line C (002) which looks wider and the intensity is lower than the peak obtained in the

graphite powder that is at $2\theta = 26.5^\circ$ with the distance between the fields is 3.35 \AA and the diffraction peak eradication at $2\theta = 11^\circ$ which looks more flat than in graphene oxide.^{6,7} The reduction process must involve the removal of the oxygen

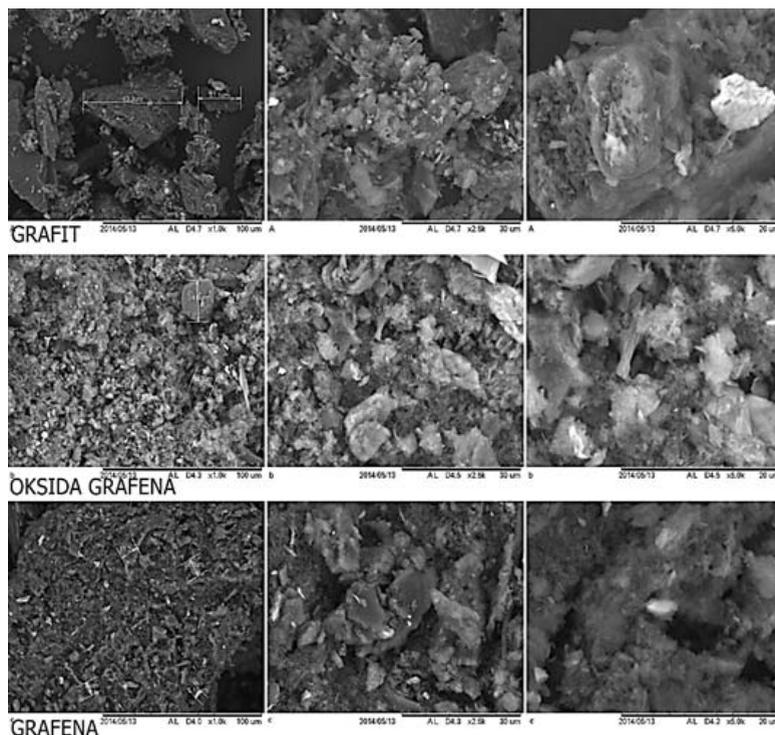


Fig. 2. SEM images of Graphite, Graphene Oxide and Graphene Nano Sheets with 1000 \times (a), 2500 \times (b) and 5000 \times magnification (c)

functional group because the graphene nano sheets conjugate structure of the sp^2 carbon bond must be reform during the reduction process, in which case the role is the opening of the epoxide ring.

Analysis of SEM-EDX

The microstructure and energy spectrum analysis data on the intensity of graphite, graphene oxide and graphene nano sheets are shown in Fig. 2 and 3, respectively.

The SEM data show that graphite has a wide and thick particle size indicated at 1000 \times magnification (Fig. 2a). The distance between the graphite particles looks wider with a far position. The result of SEM graphite at 2500 \times magnification (Fig. 2b) and 5000 \times (Fig. 2c), shows the existence of many stacks in the graphite structure indicating that graphite has a layered structure. The graphene

oxide has smaller particle size and the formed aggregates are closely related to each other than graphite which can be seen at 1000 \times magnification (Fig. 2a). The images of graphene oxide at 2500 \times magnification (Fig. 2b) and 5000 \times (Fig. 2c) indicate the existence of fewer stacks indicating that there has been exfoliation of the structure on graphite. The graphene nano sheets has a ripple surface, a smaller and uniform size of particles and pore size, has a randomly arranged aggregate with a thin layer and is tightly linked to one another to form an irregular solid (magnification 1000 \times) compare to graphite and graphene oxide. However, the graphene nano sheets structure obtained has not been single layered. It is marked on the SEM graphene nano sheets results with 2500 \times magnification (Fig. 2b) and 5000 \times (Fig. 2c) which indicates a smoother buildup and is visibly reduced by the process of exfoliation of the structure.

Graphene morphological differences with graphene oxide and graphite show that almost all oxygen groups in graphene oxide have been reduced with NH_3 . Furthermore, the EDX spectra of graphite, graphene oxide and graphene nano sheets are shown in Figure 3 – 5, respectively.

EDX spectra data of graphite, graphene oxide and graphene nano sheets were measured at a voltage of 15 kV. The spectrum is a characteristic X-ray captured by a Si detector. The graphite EDX

spectra data (Fig. 3) show that the carbon atoms (C) and oxygen atoms have the energy quantities captured by each detector at 0.15 and 0.25 keV. The large atomic intensity of C (Table 1) is due to the graphite structure consisting of the bonds of the carbon atoms. However, the graphite is not pure which is only suspended over carbon atoms, since it still finds other elements such as Al, Si and in addition, K, Al, Si and K appear probably due to the chamber effect of SEM-EDX. It is not due to the content of graphite. Furthermore, graphite was

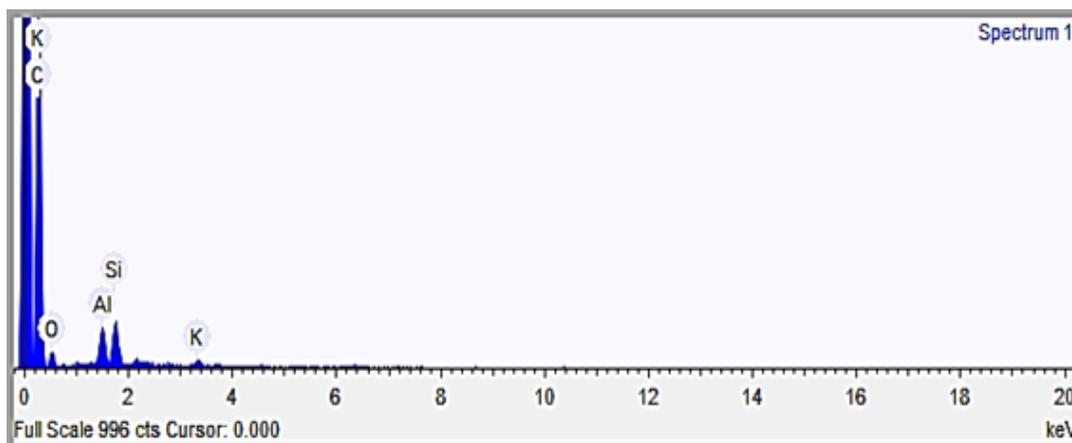


Figure 3. EDX Spectra of Graphite

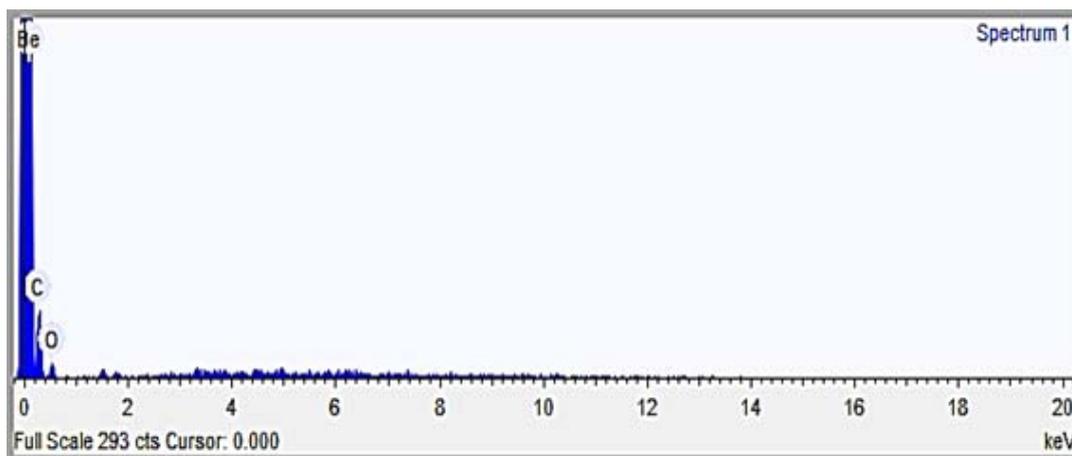


Fig. 4. EDX Spectra of Graphene Oxide

oxidized, centrifused and ultrasonicated to produce graphene oxide. The EDX spectra of graphene oxide are shown in Figure. 4.

The graphic EDX spectra of graphene oxide (Fig. 4) and the ratio of the number of elements

(Table. 1) show that the intensity of the C atom captured by the detector at 0.15 keV decreases and the oxygen atom increases at 0.25 keV. The Al, Si and K are not detected in the graphite oxide structure. The loss of Al, Si and K atoms is caused by the addition of strong sulphuric acid into the

graphite structure. The increase in oxygen atoms is due to the oxidation process of graphite by strong oxidizers (KMnO_4 , NaNO_3 and H_2O_2). Finally, graphene oxide was reduced by ammonia to generate graphene nano sheets. The EDX spectra of graphene nano sheets was shown in Figure 5.

Comparison of the number of elements of graphite, graphene oxide and graphene nano sheets can be shown in Table. 1.

The graphene nano sheets EDX spectra data (Fig. 5) show that the intensity of the oxygen atom captured by the detector at 0.25 keV

decreases. This is supported by the comparative data of the number of elements (Table. 1) showing that the grapheme nano sheets is mostly composed of atoms carbon and the percentage of the oxygen at the graphene decreases. The addition of a reducing NH_3 reduces the oxygen-functional groups that make up the graphne oxide structure. The oxygen atoms still detected in the grapheme nano sheets structure indicate that the reduction process of graphene oxide to graphene nano sheets using ammonia is not yet perfect because there are other oxygen groups in the graphene structure. That is called graphene nano sheets.

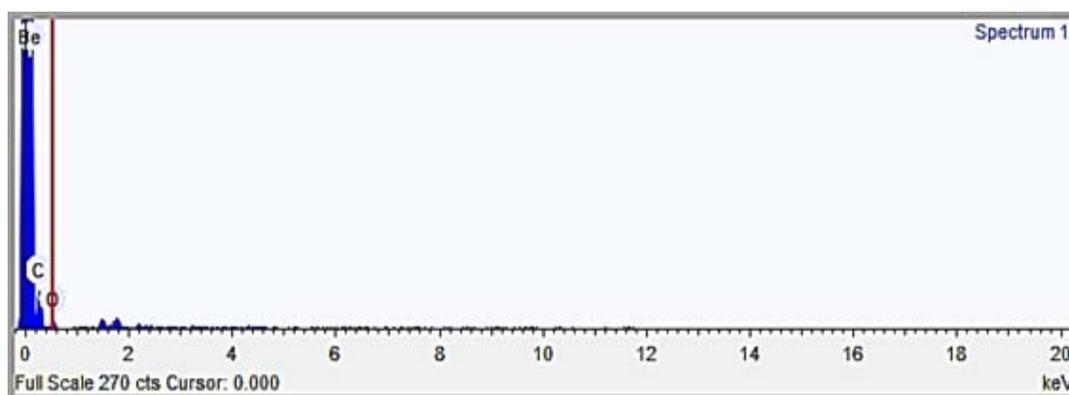


Fig. 5. EDX Spectra of Graphene Nano Sheets.

Table. 1. Comparison of elements of Graphite, Graphene Oxide and Graphene Nano Sheets (EDX Data)

Elements	Graphite	Graphene Oxide	Graphene Nano Sheets
Carbon	88.374	88.114	97.723
Oxygen	9.200	11.886	2.277
Aluminum	1.032		
Silicon	1.206		
Potassium	0.187		

CONCLUSION

Graphene nano sheets can be synthesized from graphite using ammonia reduction as well as a beginning approaching. The graphene XRD pattern shows single-layered graphene due to the emergence of the diffraction peak at C (002). Characterization of SEM-EDX show that graphene has size and shape of small, thin and aggregate where graphene structures are

closely related to each other and the reduced percentage of oxygen elements in graphene. The mechanism reaction of reduction graphene oxide used NH_3 as a reducing agent occurring in the epoxy group. NH_3 does not play a role in the de-hydroxylation, de-carbonylation and de-carboxylation processes due to the increased resistance of Gibbs energy to NH_3 if the temperature is increased above room temperature.

ACKNOWLEDGEMENT

Authors would like to thank to Lembaga Penelitian Universitas Sumatera Utara who

supported funding of our research by the research grant: Penelitian Talenta, Universitas Sumatera Utara, 2017, No. 5338/UN5.1.R/PPM/2017, Tanggal 22 Mei 2017.

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