Synthesis of reduced Graphene Oxide (rGO) using different treatments of Graphene Oxide (GO)

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Abstract. In this work, a combined chemical and mechanical method was used for the production of graphene instead of chemical method only. The use of mechanical sonication was to assists exfoliation graphene oxide (GO) besides the used of chemical reagents. Then, the reduction of GO into graphene was carried out using L-ascorbic acid. The effects sonication cause synthesis of GO undergoes peeling graphitic layer and at the same time expose the layer with oxidizing agent. The properties of GO and reduced-graphene oxide (rGO) using various routes were investigated using XRD and FTIR. The main characteristics peak was observed at 7° and 9° for GO prepared using sonication and without sonication, respectively. The decreased of 2-theta degree of GO prepared using sonication indicates that the d-value becomes bigger. Estimation of average diameter r GO (with sonication) was 24.49 nm while r GO (without sonication) was 126.2 nm. The reduction of both GO was then carried out using an environmentally reducing agent, ascorbic acid. It was found that the L-ascorbic acid was effective in removing oxygenated functional groups. The conductivity values obtained for rGO-s was 7640 S/m while rGO ws was 678 S/m.

1. Introduction
Graphene is one of new material discovered by researcher from Manchester University in 2004 and won Noble Prize in Physics for their pioneering work in year 2010 [1]. Over the past few years, graphene based flexible thin-film transistors and supercapacitor electrode has attracted great research interest due to their unique properties such as high capacity to store energy. Graphene can be synthesised from graphite and several methods such as flake fragmentation [2] and growing [3] methods. Most of the methods proposed aims to improve the quality, properties and quantity of graphene production. Method has been divided into two categories with relatively different ways that is bottom up and top down graphene [4]. In fact of that, top-down process have three method that is mechanical exfoliation, chemical exfoliation and chemical synthesis whereby single graphene sheet fragmented by separation or exfoliation with grapene oxide as intermediate phase. While, bottom-up graphene method more on some quality properties, average size and thickness produced by pyrolysis, epitaxial growth, chemical vapor deposition (CVD) and other [5].

Graphene oxide (GO) is utilized as precursor for a large-scale production of graphene-based especially in chemical exfoliation and CVD methods [6]. GO thin layer is insulator materials due to owing many oxygenated functional group and defect attribute to tunability and feasibility
incorporation [7]. The hydrophilic structure can easily disperse in water to give stable solution for single layer. Reviewed by Huang et al. [7] on graphene composite which summarize properties and combination of various chemical reported before and attraction on combination functional groups on polymer with GO. The covalent functionalization of graphene derivative is mainly based on reaction of functional groups on GO and rGO surface. This behaviour attractive on some research on GO and rGO for combination with polymer for backbone of graphene, combination with nano-metal oxide composite [8-10], combination conducting polymer for electrical enhancement [11-14], and biotribological systems [15]. Application in electrical field, rGO are commonly synthesized and used in nano-scale because of it is high in surface area contact and porosity are excellent in coating process for sensor.

Quality of rGO in almost cases is come through from the degree of reduction attainable and restoration of relevant properties (eg: electrical conductivity) [16]. While, GO quality from degree of reduction parallel with existing reactive time and temperature [6] to assists expanding graphite layer for exfoliation. Other than that, the oxidative-treatment GO do attachment of oxygen-containing functional groups during oxidation process increase interlayer between graphitic layer, thus, weakening van der Waals forces. The development method reagent used in reduction graphene oxide is very highly by using hydrazine hydrate [16-19], sodium borohydride [16, 19, 20], glucose [21], hydroquinone [22] and many more. Due to lack of quality intern of getting high conductivity and high surface area (small size particle) for demand graphene, new innovation method are combine with chemical and mechanical methods with drop of sodium nitrate reagent because it is highly fuming carcinogenic vapour. The innovation is reduction reagent by using eco-friendly reagent uses in food and pharmaceutical like ascorbic acid. L-ascorbic acid has potential as reducing agent thus serves double function in reduction of hydrophilic GO to hydrophobic rGO and conversion residual Mn (VII) ions to soluble Mn (II) ions.

Addition mechanical treatment in several part in the way to get graphene believed that highly potential in assists to breakdown van der Waals forces between graphitic layers. Ultrasonic treatment of graphite during oxidizing agent can peel apart the oxidized layers and expose the inner layers to the chemical oxidants. Typically, performance of sonication exert on GO suspension are proportional to time and also can be temperature of suspension. Temperature variable important in expand the graphitic layer and also remove oxygenated groups on basal plane. Repeated sonication process are proposed before is unsuccessful by using bath sonication but nonetheless resulted in nanoscale graphene. Another addition treatment by using ball mill effect on graphite are not much research on graphene but in CNTs are various interm to study understanding dispersion CNTs and effect on CNTs structure which reported length of CNTs shortened significantly with increasing milling time [23]. Combination mechanochemical synthesis reduced graphene for effectiveness and size has been investigated.

2. Materials and methods

2.1 Chemicals and materials
Graphite with a purity of 99% was purchased from COMAK. Sulphuric acid (H₂SO₄, 98% purity) and hydrogen peroxide (H₂O₂, with 30% purity) were supplied by R&M Chemicals. Potassium permanganate (KMnO₄) and L-ascorbic acid with purity 99% was obtained from Sigma Aldrich. Ethylene glycol (Merck) was purchased from Merck and used as dispersion solvent.

2.2 Preparation of GO using sonication method
Graphene oxide was prepared by using improved Hummer’s method as it is one of the eco-friendly method due to the removal of carcinogenic chemical, sodium nitrate (NaNO₃) [24]. Typically, 5 g of graphite were ball milled for several hours to weaken Van der Waals interaction between graphitic layers. Ball milled graphite powder were mixed with 200 ml H₂SO₄ in a beaker under ice bath condition and stirred for 1 hour. Then, 30 g of KMnO₄ was added slowly and the stirring was continued for another 24 hours for oxidation reaction to complete. The mixture was stirred for 2 hours to homogenize the solution and appear dark brown solution. 100 ml distilled water was then added slowly and the solution was sonicated for more than 5 hours at 30°C. After the sonication procedure,
the mixture was heated at 90°C for 1 hour and sufficient distilled water was added and stirs. Next, 30 ml hydrogen peroxide was added to stop the reaction. Suspension was divided into two equal parts; one washed to obtain GO and the other was further processed for preparation of rGO. After washed by HCl and distilled water, adjust pH almost to neutral. Finally, centrifuge suspension with 10,000 rpm for 20 min and GO precipitate were dried at oven.

2.3 Preparation of reduce graphene oxide (rGO)

The deoxygenation of graphene oxide to reduced graphene oxide (rGO) was carried out using L-ascorbic acid (vitamin C) as reducing agent. 10 g L-ascorbic acid was first dissolved in 100 ml of distilled water. The L-ascorbic acid solution was mix together with GO-s and GO-ws. Then, the mixture was heated at temperature 95°C for 1 hour. After heating, immediately sonicate for 15 minutes. The resultant black precipitate were simply filtered with vacuum pump and further were washed with 1M hydrochloric acid solution and distilled water to neutral pH. Finally, filter and dry in oven overnight.

2.4 Characterization and measurement

2.4.1 X-ray Diffraction (XRD) analysis

X-ray diffraction (XRD) patterns were obtained using D/Max 2200V/PC, Rigaku, Japan where CuKα as the radiation source with wavelength (λ= 0.15 nm). The XRD scans were carried out in a 2θ range from 5° to 80° at a scanning rate of 2°/min using a voltage of 40 kV and current of 40 mA.

2.4.2 Fourier transformed infrared (FTIR) study

Fourier transform infrared (FTIR) spectroscopy were recorded using Perkin Elmer Spectrum One in order to study the chemical functional groups of graphite, GO and rGO after the synthesis process.

2.4.3 Dynamic light scattering (DLS)

Particle size and zeta potential analysis of the rGO were carried out using a Nano-ZS Zetasizer (Malvern, UK) in electronic light scattering mode. 0.5 mg/ml rGO suspension in ethylene glycol was prepared and sonicated for 10 minutes to form homogenous solution.

3. Result and Discussion

X-ray diffraction (XRD) analysis was first carried out to observe any crystal structure changes after graphite has been oxidised to GO, followed by the reduction of GO to rGO. Based on figure 1, it can be seen that graphite shows a high intensity and sharp peak at 2θ= 26.7°. This indicates that crystallinity morphology and large crystallite size (with interlayer space is about 3.35 Å) of graphite. When graphite expose to oxidizing agent (KMnO₄) and intercalant agent (H₂SO₄), the graphitic interlayer d-spacing will increase drastically to weaken bond between layers. These situation called graphite intercalated compound (GIC). After the oxidation treatment of graphite to GO, the peak dissapeared and new peak appears at lower 2 theta degree which indicates that the graphite was completely convert to GO [15]. A new and sharp peak appears at 2θ= 9° for GO-s and 2θ= 11.3° GO-ws. Both are in the range of common peak between 2θ= 9°-12° [25,26]. Higher 2 theta degree and intensity when no ultrasonication was used may due to the merging of individual graphene oxide flake size more than 100 nm [27] attribute from agglomeration.

In addition, GO-ws usually forms polycrystalline material which contain wide width before going to lower of the graph. Consist of many single crystal oriented are not completely dissociate during method without sonication cause X-rays to be scattered. By introducing sonication during the preparation of GO, it reduces agglomeration of particles and weakening the Van der Waals bonding between each graphicit layer and at the same time force oxygenated group entering to the deep area. Value of d-spacing for GO (with sonication) and GO (without sonication) is 9.551 Å and 7.789 Å respectively. Evidently, existing sonication would give impact to graphicitc layer in expanding to weaken the bonding and exfoliate layer by layer. Normally, rGO and graphite can be seen almost the same about their peak ranging in 2θ= 25-27° due deoxygenated functional group with differs in peak
sharpness and particle size. Degree of reduction of rGO (L-AA) and rGO (L-AA/S) is relatively at different peak width and location of peaks. The main rGO (L-AA) peaks characterized by intense and broad at $2\theta = 26.0^\circ$ and adjacent weak peak located at $2\theta = 20.1^\circ$ and $21.0^\circ$ and $2\theta = 44.0^\circ$. rGO (L-AA/S) shows less intense and broad XRD peaks at $2\theta = 26.0^\circ$ with appear small peak adjacent at theta $2\theta = 26.0^\circ$. Amorphous crystallite particles can be estimated this rGO based on wider peak appears but in theory of adjacent two peaks are come from orientation different physical shape can be ascribe difference in number of atoms in plane. Stated crystallite size is 48 nm and 47 nm for rGO-ws and rGO-s respectively. The reduced sheet decreases, both around 3.34 Å is very close to graphite to mention this deduction intersheet hydrophobic were removed water molecule as expander during oxidation. Effectiveness in removal oxygenated functional group will reduce $d$-spacing sheet and hydrophobic properties appears.

Figure 1. XRD pattern of graphite, GO-s, GO-ws, rGO-s and rGO-ws

Figure 2- compares the functional group of graphite, GO and rGO using FTIR spectrometer. It can be seen that the graphite used does not any oxygenated functional group. Both GO contains O-H bond at 3000-3600 cm$^{-1}$. However, a broad and intense band was observed for GO-s while GO-ws contains less intense band at 3000-3600 cm$^{-1}$ (O-H stretching vibration) with intermolecular single H-bonds. The high frequency of the spectrum results of vibration or rotation of atom that may raise electron to higher energy levels. Besides the O-H bond, others bond such as at 1710 cm$^{-1}$ was observed indicates occurrence of oxidation ; C=O (carbonyl group). The presence of the oxide linkage with carbon atom reflected some interaction between graphite basal plane and KMnO$_4$, H$_2$SO$_4$ and water molecules. At wavelength 1600 cm$^{-1}$ shows that contain C=C (aromatic) molecule were still present after treatment because they stable at this condition. 1120 cm$^{-1}$ (O-H bending vibration from hydroxyl groups). Sulfur functional group found at 1030 cm$^{-1}$ and alkenes groups with bending vibration at 890 cm$^{-1}$. At 550 cm$^{-1}$ (C-Cl stretching vibration from alkyl halid group) may be contribution from washing. For all the reduced GO (Figure 2b), the intensities of the band associated to oxygen functional groups strongly decrease. rGO (L-AA) contain small amount oxygenated functional group with broad (O-H stretching vibration) and (C-O stretching vibration) at 3300-3700 cm$^{-1}$ and 1300 cm$^{-1}$ respectively. Aromatic
(C=C stretching vibration), 1600 cm⁻¹ were found in rGO (L-AA) indicates stretch band shows the remaining sp² character. Sulfur and chloride functional group are still appears but in low intensity in fingerprint area.

![Figure 2.](image)

Dynamic light scattering zetasizer plays an important role to determine the surface conductivity and particle size. Prior to testing, a solution 0.5 mg/ml rGO in ethylene glycol solvent was prepared [6]. Ethylene glycol is the best solvent to disperse rGO that remove hydrophobicity characteristic. The average diameter particle sizes was 24.49 nm and 126.2 nm for rGO-s and rGO-ws respectively. While, conductivity shows by rGO (L-AA/S) is more than (L-AA) which is 7640 S/m over 678 S/m.

4. Conclusion
In this work, it was found that the rGO prepared using combined ultrasonic and chemical method has better properties in compared to those untreated with ultrasonic. Evidently, GO-s give positive results as common review formation peak at 9° compared to GO-ws. Phenomena occurring GO-ws may due to lacking of assist in opening or expanding the graphitic interlayer spacing that just only focus on oxidation reagent. It seems like depending on chemical are not effectively in expand the graphitic interlayer. Relative amount oxygen functional group was estimated from intensities of the oxygen related band in FTIR measurements. GO-s give high d-spacing interlayer than GO-ws with value 9.551 Å and 7.789 Å. The results strengthen that the graphitic surface influences the structural, optical and electrical properties of the GO. GO synthesis in term of exfoliation control would be useful in obtaining good efficiency to reduce. As a result, rGO-s is containing high conductivity than rGO-ws.

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Reference
[1] Dresselhaus M S and Araujo P T 2010 J. Nano. Chem. 4, 6297
[2] Chen G, Weng W, Wu D, Wu C, Lu J, Wang P and Chen X 2004 J. Carbon 42, 753
[3] Pei S and Cheng H M 2012 J. Carbon N. Y. 50, 3210
[4] Ryu S, Han M Y, Maultzsch J, Heinz T F, Kim P, Steigerwald M L and Brus L E 2008 J.Nano Lett. 8, 4597
[5] Alam S, Nizam B and Maksudul U 2016 J.Int. Nano Lett
[6] Xu C, Yuan R and Wang X 2014 J. Carbon N. Y. 71, 345
[7] Huang X, Qi X, Boey F and Zhang H 2012 J. Chem. Soc. Rev. 41, 666
[8] Yun Y 2016 J. Electrochem. Sci 11, 2778
[9] Wang H, Liu Y, Li M, Huang H, Xu H M, Hong R J and Shen H 2010 J. Optoelectron. Adv. Mater. Rapid Commun. 4, 1166
[10] Lee M S, Lee K, Kim S Y, Lee H, Park J, Choi K H, Kim H K, Kim D G, Lee D Y, Nam S and Park J U 2013 J. Nano Lett. 13, 2814
[11] Dinh P and Van Hieu N 2011 J. Appl. Surf. Sci. 257, 9817
[12] Ammar A, Al-Enizi A M, Al Maadeed M A and Karim A 2015 J. Chem. 9, 274
[13] Ratautaite V, Topkaya S N, Mikoliunaite L, Ozsoz M, Oztekin Y, Ramanaviciene A and Ramanavicius A 2013 J.Electroanalysis 25, 1169
[14] Wessling B and Wessling B 2016 J. Polymer 2, 786-798
[15] Li J, Zeng X, Ren T and van der Heide E 2014 J. Lubricants 2, 137
[16] Fernández-Merino M J, Guardia L, Paredes J I, Villar-Rodil S, Solís-Fernández P, Martínez-Alonso A and Tascón J M D 2010 J. Phys. Chem.C 114, 6426
[17] Preetha K C and Remadevi T L 2015 J. Mater. Sci. Semicond. Process. 39, 178
[18] Moon I K, Lee J, Ruoff R S and Lee H 2010 J.Nat. Commun. 1, 73
[19] Shin H J, Kim K K, Benayad A, Yoon S M, Park H K, Jung I S, Jin M H, Jeong H K, Kim J M, Choi J Y and Lee Y H 2009 J. Adv. Funct. Mater. 19, 1987
[20] Gao W, Alemany L B, Ci L and Ajayan P M 2009 J. Nat. Chem. 1, 403
[21] Velasco-Soto M A, Pérez-García S A, Alvarez-Quintana J, Cao Y, Nyborg L and Licea-Jiménez L 2015 J. Carbon N. Y. 93, 967
[22] Wang G, Shen X, Wang B, Yao J and Park J 2009 J. Carbon N. Y. 47, 1359.
[23] Bastwros M, Kim G, Zhu C, Zhang K, Wang S, Tang X and Wang X 2014 J.Compos 60, 111
[24] Chen J, Yao B, Li C and Shi G 2013 J. Carbon N. Y. 64, 225
[25] Zhu C, Guo S, Fang Y and Dong S 2010 J. Nano Mole 4, 2429
[26] Abdolhosseinzadeh S, Asgharzadeh H and Seop Kim H 2015 J. Sci Rep 5, 10160
[27] Rohilla S, Kumar S, Aghamkar P, Sunder S and Agarwal A 2011 J. Magn. Magn. Mater. 323 897
[28] Ahmad A F, Humaizah F, Moin A, Munawar H, Mohd K, Rahman I A, Mohamed F, Hua C C, Ramli S and Radiman S 2013 J. Analyt Sci 17, 475