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Synthesis and characterization of graphene-like material derived from sugarcane bagasse

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Abstract. The superior ability of graphene has attracted much interest in both its development and application in various field. Graphene has been developed as material for a precursor for fabricating transparent conductive films, absorbents for environmental application, filler or additive in bioplastics, and many other applications. Graphene can be generated from carbon-based materials such as wood charcoal, sawdust, coconut shells, bagasse, rice husk, old tires, polymer-based waste, and cellulose. In this research, graphene is synthesized via Hummers route using carbon of sugarcane bagasse as raw materials. Parameter such as various addition of KMnO4 (5,10,15 gr) is observed. The characterization of the graphene such as X-Ray Diffraction (XRD), Fourier transform infra-red (FTIR) and scanning electron microscope (SEM) were used to investigate the different implication of the parameter applied during the production process. The results show that the graphene-like materials exhibit similar characteristics as published in previous works in term of crystalline structures, morphology, and its chemical bonding characteristics which can be used for diverse application as demonstrates by graphene derived from graphite exfoliation followed by reduction.

Keywords: graphene, graphene oxide, sugarcane bagasse, hummers method, biomass utilization

1. Introduction

Graphene and graphene oxide are materials that has unique chemical, optical and electrical properties because it is composed of a graphene framework and contains an oxygen functional group [1]. The materials are very promising materials to be applied in various fields such as technologies, including biosensors, drug delivery, nanoelectronics, energy storage, supercapacitors, catalysts in waste management and fillers for bioplastics [2, 3]. Bioplastics require improved physical and chemical properties for use in different applications. Several fillers such as silicate coatings and nanotubes are used to improve their mechanical, thermal, and rheological properties. Graphene and graphene oxide are possible to be applied as a filler or additive in bioplastics because it has a superior ability to produce improved physical and mechanical properties in the functional properties of bioplastics [4].

The main requirement in the synthesis of graphene and graphene oxide is that the raw materials used contain carbon atoms. This carbon source can be obtained by utilizing waste including wood charcoal, sawdust, coconut shells, bagasse, rice husks, used tires, polymer and cellulose-based waste [5-7]. One of

the wastes that can be used in the synthesis of graphene oxide is sugarcane bagasse [3, 8, 9]. Sugarcane production in 2018 is 2,174,000 tons and in 2019 it is estimated to reach 2,450,000 tons [10]. Bagasse is a by-product of the extraction (milking) process of sugarcane juice. From one factory, bagasse can be produced about 35-40% of the weight of milled sugarcane or around 735,000 tons [11]. Considering that there is so much waste, bagasse will provide added value for sugar factories if it is given further treatment, because most of the bagasse in Indonesia is only used as fuel for steam boilers in sugar factories and as a basis for making paper. One of the uses of bagasse waste that can provide a higher added value is to use it as a raw material for the manufacture of graphene oxide.

The common and widely used method to synthesize graphene and graphene oxide was developed by Hummers and Offeman in 1958, which is known as the Hummers method. Graphite oxidation can be achieved by a treatment where the graphite powder is concentrated using a H_2SO_4 solution containing $KMnO_4$ and $NaNO_3$. The advantages of using the Hummers method is that the reaction can take place completely in a few hours and safe as $KClO_3$ can be replaced with $KMnO_4$ and $NaNO_3$ to replace HNO_3 which can trigger the formation of acid mist[5, 12-14]. Although the method hold some advantages, it also have some drawbacks, including the generation of toxic gases such as NO_2 and N_2O_4 during oxidation process, the amount of Na^+ and NO_3 ion residues that are difficult during the purification process of graphene oxide. Researchers improved the Hummers method by eliminating $NaNO_3$, increasing the use of $KMnO_4$. This modification succeeded in increasing the reaction yield and reducing the spread of toxic gases by using twice the amount of $KMnO_4$ and five times the H_2SO_4 required in the Hummers method and introducing a new component H_3PO_4 in the reaction system [14]. In this paper, the use of modified Hummers method to produce graphene-like materials from sugarcane bagasse is investigated. It includes the effect of various addition of $KMnO_4$ and sonication time to the morphology, crystal structures and chemical bonding of the materials.

2. Materials and Methods

2.1. Materials
Sugarcane bagasse as raw material was obtained from the local market in Semarang, Indonesia. It was charred in furnace at 260^0C for 30 min and then ground into fine particles. Meanwhile, the chemicals such as H_2SO_4 98% (Merck), $KMnO_4$ (Merck), Ethanol (Merck), H_2O_2 30% (Merck), distilled water and deionized water were used without further treatment.

2.2. Synthesis of Graphene
The synthesis method was adapted from the modified Hummers method [5, 14]. 5 grams of charred sugarcane bagasse (CSB) was dispersed in 125 ml of 98% H_2SO_4 in an ice bath. $KMnO_4$ (5,10,15 g) then slowly added to the mixture with continues stirring and controlled temperature below 20°C. The mixture was subsequently transferred to a water bath with controlled temperature 40°C and continuous stirring for 3h which created a brownish gray colour paste. The solution then mixed with 100 mL deionized water and stirred for 15 minutes at 95°C. Subsequently, additional 100mL of deionized water was added one more time followed by 25 ml of 30% H_2O_2 which added slowly to remove the remaining $KMnO_4$. By this time, the sample colour is changes from dark brown to yellowish. The sample then filtered under warm conditions and repeatedly washed using distilled water until the pH becomes neutral. The solid sample was dried in an oven at 80°C for 6 hours. Dried solid sample then ultrasonically exfoliated in an ultrasonic bath (Krisbow, 50kHz) for several minutes which previously dissolved in deionized water.

For samples with different $KMnO_4$ (5,10,15 g) were labelled GK-05, GK-10, and GK-15 respectively and different sonication time (8 and 30 min) were labelled GU-08 and GU-30 respectively.

2.3. Characterization

The morphologies of samples were observed using scanning electron microscopy (SEM-EDX JEOL JSM-6510LA) with an accelerating voltage of 10 kV. The crystal structure was studied using SHIMADZU XRD-7000 by packed the dried sample on a glass sample plate and scanned from 2 theta 10-90 degree. Fourier transform infrared spectroscopy (FTIR) was conducted in the wave number range of 4000-400 cm^{-1} using PerkinElmer Spectrum IR 10.6.1 to observe the chemical bonding of the samples.

3. Results and Discussions

XRD analysis was employed to examine the structures of the samples for better understanding on the material synthesis from sugarcane bagasse. Figure 1 shows the XRD pattern of the graphene-like materials at various addition of $KMnO_4$ and sonication time in comparison with CBS. The diffraction pattern of CBS illustrates peaks on 26.7°, 37.7°, and 44°. Meanwhile, the pattern of treated samples GK-05, GK-10 and GK-15 shows broader range peaks at 22-26.5°, 37.7°, and 43.9° with slight shifted angle and lower intensity (Figure 1(a)).

The diffraction pattern of graphite is around 26.7° with interlayer distance 0.334 nm [8]. Li, *et.al*, 2018 mentioned that diffraction pattern at 26.5° is corresponded to graphite or the possibility of the reduced graphene oxide formation [3, 15]. While *Fahmi, et.al,* 2020 suggest that broadening peak at angle 24° indicates a non-crystalline carbon and commonly caused by either the random displacement between adjacent layers or local stacking faults produced during the treatment process. It also point out that disordered graphitic 002 and 100/101 planes are labelled for diffraction pattern at angle 22.5° and 43°, respectively [16-18].
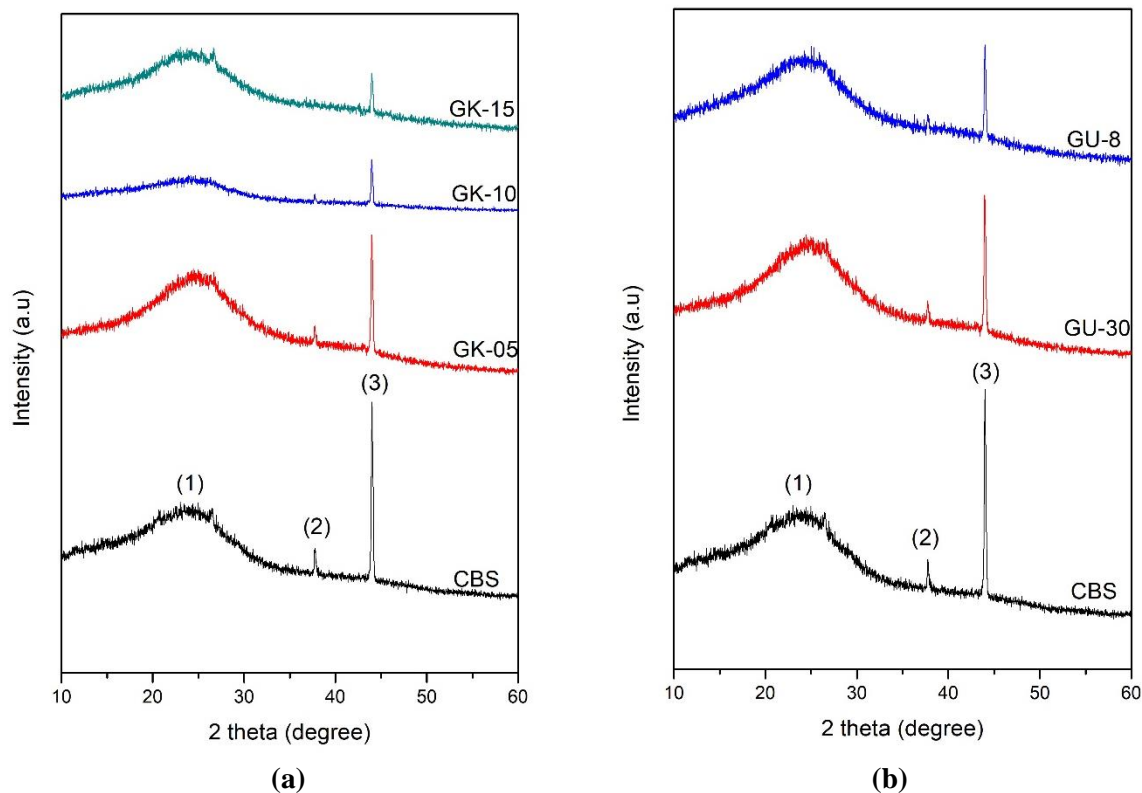

Fig. 1 XRD pattern of graphene-like materials (a) at various addition of $KMnO_4$; (b) at different sonication time

As the broader peaks appears in the diffraction pattern of treated samples (GK-05, GK-10, GK-15 and GU-08) and it has slight differences with the CBS diffraction pattern, it shows an indication that the modified Hummers methods was able to destruct the layers of carbon even in the slightest effect to become graphene-like materials. In addition, the constant decrease of the intensity of the peak at 37.7^{o}, and 43.9^{o} support the performance of the process with the peak at 43.9^{o} completely disappeared in the addition of 15g of $KMnO_4$. $KMnO_4$ is a strong oxidant, especially in acidic environment. $KMnO_4$ favor a complete intercalation for graphite oxidation [14]. Thus, the increase of $KMnO_4$ addition in this experiment leads to the high oxidation of CBS carbon layer.

The effect of sonication time apparently did not give any distinguished differences to the diffraction pattern of the graphene-like materials as illustrated in Figure 1(b). Slight reduction in the intensity was observed, however broader peaks or peak shift was found negligible. Broader peak in XRD diffraction pattern indicates micro-stress in crystallites that caused by dislocations, vacancies, shear planes. While peak shift is corresponding to lattice parameter changes due to micro-strain [19]. Thus, means that the sonication time has no effect to the crystal structure of the graphene-like materials produced via modified Hummers methods.

The morphology of the graphene-like materials, GK-05, GK-10, GK-15 and GU-08 can be observed in Figure 2. Small thin flakes of graphene-like materials obtained from modified Hummers method treatment with 5g $KMnO_4$ addition scattered in Figure 2(a) as it was detached from the layered CBS in the powerful manner.

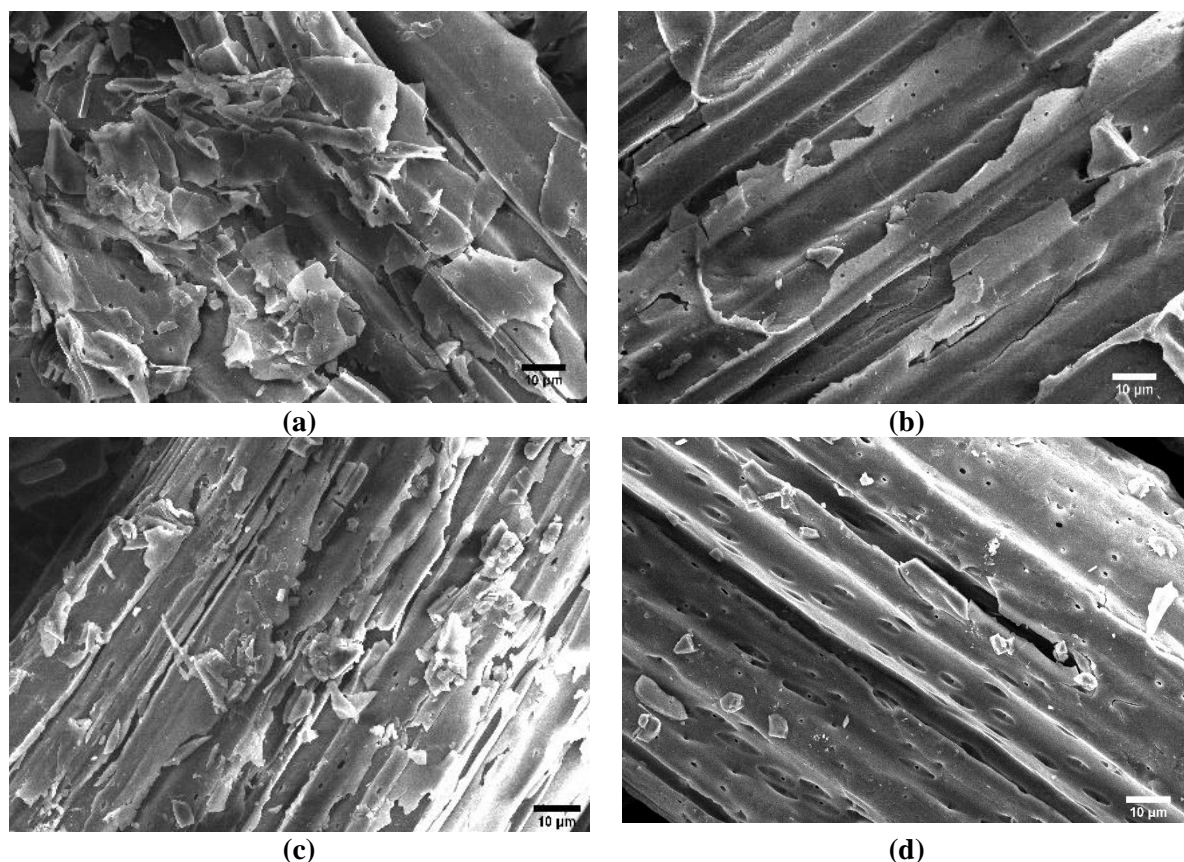**(a)**

(b)

(c)

(d)

Fig. 2 SEM images of (a) GK-05/GU-30; (b) GK-10; (c) GK-15; (d) GU-08

Figure 2(b) and (c) shows stacked of layered carbon with wrinkles and flipped side on the edge of some graphene-like materials obtained from modified Hummers method treatment with 10g and 15g $KMnO_4$ addition, respectively. Some papers reported large thickness of sheet-like structure with smooth surface and some wrinkled edge as typical graphene oxide materials [8, 9, 20]. Meanwhile, other reported thin sheets, paper-like with wrinkled morphology was a typical outlook of reduced graphene oxide [8, 21]. Refers back to Figure 2, indeed the graphene-like materials resulted in this experiment were consistent with the previously reported studies which having thin flakes and sheets with moderate thickness along with flipped edge and wrinkles. The wrinkles may indicate the oxygen functionalization (hydroxyl, epoxy and carboxy) and defects resulted from the synthesis procedure [8, 22]. The SEM result confirming the diffraction pattern observation which was discussed earlier.

The effect of $KMnO_4$ addition apparently in line with the XRD analysis results. Higher addition of $KMnO_4$ results more visible small sheets of graphene-like materials over layered carbon depict in Figure 2(a)-(c). Meanwhile it was obviously observed that high sonication time in this case 30 min can favour the exfoliation process of graphene-like materials from the layered carbon originated from sugarcane bagasse (Figure (a) and (d) in comparison). In order to investigate further the process mechanism of graphene-like materials in the controlled process parameters, the FTIR analysis was conducted with the results in Figure 3. GK-05 shows broad and strong peak at 3197.6 cm^{-1}, strong peak at 1704.8 cm^{-1}, 1602 cm^{-1}, and 1222 cm^{-1}. GK-10 shows broad and moderate peak at 3185 cm^{-1}, strong peak at 1706 cm^{-1}, 1601 cm^{-1}, and 1214 cm^{-1}. GK-15 shows board peak at 3201.7 cm^{-1}, strong peak 1705.3 cm^{-1}, 1602.8 cm^{-1}, and 1204.4 cm^{-1}.
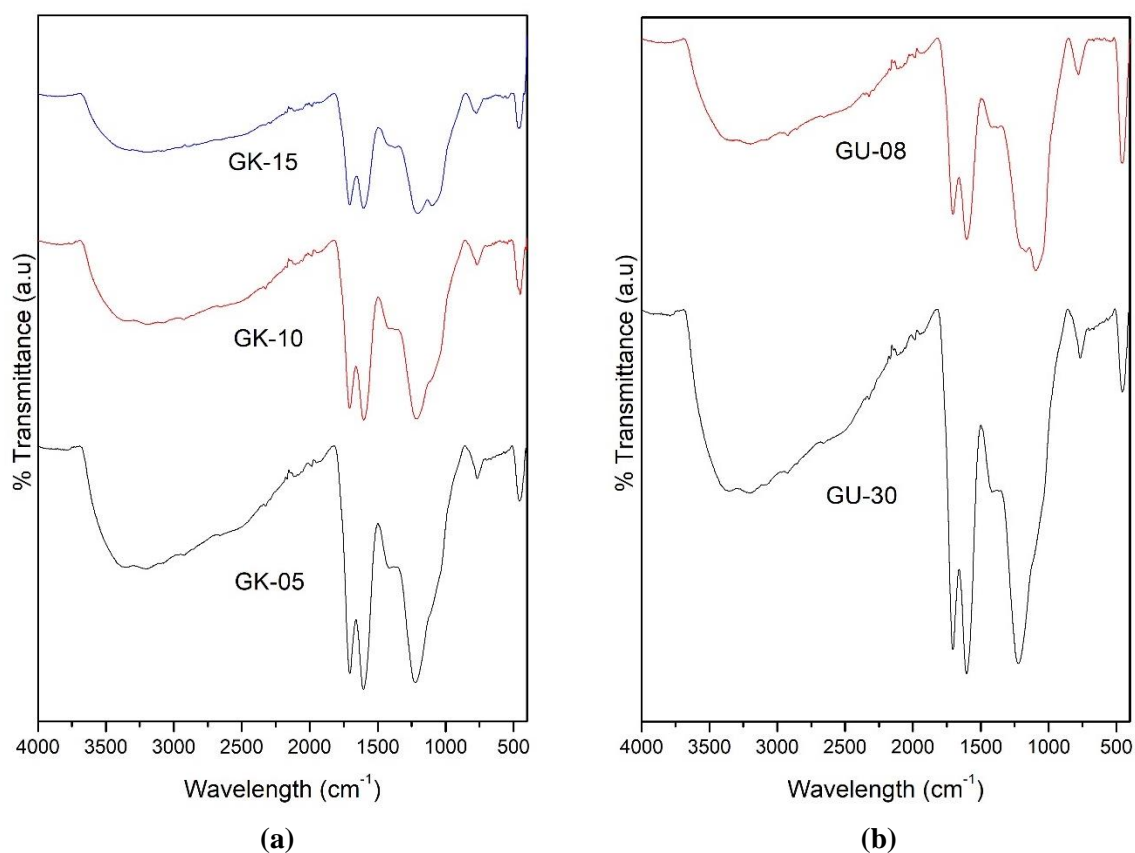

Figure 3 FTIR spectra of graphene-like materials (a) at various addition of $KMnO_4$; (b) at different sonication time

GU-08 shows broad and moderate peak at 3196.2 cm^{-1}, strong peak at 1703.2 cm^{-1}, 1603 cm^{-1}, and 1092 cm^{-1}. Wide band at around 3400 cm^{-1} for hydroxyl group may indicate the presence of oxygen containing moieties such as carbonyl, carboxylic, epoxy and hydroxyl in graphene oxide [23]. Other researcher reported indication of O-H stretching vibration in graphene oxide as a strong and wide band was observed at 3381.1 cm^{-1} [24]. Strong and wide peak at 3185-3201cm^{-1} exhibited in the samples may attributes to O-H stretching of hydroxyl group and carboxylic. As strong and broad band at 3300-2500 cm^{-1} represent O-H stretching. Moreover, Gan, *et.al,* 2019 stated that the decrease intensity of the broad band at 3400 cm^{-1} for the hydroxyl group could be an indication of the formation of reduced graphene oxide [8]. By the addition of KMnO$_4$, the intensity of the board peaks at near 3100 cm^{-1} was decreasing confirming the XRD and SEM results of the generation graphene-like materials.

Other indication was the present of strong peaks at around 1700, 1600, and 1200 cm^{-1}. According to Nethravathi and Rajamathi, 2008, narrow peak at 1730.2 cm^{-1} was normally caused by the C-O stretching of the carboxylic acid group at the fringe of graphene oxide. Meanwhile the band that is closed to 1227.6 cm^{-1} resulted in response to O-H bending vibrations [24]. Li, *et.al*, 2018 suggest that the bands observed at 1613.3 cm^{-1} and 1048.0 cm^{-1} can be attributed to the occurrence of C=C and C-O and the obvious reduction of the intensity of O-H band, C=O band and the tertiary C-OH band were confirming de-oxygenation of reduced graphene oxide. Other researcher also stated that peaks position at 1730 cm^{-1} corresponded to C-O stretching vibrations of the -COOH groups [23], meanwhile Zeng, *et.al.* 2011 found that peak at 1615 cm^{-1} that is corresponding to C=C bond (aromatic group) [25]. Peak at around 1049 cm^{-1} also can be attributed to C-O groups [26].

All the functional groups indicated in the samples based on the FTIR spectra results suggest that those are the typical groups encountered in graphene, graphene oxide or reduced graphene oxide. The reduce intensity was also observed in the 1700, 1600, and 1200 cm^{-1} that correspond to the C=O, C-O and the tertiary C-OH band signalling the transformation of layered carbon to graphene like materials. Thus, it can be stated that graphene-like material was successfully prepared from charred sugarcane bagasse (CBS) by using adaptation methods from the modified-Hummer method.

4. Conclusions

The graphene-like materials have been successfully synthesized via adaptation of modified Hummers method. The graphene-like materials exhibit similar characteristics as published in previous works in term of crystalline structures, morphology, and its chemical bonding characteristics. In the range of 5-15g of KMnO$_4$ addition, the highest ratio brings more obvious sign of the presence of graphene-like materials derived from charred sugarcane bagasse, thus the oxidizing agent in the modified Hummers method plays an important role. Meanwhile the effect of sonication time in the process found negligible. The graphene-like materials produced from sugarcane bagasse can be used for diverse application as it demonstrates similar characteristics with graphene derived from graphite exfoliation followed by reduction. This could convey new insights of the biomass waste utilization into valuable material like graphene, graphene oxide or reduced graphene oxide.

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